Enhancement of Anodic layer for Aluminum AA6061T6 by using Titanium Dioxide-Rutile Nanoparticles

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Abstract: -

In this paper, we studied the anodizing of aluminum alloy (AA6061T6) in the sulfuric acid (200 g /l) at ice bath. The anodizing layer obtained at various current densities. The best anodizing layer from these conditions modified by nano-TiO_2 Rutile which is added as dye by impregnation process. After obtained the best composite nano-anodizing layer the sealing process was done. The characterization of anodizing layer had carried out by Optical Microscope (OP), Scanning electron microscope (SEM), Microhardness, X-ray diffraction (XRD) and corrosion test was done in seawater. After sealing treatment with nano-TiO_2 powder of average particle size 25nm, corrosion resistance, wear resistance and hardness increased by 12% using direct HRF hardness.

Keywords: Anodizing, Aluminum, Nano-TiO_2, Rutile, AA6061T6.

1. Introduction

The anodizing of aluminum has the ability to promote some light metal in industry. By capitalizing on the natural phenomenon of passive film formation on aluminum in a production environment, the anodizing process has become synonymous with surface protection and durability of aluminum substrates. Anodizing can be viewed as the deliberate, controlled corrosion of the aluminum surface in sulfuric acid to yield a uniform, continuous protective oxide film. extensively studied, yet the mechanism of anodic oxidation of aluminum is still not fully established [1, 2].

The establishment of anodic film is very important for aluminum alloys to increase aluminum adhesive bonding parts, corrosion resistance and wear resistance. The porous anodic films will be made in chromic, oxalic, phosphoric and sulfuric acid Sulfuric anodizing provides corrosion resistance and is very durable. Typical applications include architecture, aerospace, manufacturing automotive and computers [3-5]. When high strength and good mechanical performance is required the 6061 aluminum alloy is the excellent in both and is outstanding for handled and mobile phones [6].

Maria Datcheva (2011) [7] worked on determination of anodized aluminum material characterization by means of nano-indentation measurements, discussed the role of temperature of electrolyte and sealing during formation of alumina films with change in their chemical composition and structure in sulfuric acid. Jude Mary Runge (2015) [8] studied enhancing anodic aluminum oxide for bonding applications for different additions of organic – inorganic and its reactions with anodic films, resulting in bonds with higher reliability. Soo Young Kang (2014) [9] studied on improvements of corrosion resistance and wear resistance by anodizing and sealing treatment with nano-diamond powder aluminum. After sealing with nano powder the corrosion and wear resistance increased.

The aim of the current research employed by impregnation of dye like solution contains of TiO_2-Rutile solution and sealing process for anodic layer of AA6061T6 aluminum alloy in order to enhance the mechanical and corrosion resistance as compare with the traditional anodizing.

2. Experimental work and Procedure

Aluminum 6061-T6 of (3mm sheet from AALCO Metals Limited, UK) was cut in disk shape samples with diameter (25.4mm). The samples were grounded one surface by various silicon carbide grit of emery paper and well-polished by using aqueous suspension of alumina grade 0.5 micron via light metal polish woven cloth for. The electrochemical cell consists of beaker 1000ml filled with sulfuric acid (98%) (Alfa Chemicals) and power supply with very fine adjustable current and voltage by using DC power supply features (PS-305DM 30V/5A, China). The cell as shown in Figure (1) consists of high purity lead as a cathode material with size (30×50mm) and the anode for the sample to be anodized. The AA6061-T6 samples where immersed in sodium hydroxide solution concentration (120g/l) for 2min. in order to buckling removal of oxidation or contamination on the surface, then immersed in deionized water and dried after spray alcohol were used. The sample then mounted with clamps in anode electrode and immersed the sample and the lead electrode in the sulfuric acid solution and applied various current density as shown in Table (1). The beaker where surrounded with ice bath to keep the operation temperate low as possible. Titanium Dioxide-Rutile (CAS No. 13463-67-7) nano-powder with average grain size 25nm, 99.9% purity used as sealing agent. The powder provided from Micxy Reagent, China.

The characterization for anodized layer were done by using various apparatus. XRD-6000 with Cukα (λ=1.5406A°) by Shimadzu company. The scanning electron microscope (SEM) model AIS2300C with 3.0 nm at 30kV, SERON Technologies Inc, Korea. AFM from PHYWE system, Germany, Electrochemical corrosion test (ECT) was used a Tafel extrapolation method by “Wenking Mlab with multi channels-Potentiostat and SCI-Mlab from Bank Electroniks-Intelligent control GmbH, Germany and optical microscope (OP) from Nikon Eclipse LV100N, Japan.

