ANALYSIS OF THE PROPERTIES OF THE Al_2O_3 / IF-WS_2 SURFACE LAYERS OBTAINED IN THREE-COMPONENT' ELECTROLYTE

Joanna KORZEKWA [1], Aneta GĄDEK-MOSZCZAK [2], Marek BARA[1], Dariusz BOCHENEK[1]

[1]*University of Silesia, Faculty of Computer and Materials Science,Sosnowiec, Poland, EU,*
joanna.korzekwa@us.edu.pl, marek.bara@us.edu.pl, dariusz.bochenek@us.edu.pl

[2]*Cracow University of Technology, Faculty of Mechanical Engineering, Cracow, Poland, EU,*
aneta.gadek-moszczak@mech.pk.edu.pl

https://doi.org/10.37904/metal.2019.903

Abstract

Anodic oxidation of aluminum alloy in a ternary solution of SAS (sulfuric, adipic and oxalic acids) was carried out in order to obtain the aluminum oxide layer (Al_2O_3) and Al_2O_3 with inorganic fullerene-like tungsten disulfide (IF-WS_2) named in article as Al_2O_3/IF-WS_2. The micro-hardness, thickness, geometric structure of the surface (SGP) and the microstructures of Al_2O_3 and Al_2O_3/IF-WS_2 were investigated. The influence of electrolysis time, temperature and type of electrolyte on the micro-hardness of coatings was studied using the Taguchi statistical method. A L_2 orthogonal array with the three main factors of control at two levels each was studied. Signal-to-noise ratio showed that the great influence of temperature on micro-hardness. The optimized electrolysis conditions were defined.

Keywords: Aluminum oxide layer, inorganic fullerene-like tungsten disulfide, microstructures, hardness

1. INTRODUCTION

The light weight, a quite large corrosion resistance, a simplicity of surface treatment and forming, a total process ability as a secondary raw material there are just few benefits of aluminum alloys which are widely used in motorization, aircraft or food industry. In same case the pros of aluminum could stay also its cons, for example simplicity of forming makes aluminum a material susceptible to mechanical deformation. Aluminum alloys has high friction coefficient wherefore without appropriate surface treatment it is unsuitable as friction material. To improve poor wear or/and corrosion resistant of aluminum the various method such as ion implantation [1], lubricating additives [2], anodic oxidation [3,4], catalytic chemical vapor deposition (CCVD) [5], electroplating [6], conversion coating [7,8], and polymer coating [9,10], have been applied. In oil-less tribological coupling, or more precisely in coupling with lack of lubrication fluid, the choice of type of materials for tribological pair plays an important role. In order to improve the properties of the anodic oxide coatings, their modifications are made. The authors of the works [12-14] described the microstructure and effects of improvement of tribological properties caused by the modification of Al_2O_3 oxide layer by graphite additive. It has been reported that the lubricating mechanism was that PTFE particles embedded in porous anodic aluminum oxide film smeared a transfer film on the sliding path and the micro-pores could support the supplement of solid lubricant during the sliding, which prolonged the lubrication life of the aluminum alloys [15]. Gyu-Sun Lee at al. showed that the effect of oxide layer developed by tribochemical reaction on the surface is greater than lubricant reservoir effect of the pore [16]. The objective of the present work is to present the investigation concern a micro-hardness, a thickness, a geometric structure of the surface (SGP) and the microstructures of Al_2O_3 and Al_2O_3/IF-WS_2. The experiment was carried out using the Taguchi experimental design.

