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The effect of sulfuric acid on pore initiation in anodic alumina formed in oxalic acid

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Abstract

In this work, a tracer study on pore initiation in anodic alumina in oxalic acid was performed. Effects of some experimental parameters such as applied electrical potential, electrolyte composition and heat pretreatment were evaluated. Electrochemical and morphological experiments were performed using potentiostatic anodizing and scanning electron microscopy (SEM) techniques, respectively. Effect of electrolyte composition on current density was discussed. In various electrical potentials, electrolyte composition had different effects on current density. Addition of sulfuric acid into oxalic acid increased porosity. Also, distribution of pore size and pore diameter were influenced by presence of sulfuric acid. Effect of electrolyte composition on the morphology of aluminum surface layer depended on the electric potential. Current density and porosity of aluminum surface layer was decreased by heat pretreatment.

Keywords: Thin films, anodized aluminum oxide, porosity, electrolyte composition

Introduction

Aluminium anodizing is an electrochemical process in which a porous oxide layer is produced by anodic oxidation of aluminum metal in an electrolytic solution and simultaneous electric field-assisted chemical etching of the resultant oxide. Anodization of aluminum surfaces for protection or decoration has been

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employed commercially for at least 80 years [1]. The interest in these porous structures has been recently increased to the emerging field of nanotechnology. The nanoporous materials provide an ideal structure for the possible growth of nanowires and thus provide order and structure in an otherwise chaotic regular nanowire growth pattern [2]. Besides, current density, electrical potential, sample surface condition and electrolyte composition are also important factors that deeply influence the film morphology. For example, two or more different electrolytes are often mixed to serve as a new electrolyte, by which the morphology and property of the produced film can be improved [3-6]. As for the acidic electrolytes, they can be classified into two sorts: one is inorganic acid solution such as sulfuric, phosphoric as well as chromic acid; the other is organic carboxylic acid solution including oxalic, malonic, tartaric and citric acid, etc. Compared to the inorganic acid electrolyte, the acidity of organic carboxylic acid electrolyte is relatively weak. Moreover, the carboxylic acid electrolyte usually presents evident viscosity that can additionally influence the anodization to a large extent [7,8]. So, the anodization in organic acid electrolyte differs greatly from that carried out in inorganic acid electrolyte exhibiting its own particular characters. Triangular and densely arranged anodic alumina nanoporous structures with a periodicity constant ranging from about 50 to 500 nm can be fabricated by anodization of aluminum carried out in sulfuric, oxalic and phosphoric acids [9-16]. Typical dimensions of the anodic aluminum oxide nanohole array under self-organization conditions depend on the electrolyte and applied anodizing potential. Moreover, the anodizing electrolyte is related to a specific range of anodizing potential and corresponding inter-pore distance of the porous anodic alumina film. For aluminum anodizing, performed in oxalic acid, applicable potential range should be between 30 and 100 volts. Highly regular pore structures can be formed only in a quite narrow processing window, different for each anodizing electrolyte. For example, the optimal potential for long-range ordering is 25 volt in sulfuric acid, 40–45 volts in oxalic acid, and 195 volt in phosphoric acid electrolyte [9]. In recent years, mixed electrolytes such as oxalic/chromic acid [17], nitric/sulfuric acid and boric/sulfuric acid [18,19], instead of single electrolytes, were investigated. The improved mechanical properties of oxide layer obtained on aluminum in mixed oxalic/sulfuric acid electrolyte were studied using experimental design [20-23]. Based on author's knowledge, pore initiation study for anodic alumina oxide nanoporous structure formation in mixture of oxalic/sulfuric acid electrolyte was not reported. Pore initiation stage has a critical role in characteristics of anodic alumina nanoporous structure [24]. Therefore، the effect of sulfuric acid on pore initiation stage in oxalic acid was presented in this work.

