

# ANALYSIS OF PHYSICAL FACTORS ON CHOSEN PROPERTIES OF ANODIC ALUMINA OXIDE (AAO) LAYERS AND ENVIRONMENT

Received – Prispjelo: 2015-12-16

Accepted – Prihvačeno: 2016-04-20

Preliminary Note – Prethodno priopćenje

In the contribution is evaluated an impact of physical factors of anodizing process, namely the temperature of an electrolyte, anodizing time and voltage, on the change of values of Vickers microhardness and thickness of formed layer of experimental materials Al99-5. By increasing of electrolyte temperature, the values of layer microhardness and thickness layer increase, namely about 0.78 % at the increasing of electrolyte temperature by 1 °C. By lengthening of anodizing time grows the value of layer thickness, but only to the value of the critical deposition time, when chemical dissolution of the layer start to be more prominent. By voltage increasing, values of layer thickness and micro-hardness are increased in the range of the used experimental values.

*Key words:* anodizing of aluminium, microhardness, layer, thickness, environment

## 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, photo voltaic solar cells, filters [1,2], chemical sensors [3], photonics [4] and metallic nanowires [5, 6].

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

Depending on the considered anodizing conditions, these properties can be varied to a wide extent; therefore 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 [7 - 9]. 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 [10].

In the literature may be found the results for the various alloys as shown in Table 1. The results in this table show that in addition to physical and chemical factors engaged in the process of anodizing oxidation on the final value of the technological properties of the layer, the most of all microhardness affects on the type and quantity of alloyed elements in the alloy, and electrochemical properties and kinds of aluminium matrix and alloys. For example, alloyed elements, such as copper and magnesium, decrease the value of microhardness, significantly compared to the effect of silicon. For the ternary compositions, however, also show interactive effects (AlMg<sub>3</sub> vs. AlSi<sub>7</sub>Mg) [9].

Table 1 **Vickers microhardness of anodic oxide layers on different aluminium alloys [8]**

Substrate composition / wt.%	Vickers microhardness / HV	Anodizing conditions and /or reference
Al99-7	600 (HV <sub>0,020</sub> )	[7]
	481 (HV <sub>0,015</sub> )	[9]
	541 ± 28 (HV <sub>0,025</sub> )	[8]
Al99-5	147 (HV <sub>0,010</sub> )	This study
AlMg <sub>5</sub>	460 (HV <sub>0,015</sub> )	[9]
AlSi <sub>10</sub> Cu <sub>3</sub>	227 ± 78 (HV <sub>0,025</sub> )	[8]
AlSi <sub>10</sub>	489 ± 63 (HV <sub>0,025</sub> )	[8]

In this contribution was evaluated the effect of physical factors (temperature of the electrolyte, anodizing time and voltage) on to change of the values of Vickers microhardness and thickness of the created AAO layer. In order to not affect of the measurement results by chemical composition of the experimental material, there was used aluminium Al99-5.

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## MATERIAL AND EXPERIMENTAL METHODS

Aluminium sheet Al99.5 of thickness 0,5 mm was used as an experimental anode material. The chemical composition of experimental material is shown in Table 2.

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  $50 \pm 2$  °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  $55 \pm 2$  °C for 1 minute.

Table 2 **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 individual experiments were performed in an electrolyte composed of  $H_2SO_4$  with a mole concentration of  $1,428 \text{ mol}\cdot\text{dm}^{-3}$  and  $C_2H_2O_4$  with the molar concentration  $0,183 \text{ mol}\cdot\text{dm}^{-3}$  at three different values of current densities  $3 \text{ A}\cdot\text{dm}^{-2}$ ,  $4 \text{ A}\cdot\text{dm}^{-2}$  and  $5 \text{ A}\cdot\text{dm}^{-2}$ . When analysing the dependence of microhardness and thickness of the layer versus electrolyte temperature, the anodizing time was 25 minutes and a voltage 12 V. In examining of the impact of the anodizing oxidation period was the electrolyte temperature  $15$  °C and the voltage 12 V and at analysing of the impact of tension, the electrolyte temperature is  $20$  °C and the period of anodic oxidation terms 30 minutes.