2. METHODOLOGICAL BASES

Macroscopic images of the samples were made with Omnivision OV12A10 camera (Xiaomi Redmi 5 Plus) and Olympus BX60M optical microscope with Motic camera while images of the structure and morphology of the formed surface oxide layers was carried out using JEOL JSM-7100 TTL LV Field Emission Scanning Electron Microscope. The thickness of the layers was measured with Dualscope MP40 by Fischer, using the eddy current method. 10 measurements were performed along the length of the sample and then the average value was calculated. The micro-hardness tests in cross-sections of the samples were performed using Neophot 21 microscope with Hanemann adapter (Vickers indenter) at a load of 0.3 N. The ImageJ software was used for image analysis. SGP measurements of oxide layers were made by the Taylor Hobson Talysurf 3D pin profilometer with the accuracy of 2 %. The results of the parameters were developed by using the TalyMap Universal 3D software. The stereometric analysis was performed on an area of 2 mm x 2 mm. The Taguchi experimental design has been applied for analyzing the influence of the technological process parameters on micro-hardness of Al_2O_3 and Al_2O_3/IF-WS_2 coatings. Three control factors were considered: temperature, time and type of electrolyte. The L_2 orthogonal array with the three main factors at two levels each was used for the study. The signal to noise (S/N) ratio and effects of control parameters were used to determine an expected S/N ratio under optimum condition. The statistical analysis of the result was performed using the STATISTICA 12.0 software.

3. MATERIALS AND SAMPLE PREPARATION

The starting material for the process was EN-AW-5251 aluminum alloy. Samples were etched sequentially with 5% KOH solution for 45 minutes, and 10 % HNO_3 solution for 10 minutes, at room temperature. After each step of etching, the sample was placed in distilled water to remove residual acid. The electro-oxidation of the aluminum alloy was carried out in a ternary solution of SAS (18 % sulfuric (33 ml/l), adipic (67 g/l) and oxalic acids (30 g/l)) and in that way the Al_2O_3 samples no 1 and 4 was obtained. The Al_2O_3/IF-WS_2 samples no 2 and 4 was obtained in SAS solution with the same proportion as above and with admixture of 15 g of the commercially available IF-WS_2 nanoparticles (NanoMaterials Ltd) per 1 liter of electrolyte. The hard anodizing process was performed at 3 A/dm^2 current density. The details concerning the serial number of samples, IF-WS_2 content in the bath acid and time of anodizing are presented in **Table 1**. In order to ensure homogeneity of the suspension and to prevent settling of the IF-WS_2 nanopowder, mechanical stirring was applied during the electrolysis process.

Table 1 Factor settings for Taguchi L_2 design

Experiment/ Sample No	Temperature (°C)	Time (min)	Electrolyte
1	25	30	Pure
2	25	60	with IF-WS_2
3	30	30	with IF-WS_2
4	30	60	Pure

4. RESULTS AND ITS DISCUSSION

The SEM images of the microstructure of the surface layer were shown in **Figure 1**. The size of the pores for each sample was assessed by their area. The sample 1-3 have similar pores size - the mean square area of the pores obtained a value 170 nm^2 for sample 1, 215 nm^2 for sample 2 and 208 nm^2 for sample 3. Pores of sample 4 have distinctly largest mean area equal to 550 nm^2. The extend anodizing time has influence on the increasing of the mean square area of the pores.

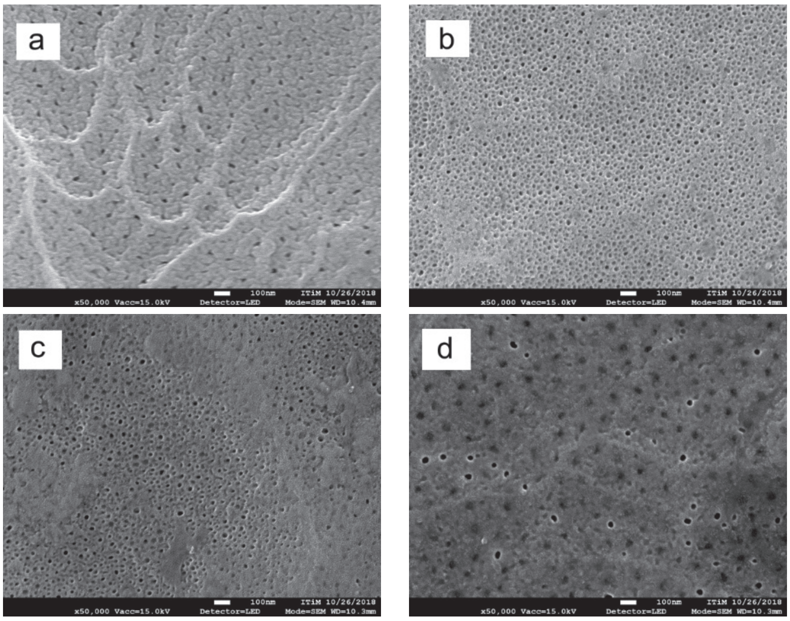

Figure 1 SEM images of the microstructure of surface layers
(a) sample 1, (b) sample 2 (c) sample 3, (d) sample 4