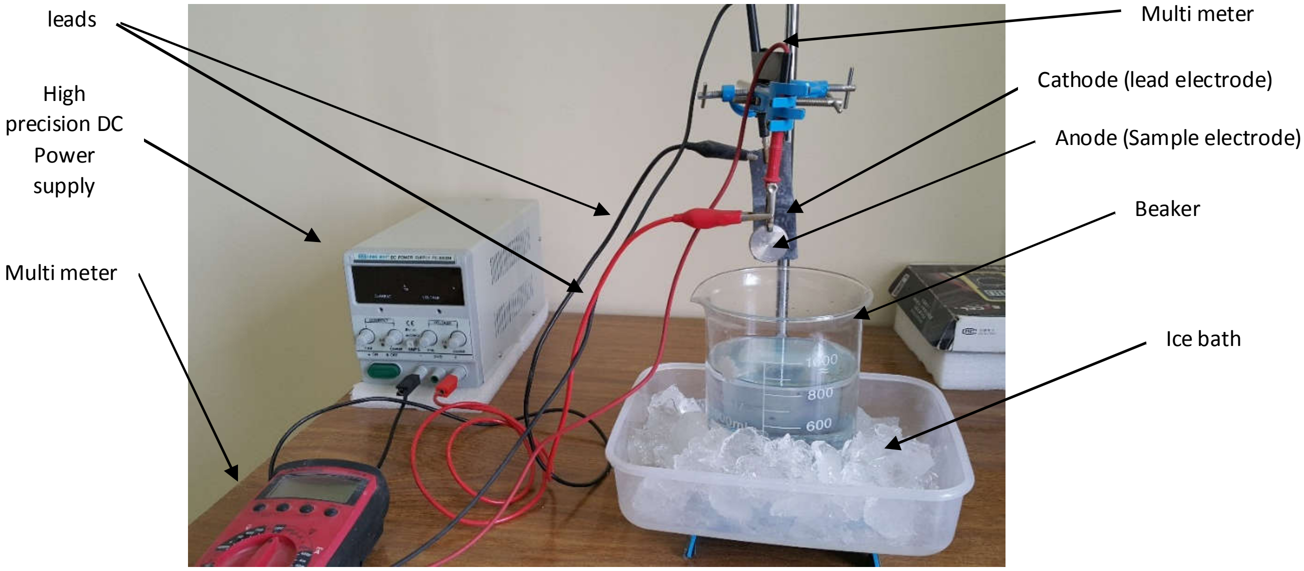


Fig. 1 The electrochemical cell used for anodizing research.

Table.1 Anodizing current and voltage variables.

Sample name	Applied current (Amp)	Voltage (volt), Initial/ final
A	1	15.6/13.6
B	1.2	21.9/16.9
C	1.5	20.4/16.7
D	1.8	18/15.7
E	2	16.8/15.2

Table. 2 Sealing process of anodic layer

Samples	Description
A1	Sample A with normal surface sealing via water
A2	Sample A with surface sealing by NPs of TiO_2-R

3. Results and Discussions

From figures (2-6) SEM cross section of the anodizing layers' thickness range between 3 to 25 µm, hard anodizing layer 25µm found in sample number A. The current was found 1 A and initial and final voltages were 15.6 V and 13.6V respectively in ice bath of 271g/80ml sulfuric acid as showing in Figure (1b), in Figure (1a) represent other side of sample which not polished, thus shows thin white layer in between anodizing layer and substrate which is represent a some of sulfate salts deposited in the grooves of rough surface. We can conclude that the well-polished surface with sodium hydroxide buckling very effective to obtain adherent anodizing layer. Increasing the current to (1.2A) has reverse effect of the anodizing layer which decreases to 14-16 µm also the final voltage increased slightly was clearly shown in Figure (2a-b). For 1.5A the initial voltage approximately stable but the anodizing layer seems containing with big porous voids instead of columnar pore structure that shown in Figures (3a-b).

Increasing the current 1.8A the applying voltage decrease due to breaking down the anodizing layer and with some sulfide salts started deposit with very thin about 8 µm anodizing layer (Figures (4a-b)). In Figure (5b) with elevated current to 2A the anodizing diminishes about 8 µm while very thin few microns in other side (Figure 5a) with participate sulfide salts within and above the anodizing layer, that confirm by dropping the initial applying voltage for the cell.