After anodizing, the samples were immediately rinsed in cooled (approximately  $10$  °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).

## RESULTS AND DISCUSSION

By the experimental analysis of the influence of the electrolyte temperature on values of Vickers microhardness  $HV_{0,01}$  and layer thickness ( $th$ ) at the current densities of 3 to  $5 \text{ A}\cdot\text{dm}^{-2}$ , (Figure 1) were used the electrolyte temperature from  $-1,78$  °C to  $45,78$  °C, the constant anodizing oxidation time was 25 minutes and a voltage 12 V. At a current density  $J_1 = 3 \text{ A}\cdot\text{dm}^{-2}$  occurs the growth of microhardness values of the layer by rising of the electrolyte temperature, while this layer growth is linear one. The difference of the microhardness value at the lower limit of the experimental interval of the electrolyte temperature ( $-1,78$  °C) and the upper limit of used electrolyte temperature presents an increase about 37 %.

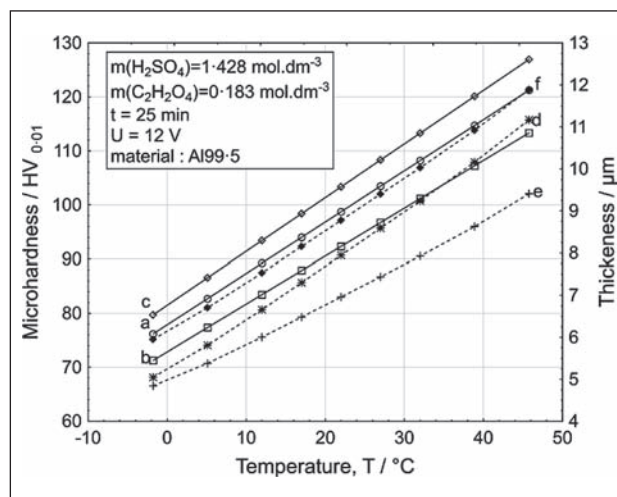
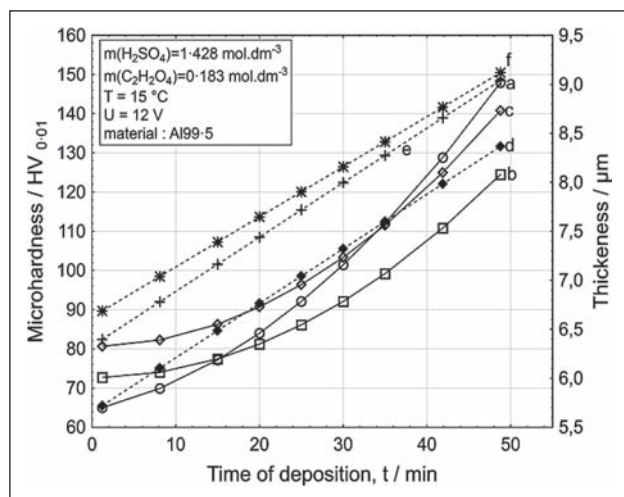