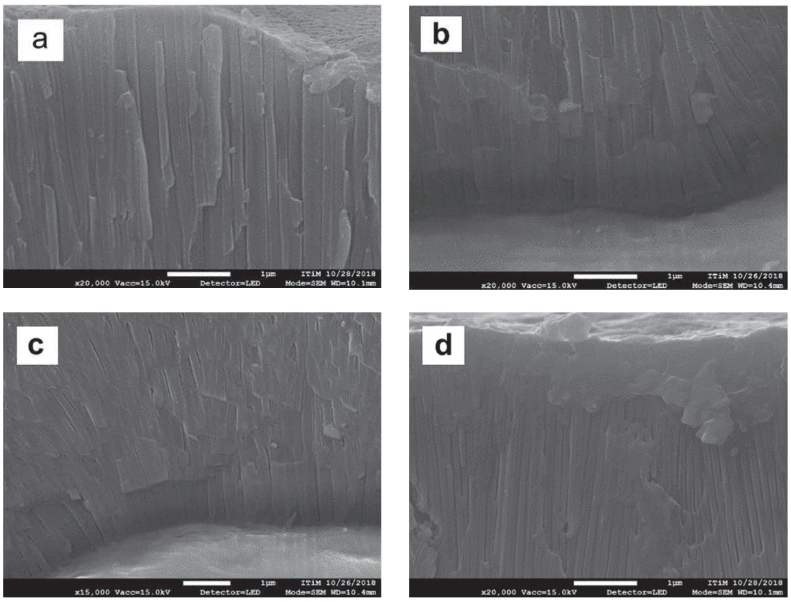

Figure 2 SEM images of the fresh structure of surface layers
(a) sample 1, (b) sample 2 (c) sample 3, (d) sample 4

The SEM images of the fresh structure of the surface layer were shown in **Figure 2**. The mean diameter of the fibers was measured for each sample. The values of mean fibers diameter in the sample 1 and 2 are similar and is equal to 180 nm. Mean fibers diameter for sample 3 is 110 nm. The lowest diameter of the fibers has sample 4 - 80 nm. From the knowledge it is known that in Al_2O_3 coatings, obtained on aluminum alloy, the micro-hardness decreases in gradient as the distance from the ground increases. It is related to decrease the diameter of nanofibers likeways. Therefore, the Vickers indentation imprints were taken in the same distance on each coating. Example picture and measurement of Vickers indentation imprint for the sample 2 is shown at **Figure 3**.

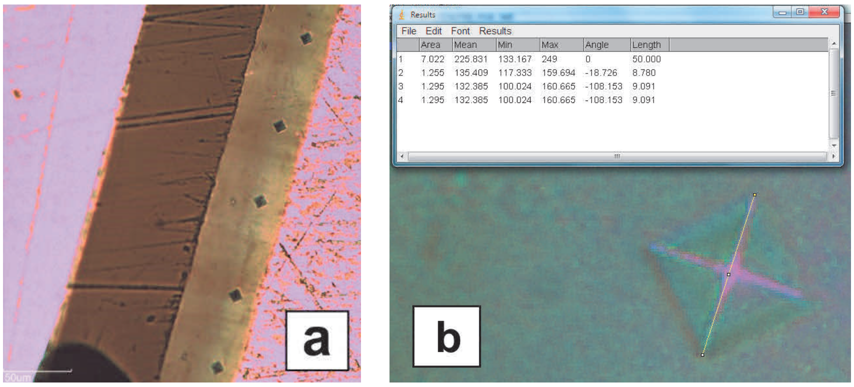

Figure 3 (a) Vickers indentation imprint at 0.3 N for the sample 2, (b) example measurement of diagonals performed in ImageJ software