The sample A of anodized layer of 25 µm sealed by using traditional sealing technique in boiling water bath for 10 min. On other hand, other sample with similar anodizing conditions are immersed in titanium dioxide-rutile (TiO_2-R) nanoparticles (NP) 1gm/50ml in deionized water after sonication with low power sonicator 40kHz overnight followed by sealing by boiled the TiO_2-R solution for 10min. The NPs of TiO_2-R are capable by impregnation method [10] make it very excellent candidates used as absorbable materials. In Table 2 the shows two samples of sealing treatment. Initial surface test and characterization for functionalized anodizing sealing samples using ball-on-disk for wear test apparatus. The purpose to use this kind of test, to characterize the tracking ball bath as a comparison. The speed test was 80 rpm and 100g applying load. The OM found groove along the traveling direction (see Figure 7). Sample A2 of NPs of TiO_2-R sealing found a uniform ductile groove of 8mm steel ball created on the top surface and the hardness was 67HRF (Rockwell F-type-steel ball diameter 1/16 inches, 60kg load, for 5-7 impression) as shown in Figure 6a, while non-uniform with oxide layers' debris found in sample A1 as shown in Figure (7b) and the hardness was found 60HRF.

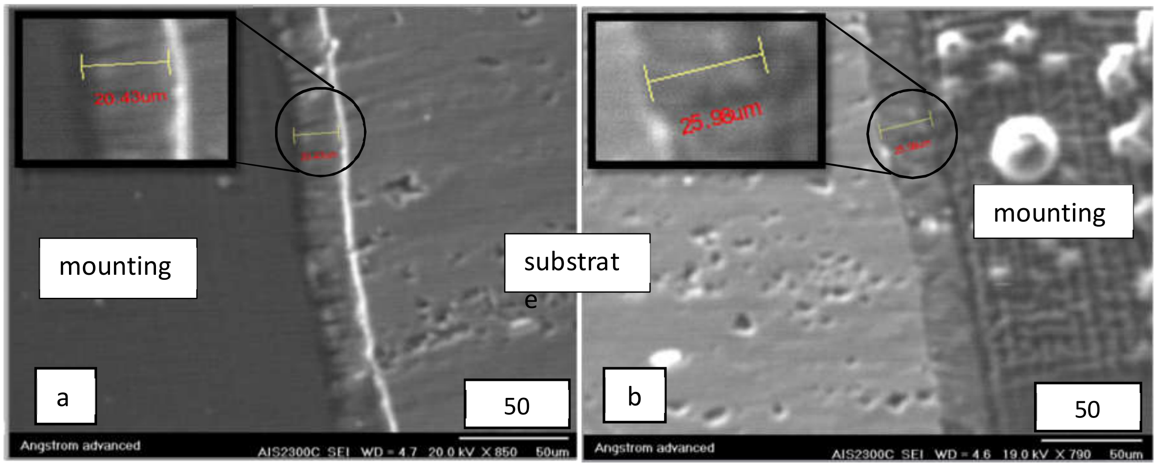


Fig. 2 SEM-Micrograph for sample (A) a cross-section of anodizing layer of AA6061T6, (a) the rough side, (b) well-polished side.

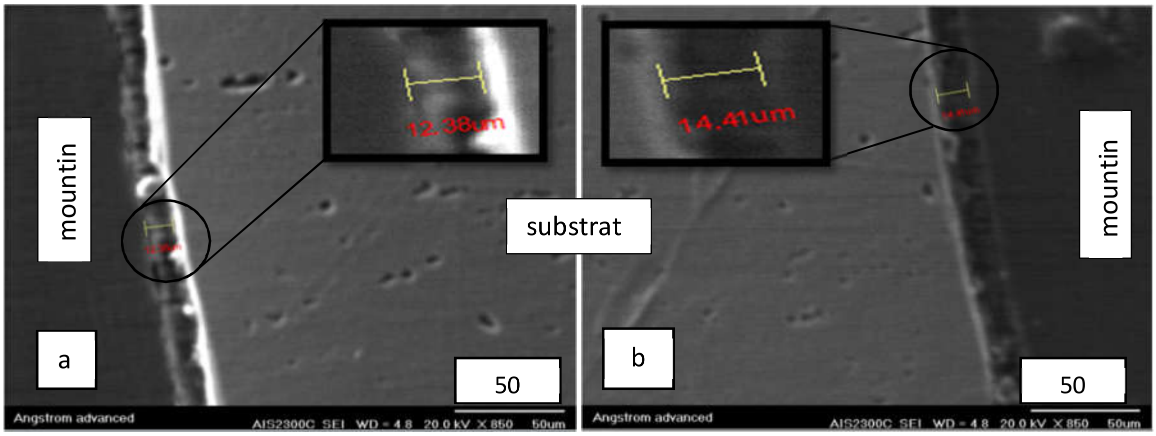


Fig. 3 SEM-Micrograph for sample (B) a cross-section of anodizing layer of AA6061T6, (a) the rough side, (b) well-polished side.