Experimental

General

Aluminium sheets (99.99% purity, 300 µm thick) were used in order to grow anodic porous layers. High purity metal was preferred in order to minimize breakdown phenomena and the formation of flaws or cracks in the porous matrix. Prior to anodizing, the samples were degreased with acetone and then washed with deionized water. Anodization was performed in a two-electrode cell with an aluminum sheet as the cathode. The electrolyte was agitated at constant rate in all experiments. The exposed sample surface area was 2 cm^2 and the rest sample surface was coated with insulting glue. Anodization was performed under a potentiostatic mode in oxalic acid solutions with different concentrations. The electrolytes were prepared with analytical grade oxalic acid and deionized water. The current response was recorded against the anodizing time. For the purpose of comparison, the anodization in presence of different concentrations of sulfuric acid in oxalic acid solution was also performed. The applied potentials are set at 5 - 40 volts. Heat pretreatment of aluminum sheets was carried out in air for 1 h at 200 $^{\circ C}$. The film structure was evaluated with a field-emission scanning electron microscope (Oxford، ZEISS). The film was made conductive by deposition with sputtering of an extremely thin layer of gold on its surface.

Results and discussion

Anodizing of aluminum samples was performed in oxalic acid bath at different experimental conditions to analyze their influence. Since the aim of this study is to obtain the relationship between pore initiation stage and experimental parameters, effectiveness of these variables was assessed by analyzing current transients and alumina layers morphology at different experimental conditions.

Electrochemical studies

Anodizing aluminum samples in 0.3 M oxalic acid solution can lead to a well-ordered nanopore structure even at room temperature. Therefore, potentiostatic anodizing was performed at room tempetature.

Effect of potential

To investigate the influence of applied potential on characteristics of current transients, four series of anodizations were performed at 20, 30, 40 and 50 volts. At each potential, the four stages of the porous structure development under anodizing potentials are shown from the current density–time curves in Figure 1. A high electric field at the commencement of anodizing at constant potential leads to a relatively large current surge. This increasing current falls to a low value (i_{min}) when the barrier layer is formed. Pores have been considered [25] to be initiation in this decreasing current stage and their growth is believed to take place in the next stage, i.e. by the time the current has risen and steadied out. As shown in Figure 1, the current densities at 40 and 50 volts were higher than the current densities at 20 and 30 volts. As mentioned above, highly regular pore structures can be formed only in a quite narrow processing window of applied electrical potentials. In oxalic acid electrolyte, these potentials are greater than 40 volts. Therefore, it was expected that pore initiation stage was accrued in these potentials. On the other hand, high current densities, high electrode and electrolyte temperatures, long duration of anodizing and electrolyte composition may be caused burning at the surface of aluminum [26]. Therefore, anodizing at lower potentials with appropriate current densities can be achieved by using mixing electrolytes.

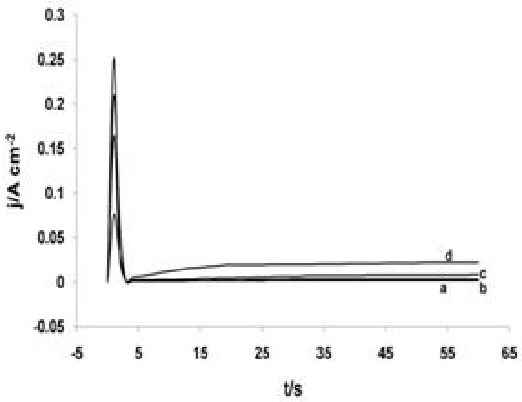

Figure 1. Anodizing current density– time transients at, a (20), b (30), c (40) and d (50) V in a solution containing 0.3 M oxalic acid