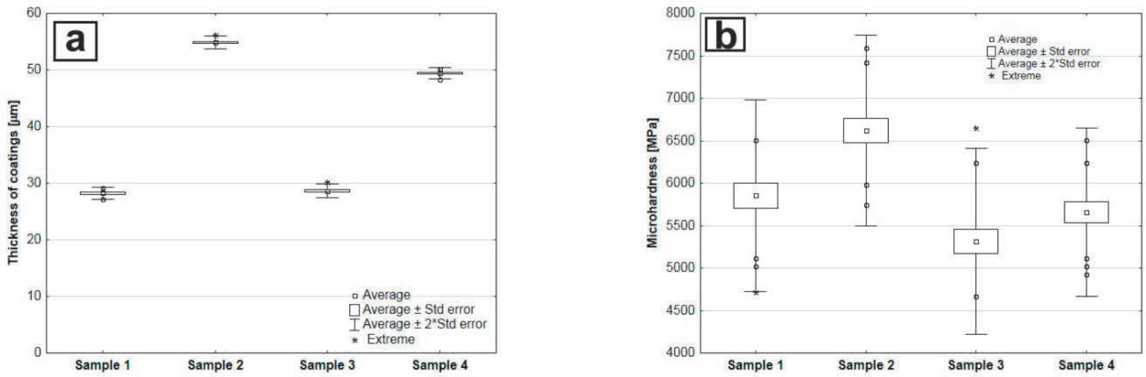

Figure 4 The thickness (a) and the micro-harness (b) of oxide coatings

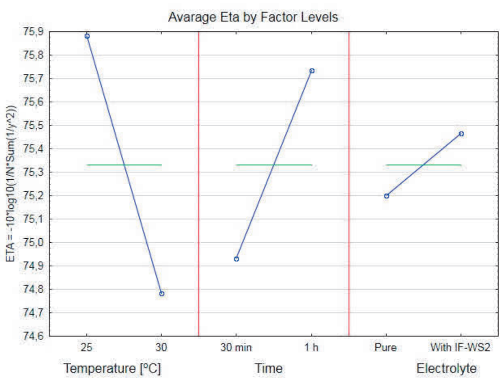

Figure 5 Analysis of effects of control parameters on S/N ratio

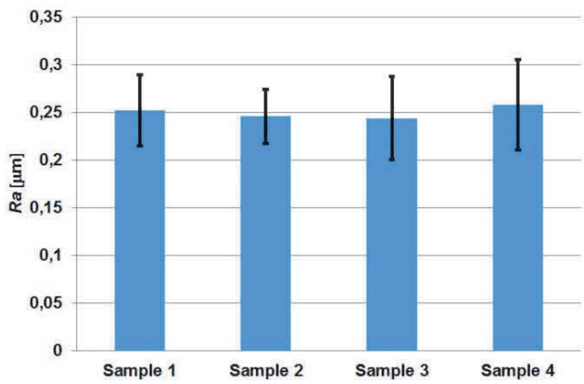

Figure 6 The surface roughness parameters *Ra*

The results of micro-harness and thickness of coatings are presented in **Figure 4**. Thickness of coatings strongly depends on time of electrolysis. For samples 1 and 3 the values was ~28 μm and ~29 μm respectively and for samples 2 and 4 the values was ~55 μm and ~50 μm respectively, which was expected (**Figure 4b**). Take into consideration the fact mentioned above the micro-hardness of the coating could be compared. From the applications point of view in oxide coatings the high micro-hardness is required, therefore the S/N ratio calculation according „larger the better“ was used. The results of effects on S/N ratio are shown in **Figure 5**.