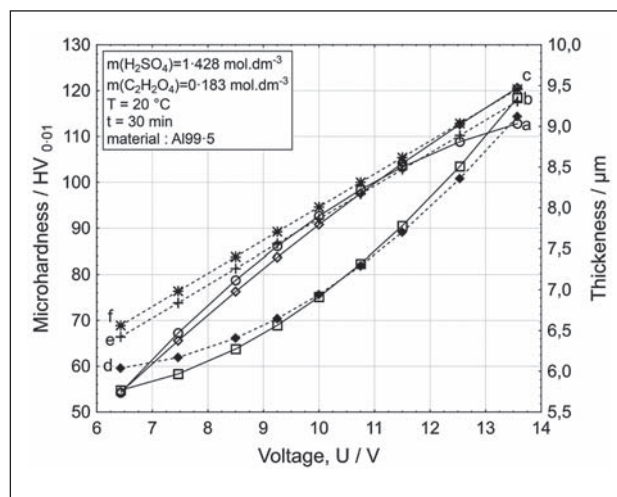
Figure 1 Dependence of value  $HV_{0,01}$  and layer thickness from the electrolyte temperature (a -  $HV_{0,01}$  for  $J_1 = 3 \text{ A}\cdot\text{dm}^{-2}$ , b -  $HV_{0,01}$  for  $J_2 = 4 \text{ A}\cdot\text{dm}^{-2}$ , c -  $HV_{0,01}$  for  $J_3 = 5 \text{ A}\cdot\text{dm}^{-2}$ , d -  $th$  for  $J_1 = 3 \text{ A}\cdot\text{dm}^{-2}$ , e -  $th$  for  $J_2 = 4 \text{ A}\cdot\text{dm}^{-2}$ , f -  $th$  for  $J_3 = 5 \text{ A}\cdot\text{dm}^{-2}$ )

By increasing of the current density on the value 4 and  $5 \text{ A}\cdot\text{dm}^{-2}$ , there remains the percentage growth of the microhardness value with the electrolyte temperature approximately the same on the level of 37 %. Regarding to the approximately linear character of this dependence, it can be said that by the increasing of the temperature about  $1$  °C, also the microhardness value will increase about approximately 0,78 %. If at the temperature  $-1,78$  °C will be increased the current density from 3 to  $4 \text{ A}\cdot\text{dm}^{-2}$ , there will be decreased the value of the microhardness layer about 6,5 % and decreased the value of the layer thickness about 4 %. By further increasing of the current density to  $5 \text{ A}\cdot\text{dm}^{-2}$  at the same temperature, there will be increased microhardness values of about 11,85 % and to increasing of the value of layer thickness almost about 23 % on the value  $5,95 \mu\text{m}$ . If an influence of the current density will be monitored at the practical "critical" anodizing oxidation temperature  $22$  °C, conclusion will be that at increasing of current density from 3 to  $4 \text{ A}\cdot\text{dm}^{-2}$ , it will be led to decreasing of microhardness layer value at about the same value as at temperature  $-1,78$  °C and it means on 6,5 %, but the value of the thickness layer will be decreased on about 12,38 %. By increasing of the current density on  $5 \text{ A}\cdot\text{dm}^{-2}$ , there occurs the increasing of microhardness value on 11,95 % and the increasing of the value of the layer thickness is more than 26 %. At the experimental analysis of the impact of anodizing oxidation time to change the value of Vickers microhardness  $HV_{0,01}$  and the layer thickness ( $th$ ) at current densities of 3 to  $5 \text{ A}\cdot\text{dm}^{-2}$  (Figure 3), there were used anodizing oxidation times of 1,22 minutes till 48,78 minutes, the constant electrolyte temperature  $15$  °C and a voltage 12 V.

From the mentioned Figure 2 influences strongly nonlinear dependence of microhardness of layers with increasing of duration of anodizing oxidation. At a current density  $3 \text{ A}\cdot\text{dm}^{-2}$  is observed in the range 1 minute



**Figure 2** Dependence of  $HV_{0,01}$  and layer thickness values on anodizing oxidation time (a -  $HV_{0,01}$  for  $J_1 = 3 \text{ A}\cdot\text{dm}^{-2}$ , b -  $HV_{0,01}$  for  $J_2 = 4 \text{ A}\cdot\text{dm}^{-2}$ , c -  $HV_{0,01}$  for  $J_3 = 5 \text{ A}\cdot\text{dm}^{-2}$ , d -  $th$  for  $J_1 = 3 \text{ A}\cdot\text{dm}^{-2}$ , e -  $th$  for  $J_2 = 4 \text{ A}\cdot\text{dm}^{-2}$ , f -  $th$  for  $J_3 = 5 \text{ A}\cdot\text{dm}^{-2}$ )



**Figure 3** Dependence of  $HV_{0,01}$  and layer thickness values on of the voltage

to 22,15 minutes an increase of the microhardness layer of 15,8 %, whereas in the range from 15 to 48,78 minutes, this increase is more than 47 %.