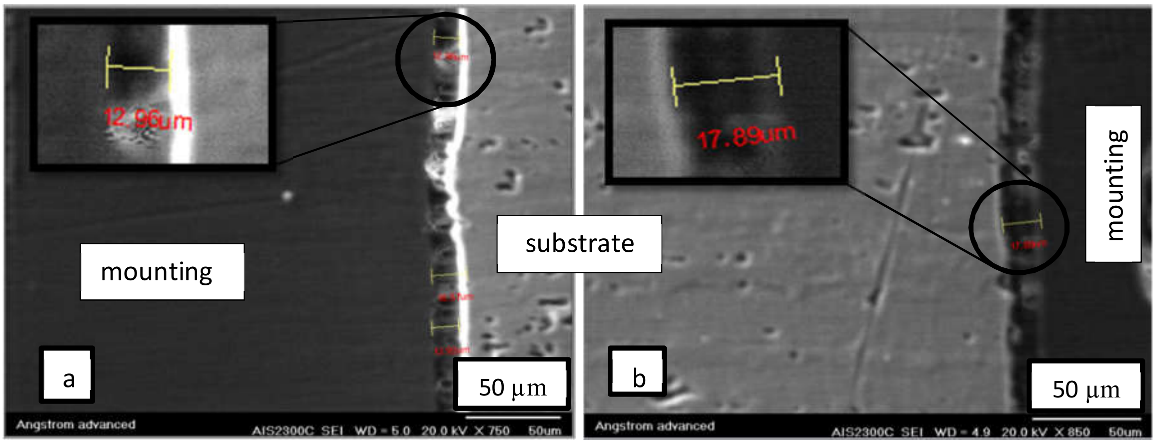


Fig. 4 SEM-Micrograph for sample (C) a cross-section of anodizing layer of AA6061T6, (a) the rough side, (b) well-polished side.

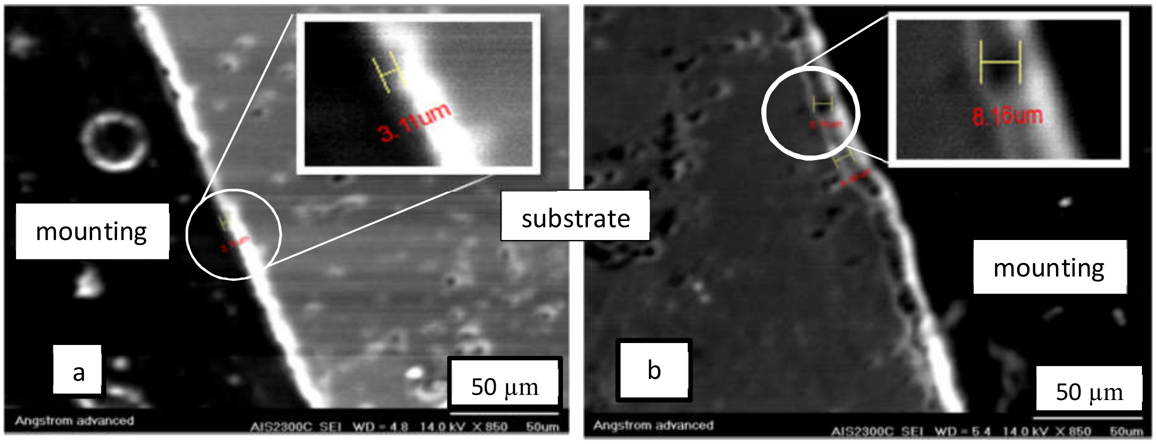


Fig. 5 SEM-Micrograph for sample (D) a cross-section of anodizing layer of AA6061T6, (a) the rough side, (b) well-polished side.