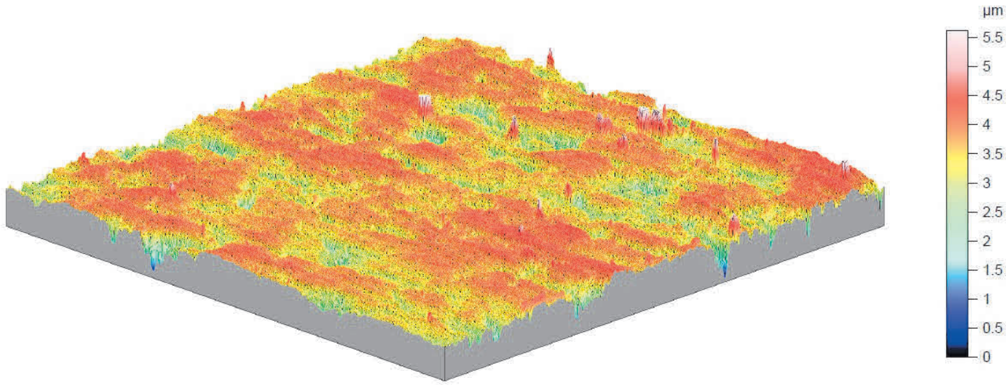

Figure 7 Example of isometric image of surface layers -sample 2 (b)

The great significance of temperature and then time is observed. Moreover Taguchi method could be also used for proposing the expected S/N ratio under optimum conditions of technological route (**Table 2**).

Table 2 Expected S/N Ratio under optimum condition

	Expected S/N Ratio under optimum condition Average= 75.33 Sigma =0.80	
Factor	**Level**	**Effect size**
Temperature	25°C	0.550
Time	1h	0.402
Electrolyte	With IF-WS_2	0.132
Expected S/N		76.42

In order to comprehensive analysis of the properties of the Al_2O_3 and Al_2O_3/IF-WS_2 surface layers the results of *Ra* roughness parameters were shown in **Figure 6**. According to bar graph the values of *Ra* were comparable within the limits of error regardless of technological parameters. In **Figure 7** the example of isometric image of surface layers was shown.

5. CONCLUSIONS

The Al_2O_3 and Al_2O_3/IF-WS_2 surface layers were obtained in a three-component’ SAS electrolyte. The *Ra* roughness parameters of obtained coatings were comparable within the limits of error. The thickness of coatings depends on time of electrolysis. The extend anodizing time has influence on the increasing of the mean square area of the pores. Taguchi statistical method was carried out and showed that the great significance influence on micro-hardness has the temperature and then time. The expected S/N ratio showed that the optimum conditions are: temperature and time of electrolysis 25°C and 1 h respectively and electrolyte with IF-WS_2. The results and recognized problems appear to be useful for similar problems in research [17] and industrial area [18,19].

REFERENCES

[1] CRISTÓBAL, M.J., FIGUEROA, R., MERA, L. and PENA, G. Tribological behaviour of aluminium alloy AA7075 after ion implantation, *Surface & Coatings Technology.* 2012. Vol. 209, pp. 124-130.

[2] LEE, J., SHIN, S., JIANG, Y., JEONG, C., STONE, H.A. and CHOI, C.-H. Oil-Impregnated Nanoporous Oxide Layer for Corrosion Protection with Self-Healing*, Advanced Functional Materials*. 2017. Vol. 27, Issue 15, 1606040

[3] TUA, J.P., JIANG, C.X., GUO, S.Y., ZHU, L.P., FU, F.M. and ZHAO, X.B. Friction and wear properties of aligned film of amorphous carbon nanorods on anodic aluminum oxide template in vacuum, *Surface & Coatings Technology*. 2005. Vol.198, pp.464- 468.

[4] CHOUDHARY, R.K., MISHRA, P., KAINA, V., SINGH, K., KUMAR, S. and CHAKRAVARTTY, J.K. Scratch behavior of aluminum anodized in oxalic acid: Effect of anodizing potential. *Surface & Coatings Technology*. 2015. Vol. 283, pp.135-147.

[5] DEJUN, K., JINCHUN, W. and HAO, L. Friction and wear performances of 7475 aluminium alloy after anodic oxidation. *Rare Metal Materials and Engineering*. 2016. Vol. 45(5), pp.1122-1127.