The effect of electrolyte composition

The most influential factor in the performance of inorganic acids during anodizing process is their acidity that depends on their concentration. In the case of organic acids, their viscosity has critical role [27]. The effect of electrolyte composition was studied at 20, 30 and 40 volts. At higher electrical potentials than these voltages, due to the addition of sulfuric acid to the electrolyte, the surface of electrode burns. On the other case at lower potentials, we did not observe any effect. In each potential, anodizing was performed in solutions containing various amounts of oxalic and sulfuric acids. Figure 2 shows the current densities transients at 40 volts in three different composition electrolytes. It was concluded from Figure 2 that in presence of sulfuric acid (Figure 2(c)), current density increased about 160.87%. Dilution, with increasing of deionized water, decreased the current density (Figure 2(b)). Dilution has two outcomes, decreasing of concentration of sulfuric/oxalic acids and viscosities of oxalic acid, these effects have different influences on the current density. With the decrease of viscosity of oxalic acid, it is expected that current density would increase [27]. On the other hand, current density may decrease due to the decrease of acidity. It seems that the decrease of acidity was our influential parameter. The effect of electrolyte composition on the surface layer morphology will be discussed in the following sections.

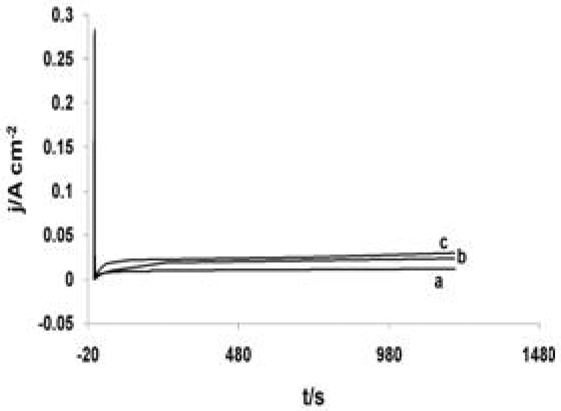

Figure 2. Anodizing current density– time transients at 40 V in solutions containing: a (0.3 M oxalic acid), b(0.15 M oxalic acid + 0.011 M sulfuric acid), c (0.3 M oxalic acid + 0.022 M sulfuric acid)

The effect of electrolyte composition on the current density at 30 volts was presented in Figure 3. It was revealed that addition of sulfuric acid increased the current density to about 191% at 30 volts (Figure 3(c)). Similar behaviors were observed at 30 volts. The only difference was the amount of sulfuric acid.

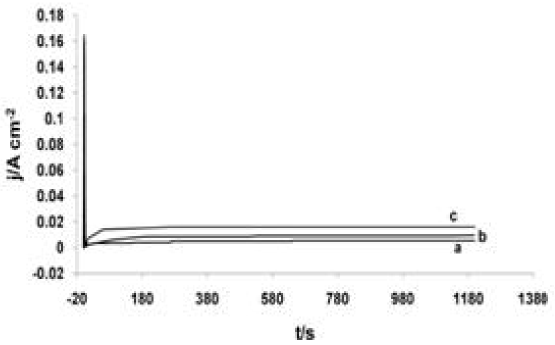

Figure 3. Anodizing current density– time transients at 30 V in solutions containing: a (0.3 M oxalic acid), b(0.15 M oxalic acid + 0.017 M sulfuric acid), c (0.3 M oxalic acid + 0.034 M sulfuric acid)

Figure 4 shows the current densities transients at 20 volts in different electrolytes. With the increase of sulfuric acid, the current densities will increase to about 387.5% (Figure 4(b)). Unlike what was observed at 30 and 40 volts, the current density was increased due to dilution (Figure 4(c)). Furthermore, in the absence of oxalic acid, the current density increased (Figure 4(d)). According to our observations, it was concluded that viscosity of oxalic acid decrease was the most significant parameter at 20 volts. On the other hand, aluminum anodizing process analysis at 20, 30 and 40 volts revealed that in these potentials, electric field-assisted chemical etching has different rates. At 20 volts, due to low rate of electric field-assisted chemical etching, decreasing of viscosity of oxalic acid could increase the current density. However, at 30 and 40 volts, due to the high rate of electric field-assisted chemical etching, dilution could decrease the current density. Accordingly, it was concluded that with mixing of electrolyte, appropriate current densities in relative low potentials could be achieved.