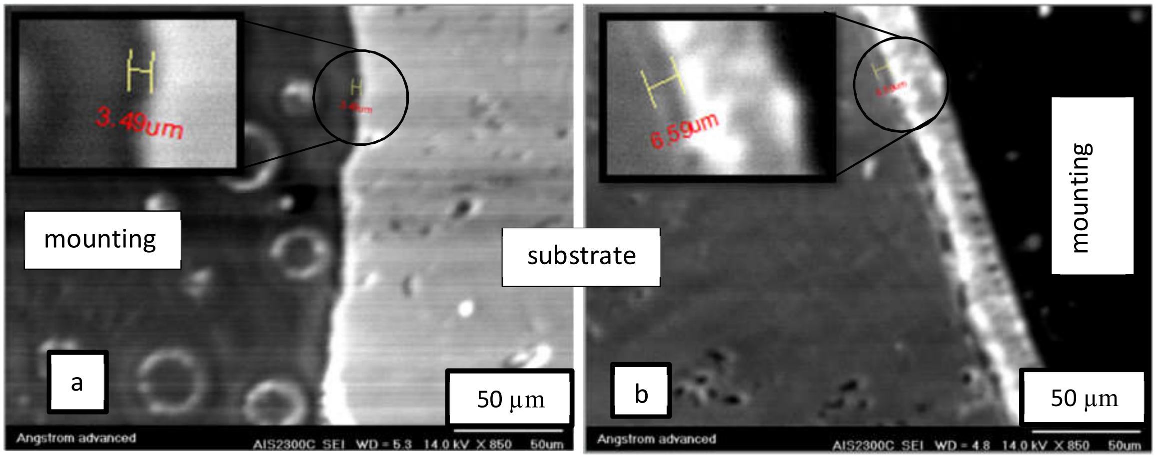


Fig. 6, SEM-Micrograph for sample (E) a cross-section of anodizing layer of AA6061T6, (a) the rough side, (b) well-polished side.

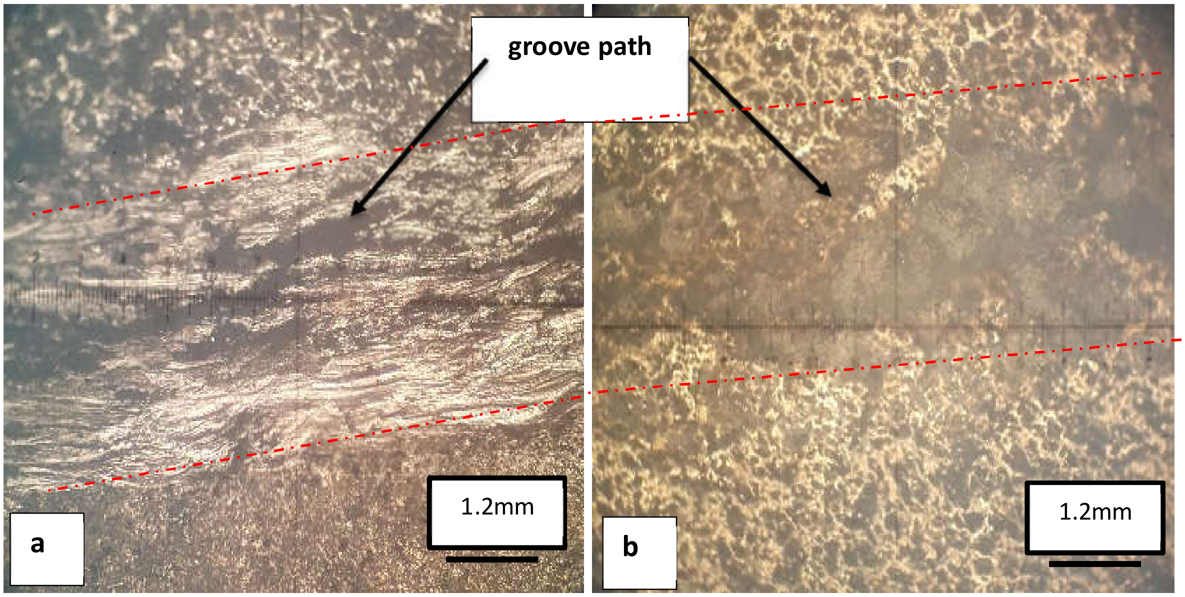
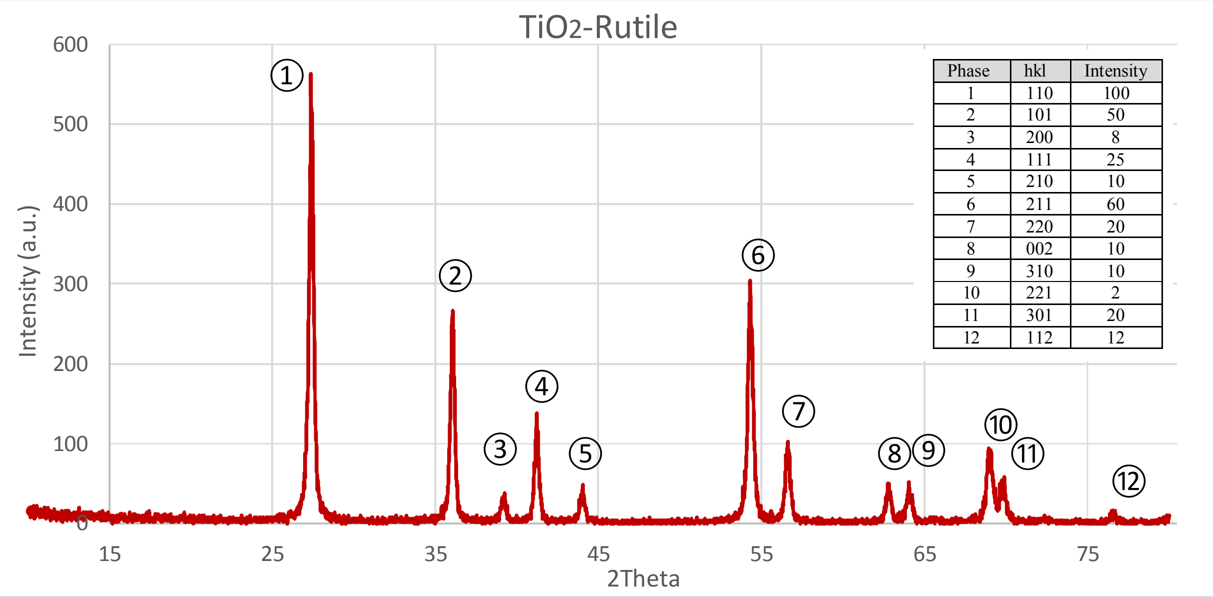