[6] TSYNTSARU N., KAVAS B., SORT J., URGEN M. and CELIS J.-P. Mechanical and frictional behaviour of nano-porous anodised aluminium. *Materials Chemistry and Physics*. 2014. Vol. 148, pp.887-895.

[7] HILTY, R. D. and MASUR, L.J. On the Formation of Lightweight Nanocrystalline Aluminum Alloys by Electrodeposition. *The Minerals, Metals & Materials Society*. 2017. Vol. 69, No. 12, pp. 2621-2625.

[8] QI, J.-T., HASHIMOTO, T., WALTON, J.R., ZHOU, X., SKELDON P. and THOMPSON, G.E. Trivalent chromium conversion coating formation on aluminium. *Surface & Coatings Technology*. 2015. Vol. 280, pp.317-329.

[9] ZHONG, Xin, WU, Xiaosong, JIA, Yuyu and LIU, Yali. Self-repairing vanadium-zirconium composite conversion coating for aluminum alloys. *Applied Surface Science.* 2013. Vol. 280, pp.489-493.

[10] RENAUD, A., BONNAUD, L., DUMAS, L., ZHANG, T., PAINT, Y., FASANO, F., KULYK, O., POSPISILOVA, E., NYSTEN, B., DELCORTE, A., BONIFAZI, D., DUBOIS, P., OLIVIER, M.-G. and POORTEMAN, M. A benzoxazine/substituted borazine composite coating: A new resin for improving the corrosion resistance of the pristine benzoxazine coating applied on aluminum. *European Polymer Journal.* 2018. Vol. 109, pp. 460-472.

[11] LEE, Ch.-H., LEE, Y.-B., KIM, K.-M., JEONG, M.-G. and LIM, D.-S. Electrically conductive polymer composite coating on aluminum for PEM fuel cells bipolar plate. *Renewable Energy*. 2013. Vol. 54, pp. 46-50.

[12] KMITA, T. and BARA, M. Surface oxide layers with an increased carbon content for applications in oil-less tribological systems. *Chemical and Process Engineering*. 2012. Vol. 33 (3), pp. 479-486**.**

[13] BARA M., SKONECZNY W. and KAPTACZ S. Tribological properties of ceramic-carbon surface layers obtained in electrolytes with a different graphite content. *Maintenance and Reliability*. 2008. Vol. 4, pp. 66-70.

[14] KMITA T., SZADE J. and SKONECZNY W. Gradient oxide layers with an in-creased carbon content on an EN AW-5251 alloy”. *Chemical and Process Engineering*. 2008. Vol. 2, pp. 375-387.

[15] ZHANG, D., DONG, G., CHEN, Y. and ZENG, Q. Electrophoretic deposition of PTFE particles on porous anodic aluminum oxide film and its tribological properties. *Applied Surface Science.* 2014. Vol. 290, pp.466-474.

[16] LEE G.-S., CHOI, J.H., CHOI, Y.C., BU, S.D. and LEE, Y.-Z., tribological effects of pores on an anodized Al alloy surface as lubricant reservoir. *Current Applied Physics*. 2011. Vol. 11, pp. S182-S186.

[17] SZCZOTOK, A., RADEK, N. and DWORNICKA, R. Effect of the induction hardening on microstructures of the selected steels. In METAL *2018: 27th Int. Conf. Metallurgy and Materials*. Ostrava: TANGER, 2018, pp. 1264-1269.

[18] OPYDO, M., KOBYLECKI, R., DUDEK, A. and BIS, Z. The effect of biomass co-combustion in a CFB boiler on solids accumulation on surfaces of P91 steel tube samples. *Biomass & Bioenergy* 2016, vol. 85, pp.61-68.

[19] BĄKOWSKI, H. Wear mechanism of spheroidal cast iron piston ring-aluminum matrix composite cylinder liner contact. *Archives of Metallurgy and Materials* 2016, vol. 63 (1), pp. 481-490