The effect of heat pretreatment

In pore initiation studies, the characteristics of surface layer has critical role. Therefore, the effect of electrolyte composition was studied at heated pretreatment surfaces. Figure 5 shows the current density transients at heated pretreatment surfaces in experimental conditions similar to Figure 2. Considerable decrease in current densities was observed. It seems clear that this decrease is caused by changes in the surface structures. Both pre- and post-heat-treatment at temperatures could induce the formation of crystalline γ′-Al_2O_3 in the outer layer of anodized oxide and consequently it will increase the relative dielectric constant of the film. The differences in the morphology and crystalline characteristics between the anodized oxide subjected to pre- and/or post-heat-treatments led to variations in the electrochemical properties. The pre-heat-treatment could economize the required charge to anodize the oxide and retard the growth of film thickness during anodizing. Thermal-induced phase transformation from amorphous to crystalline oxide of the anodized film, due to post-heat- treatment, could leave some defects and substantially decrease the electrical resistance of the oxide layer [28]. The effect of heat pretreatment on morphology and porosity of surface layer will be discussed in the next section.

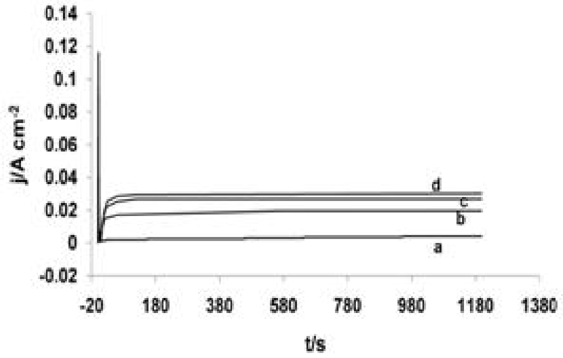

Figure 4. Anodizing current density– time transients at 20 V in solutions containing: a (0.3 M oxalic acid), b (0.3 M oxalic acid + 0.727 M sulfuric acid), c(0.15 M oxalic acid + 0.363 M sulfuric acid), d(0.727 M sulfuric acid)

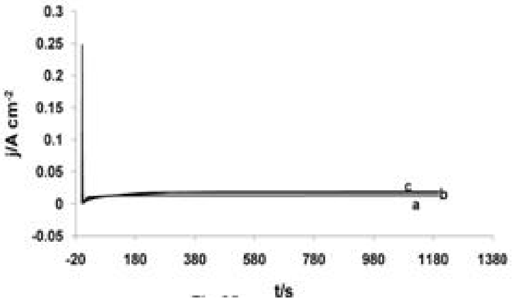

Figure 5. Anodizing current density– time transients at heated pretreatment surfaces in solutions containing: a (0.3 M oxalic acid), b(0.15 M oxalic acid + 0.011 M sulfuric acid), c (0.3 M oxalic acid + 0.022 M sulfuric acid) at 40 V

Morphological studies

The structure of anodic aluminum oxide can be described as a close-packed hexagonal array of parallel cylindrical nanopores perpendicular to the surface on top of the underlying Al substrates. The pore structures are characterized by parameters such as: pore organization (hexagonal), pore diameter, interpore distance (cell diameter), wall thickness, and pore length and barrier layer thickness. All these properties are influenced by formation of pores. The effect of sulfuric acid on pore initiation stage at surface of aluminum at 40 volts was presented in Figure 6. The increase in porosity was considerable. Growth of these initial pores during the anodizing process could be significant. Figure 7 shows pore size distribution diagrams calculated from FE-SEM top-view images (Figure 6). It was concluded from Figure 7 that distribution of pore size and pore diameter were influenced by the presence of sulfuric acid. It is noticeable that adding sulfuric acid has similar effect on the pore size distribution at 30 volts.