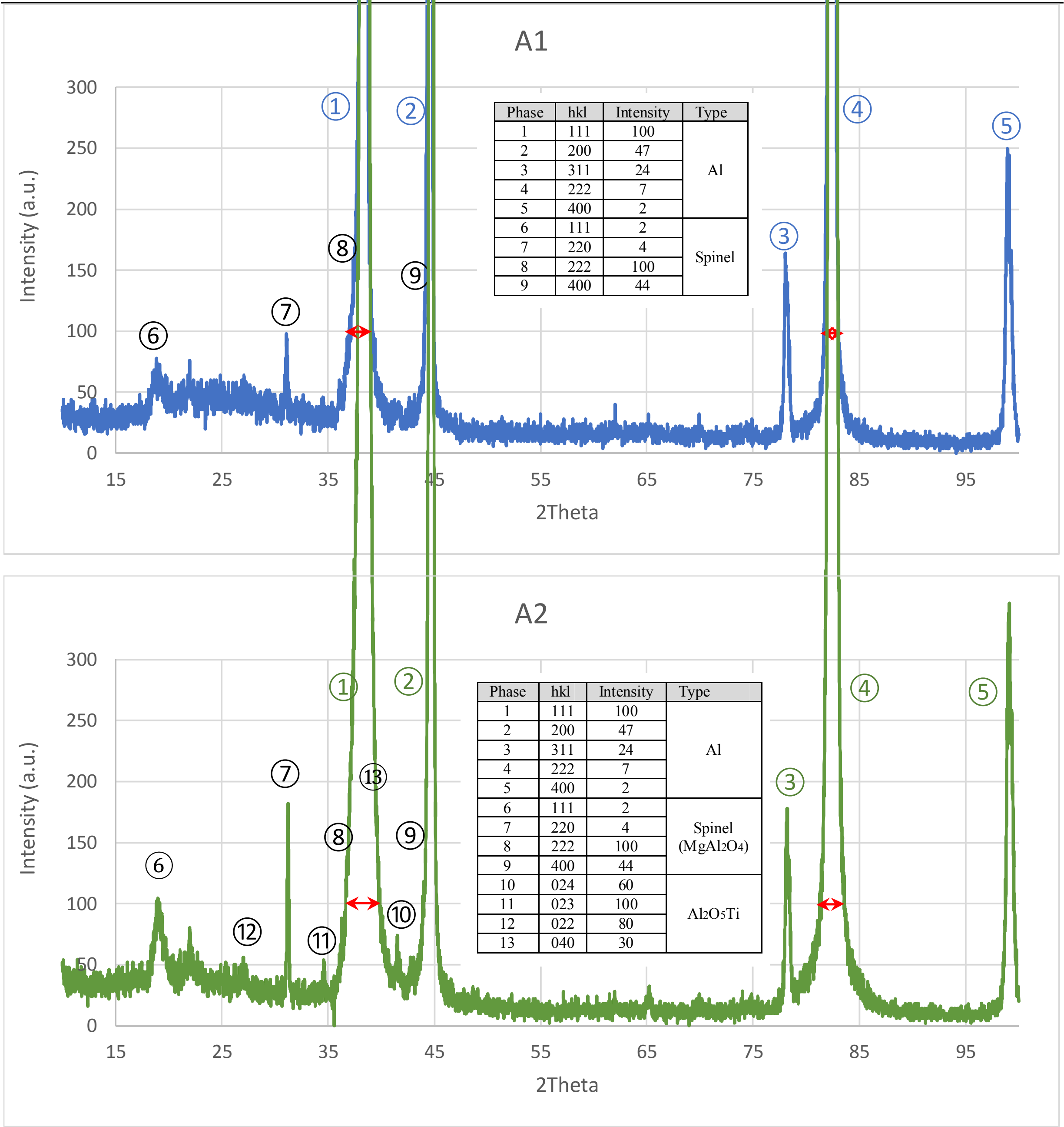
Fig.7 OM graph for samples A1 and A2 after wear groove path creation. On left (a) represent sample A2 and on the right (b) is sample A1.