The overall average increase of the microhardness layer value by varying the anodizing oxidation time is at a current density  $3 \text{ A}\cdot\text{dm}^{-2}$  in the whole range of used values of 56,07 %. By increasing of the current density on the value  $4 \text{ A}\cdot\text{dm}^{-2}$  is the average increase of microhardness layer on 41,59 % and by further increase of the current density to  $5 \text{ A}\cdot\text{dm}^{-2}$  is value 42,73 %. The non-linear dependency manifests by slightly increase of the microhardness values at the both current densities (4 and  $5 \text{ A}\cdot\text{dm}^{-2}$ ) in the range from 1,22 to 15 minutes about 6 %. In the interval of the used times of anodizing oxidation from 15 to 48,78 minutes is an increase of  $HV_{0,01}$  more significant, the value 37,79 % is at  $J_2 = 4 \text{ A}\cdot\text{dm}^{-2}$  respectively 42,72 % at  $J_3 = 5 \text{ A}\cdot\text{dm}^{-2}$ . The dependence of the change of the layer thickness on the anodizing oxidation time is linear one. The average change of the value of the layer thickness is without on the anodizing oxidation time at the current density  $3 \text{ A}\cdot\text{dm}^{-2}$  more than 31 %, at the current density  $4 \text{ A}\cdot\text{dm}^{-2}$  almost 30 % and at the current density  $5 \text{ A}\cdot\text{dm}^{-2}$  more than 27 %.

During the scientific research, at the experimental analysis of voltage on the change of Vickers microhardness value  $HV_{0,01}$  and layer thickness ( $th$ ) at the current densities from 3 to  $5 \text{ A}\cdot\text{dm}^{-2}$  (Figure 3), were used constant temperature of the electrolyte  $20 \text{ }^\circ\text{C}$  and constant anodizing oxidation time 30 minutes.

From Figure 3, it clearly shows a nonlinear dependence of changes of the value microhardness layer from increasing values of the voltage. In the interval of used voltage values from 6,43 V to 13,57 V, it can be seen that at a current density  $3 \text{ A}\cdot\text{dm}^{-2}$  at the upper limit of the used experimental interval the voltage value of the microhardness is gradually stabilized. At a current density

$4 \text{ A}\cdot\text{dm}^{-2}$ , it is observed the significant non-linear growth of the microhardness layer value in the whole interval of used voltage values. At a current density  $5 \text{ A}\cdot\text{dm}^{-2}$  is a total growth of the microhardness layer almost 55 %.

## CONCLUSION

The mechanism of anodizing oxidation of the aluminium and its alloys remains despite significant efforts of researchers elucidated. The attempt of authors were partial introduce the dependencies of physical factors affected in the process on the change of the value of the created layer thickness and its microhardness. From the mentioned problem, we can make a conclusion:

- by increasing of the electrolyte temperature is growing mean value of layer microhardness, also the layer thickness at all used current densities ( $3 \text{ A}\cdot\text{dm}^{-2}$ ,  $4 \text{ A}\cdot\text{dm}^{-2}$ ,  $5 \text{ A}\cdot\text{dm}^{-2}$ ),
- by increasing of the electrolyte temperature about  $1 \text{ }^\circ\text{C}$ , the microhardness values will grow approximately about 0,78 %,
- by increasing of the anodizing oxidation time, the value of the created generated layer microhardness grows while the character of the relation is strongly nonlinear,
- by increasing of the anodizing oxidation time, the value of the layer thickness is growing,

## Acknowledgement

The work was supported by Ministry of Education of Slovak republic, VEGA 1/0537/15.

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