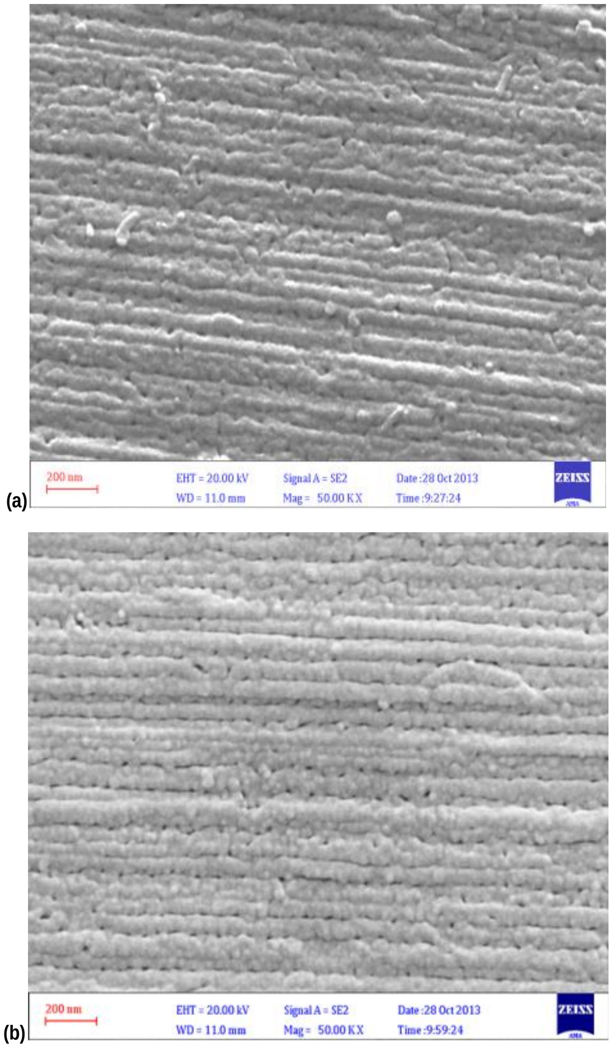

Figure 6. Top-view FE-SEM images of aluminum surfaces anodized in solutions containing: a (0.3 M oxalic acid), b (0.3 M oxalic acid + 0.022 M sulfuric acid) at 40 V

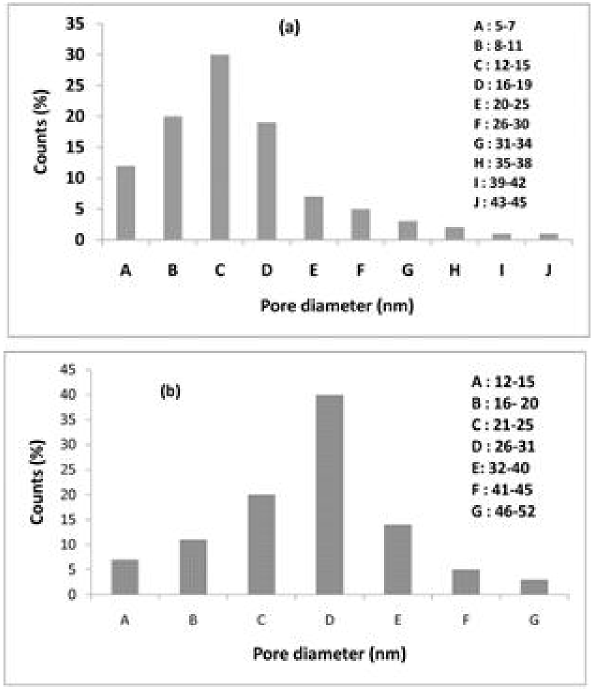

Figure 7. Pore size distribution diagrams of anodized aluminum in: a (0.3 M oxalic acid), b (0.3 M oxalic acid + 0.022 M sulfuric acid) at 40 V

In order to investigate the effect of potential on the morphology of aluminum surface, top-view FE-SEM images of aluminum surfaces anodized at 20 volts was shown in Figure 8. In this case, the pores were smaller than the case of 40 volt. It seems that pores are formed in the initial stages. Therefore, it can be concluded that pore size distribution was not affected by the addition of sulfuric acid at 20 volts. It seems that performance of the electrolyte was depended on the electric potential. The effect of heat pretreatment on the morphology of surface layer was shown in Figure 9. Comparison of Figure 9 and Figure 6(b) revealed that the porosity of surface layer was decreased by heat pretreatment.