Phase	hkl	Intensity
1	110	100
2	101	50
3	200	8
4	111	25
5	210	10
6	211	60
7	220	20
8	002	10
9	310	10
10	221	2
11	301	20
12	112	12

Fig. 8 XRD graphs for samples A1, A2 as comparing with TiO_2-Rutile powder.

XRD analysis for samples A1 and A2, where found very high characteristics peaks of aluminum, (111), (200) and (222) with small peak (311). On other hand, TiO_2-R Nano-powder has peaks (110), (101), (111), (211), (200) and (211) these three graphs shown in Figure 8 Figure 9 shows the combining graphs for samples A1 and A2. It is also noted that both lines of two samples are matches based on aluminum peaks. Boarding of A2 peaks than the A1 are notable, that because the peak contains Ti, O nanostructure which significantly boarding as influence of the lattice defects [11]. TiO2-R exhibits affinity to react with aluminum oxide during sealing bath. Aluminum titanium oxide Al_2Ti-O_5 phase generated as results of sealing process.



Phase	hkl	Intensity	Type
1	111	100	Al
2	200	47	
3	311	24	
4	222	7	
5	400	2	
6	111	2	Spinel
7	220	4	
8	222	100	
9	400	44	

Phase	hkl	Intensity	Type
1	111	100	Al
2	200	47	
3	311	24	
4	222	7	
5	400	2	
6	111	2	Spinel ($MgAl_2O_4$)
7	220	4	
8	222	100	
9	400	44	
10	024	60	Al_2O_5Ti
11	023	100	
12	022	80	
13	040	30	

Fig. 9 XRD graphs for samples A1, A2, the red diffraction lines indicate Aluminum Titanium Oxide Al2Ti-O_5 phase.

AFM has confirmed the sealing process with nano TiO_2-R. In Figure 10, topography for A1 sample has many small open pores and has large pores of average 5micron for traditional water bath sealing processes. Contrary, less small open pores with smoother surface exists in sample A2 that seen in Figure 11, as compared between both surfaces the surface roughness for TiO_2-R sealing treatment less than sample A1 which are Ra=318nm and Ra=185nm respectively.