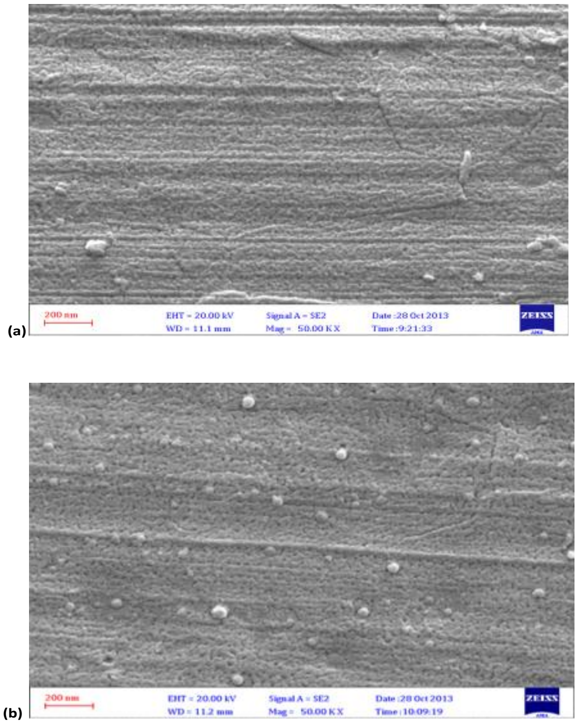

Figure 8. Top-view FE-SEM images of aluminum surfaces anodized in solutions containing: a (0.3 M oxalic acid), b (0.3 M oxalic acid + 0.727 M sulfuric acid) at 20 V

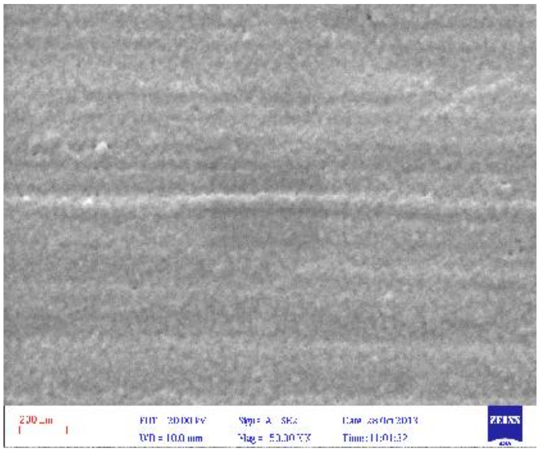

Figure 9. Top-view FE-SEM images of heated pretreatment surfaces in solutions containing (0.3 M oxalic acid + 0.022 M sulfuric acid) at 40 V

Conclusion

The effect of sulfuric acid on the pore initiation stage of aluminum anodizing in oxalic acid bath was studied by potentiostatic anodization. Electrochemical experiments were followed by morphological examination by SEM. The following conclusions can be made.

In the process of anodizing by mixing of electrolyte, appropriate current densities in relative low potentials can be achieved.

[1] In various electrical potentials, electrolyte composition has different effects on the current density.

[2] In oxalic bath, distribution of pore size and pore diameter were influenced by the presence of sulfuric acid.

[3] The effect of electrolyte composition on the morphology of aluminum surface layer is depended on the electric potential.

[4] Current density and porosity of aluminum surface layer was decreased by heat pretreatment.

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References

[1] Anodisation of aluminium: New applications for a common technology. Nano Wizard Application Report, Cambridge, UK, September **2003**.

[2] A.M.M. Jani, D.Losic, N.H. Voelcker, *Prog. Mat. Sci.*, **2013**, *8*,636-704.

[3] S. Mezlini, K. Elleuch, S. Fouvry, Ph. Kapsa, *Surf. Coat. Technol.*, **2006**, *200*, 2852-2856.

[4] V. Lopez, E. Otero, A. Bautista, J.A. Gonzalez, *Surf. Coat. Technol.*, **2000**, *124*, *76*-84.

[5] A. Jagminas, D. Bigeliene, I. Mikulskas, R. Tomasiunas, *J. Cryst. Growth.*, **2001**, *233*, 591-598.

[6] O. Lunder, J.C. Walmsley, P. Mack, K. Nisancioglu, *Corros. Sci.*, **2005**, *47*, 1604-1624.

[7] R. Giovanardi, C. Fontanesi, W. Dallabarba, *Electrochim. Acta.*, **2011**, *56, 3128*-3138.

[8] W. Lee, K. Nielsch, U. Go◌sele, *Nanotechnology.*, **2007**, *18*, 475713(8pp).

[9] G.D. Sulka, in: A. Eftekhari (Ed.), Nanostructured Materials in Electrochemistry, Wiley-VCH, Weinheim, **2008**, p. 1.

[10] G.D. Sulka, S. Stroobants, V. Moshchalkov, G. Borghs, J.P. Celis, *J. Electrochem.Soc.*, **2002**, *149*, D97-D103.

[11] G.D. Sulka, S. Stroobants, V. Moshchalkov, G. Borghs, J.P. Celis, *J. Electrochem. Soc.*, **2004**, *151*, B260-B264.

[12]G.D. Sulka, M. Jaskuła, *J. Nanosci. Nanotechnol.*, **2006**, *6*, 3803-3811.

[13] G.D. Sulka, K. Parkoła, *Thin Solid Films.*, **2006**, *515*,338-345.

[14] G.D. Sulka, K.G. Parkoła, *Electrochim. Acta*., **2007**, *52*, 1880-1888.

[15] G.D. Sulka, W.J. St˛epniowski, *Electrochim. Acta.*, **2009**, *54*, 3683-3691.

[16] L. Zaraska, G.D. Sulka, M. Jaskuła, *J. Phys. Conf. Ser.*, **2009**, *146*, 1-6.

[17] V. Moutarlier, M.P. Gigandet, J. Pagetti, B. Normand, *Surf. Coat. Technol.*, **2004**, *182*, 117-123.

[18] H.H. Shih, S.L. Tzou, *Surf. Coat. Technol.*, **2000**, *124*, 278-285.

[19] L. Domingues, J.C.S. Fernandes, M.D.C. Belo, M.G.S. Ferreira, L.G. Rosa, *Corros. Sci.*, **2003**, *45*, 149-160.

[20] W. Bensalah, K. Elleuch, M. Feki, M. Wery, H.F. Ayedi, *Surf. Coat. Technol.*, **2007**, *201*, 7855-7864.

[21] W. Bensalah, K. Elleuch, M. Feki, M. Wery, H.F. Ayedi, *Mater. Des.*, **2009**, *30*, 3141-3149.

[22] W. Bensalah, K. Elleuch, M. Feki, M. Wery, H.F. Ayedi, *Mater. Des.*, **2009**, *30*, 3731-3733.

[23] W. Bensalah, M. Feki, M. Wery, H.F. Ayedi, *J. Mater. Sci. Technol.*, **2009**, *25*, 508-512.

[24] A. B. Wieche´c, M.G. Burke, T. Hashimoto, H. Liu, P. Skeldon, G.E. Thompson, H. Habazaki, J.J. Ganem, I.C. Vickridge, *Electrochim. Acta*., **2013**, *113*, 302-306.

[25] I.T. Kaplanoglou, S. Theohari , T. Dimogerontakis, Y.M. Wang, H.H. Kuo, S. Kia, *Surf. Coat. Technol*., **2006**, *200*, 2634-2641.

[26] T. Aerts, I. De Graeve, H. Terryn, *Surf. Coat. Technol*., **2010**, *204*, 2754-2760.

[27] J. Ren, Y. Zuo, *App. Surf. Sci.*, **2012**, *261*, 193-200.

[28] J.K. Chang, C.M.Lin, C.M. Liao, C.H.Chen, W.T.Tsai, *J. Electrochem. Soc.*, **2004**, *151*, B188-B194.