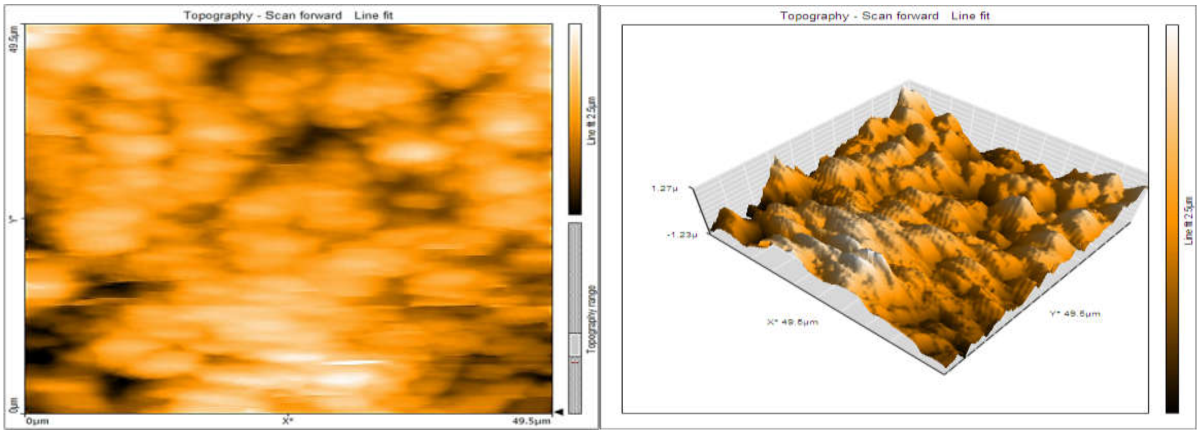


Fig. 10, AFM micrograph and topography for sample A1, in left graph 2D of pores exists after water bath sealing processes the average pores size is 5micron, In the right 3D of topography surface roughness (Ra=318nm).

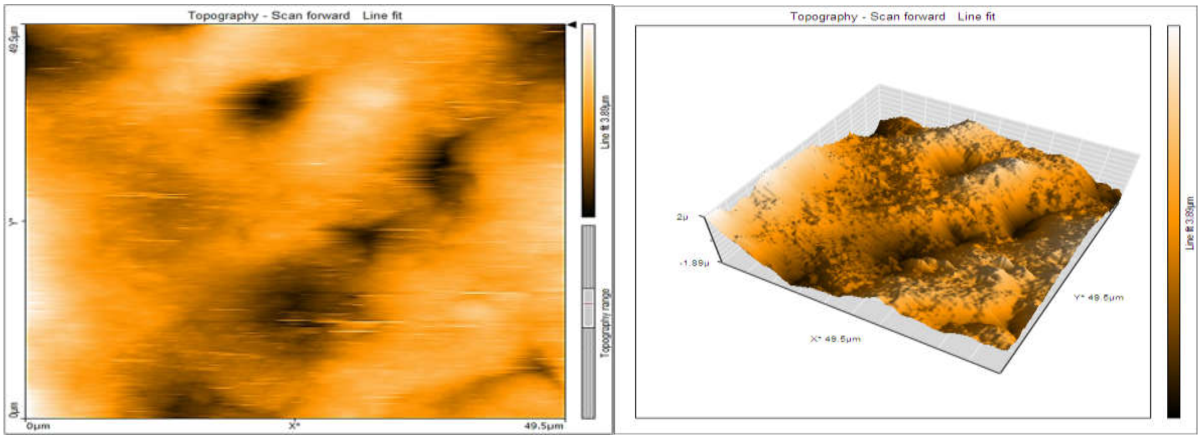


Fig. 11, AFM micrograph and topography for sample A2, in left graph 2D revels less pores after nano TiO2-R solution bath sealing processes, In the right 3D of topography surface roughness (Ra=185nm).

Electrochemical corrosion test by using Tafel extrapolation method in order to calculate $i_{corr.}$ and corrosion rate in MPY in sea water of 3.5wt% NaCl of pH was 6.8.

The parameters latter will use to calculate corrosion rate by using CR equation below [12].

$$CR(mpy) = 0.13 \times i_{corr.} \times Eq.wt/\rho \quad \ldots\ldots (1)$$

Where;

CR(mpy) is mill-inches per year, $i_{corr.}$ is the corrosion current density ($\mu A/cm^2$), Eq.wt; refers to equivalent weight of the corroding species, ρ ; is the density of the corroding specimens, (g/cm^3).

The values for the corrosion potentials and corrosion current densities were estimated from the intersection of the anodic and cathode Tafel lines. For Figure12, of sample A1 the i_{corr}. 191.37 ($\mu A/cm^2$) and corrosion rate is 82.8mpy. i_{corr}. For sample A2 (Figure 13) is 96.41($\mu A/cm^2$) so that the corrosion rate is 41.7mpy. This conclude the sealing with present of nano TiO_2-R promote the corrosion resistance or reduce the corrosion rate.

4. Conclusion

It's successfully found the NP of TiO_2-R sealing process achieved efficient technique for increasing some mechanical and functionally modified the surface anodizing layer. Hardness test HRF increased slightly, corrosion rate enhanced with generated Al_2Ti-O_5 phase. Micro pores tend to filled with NP and smaller proses diminishes. That type of sealing modification with NP of TiO_2-R promised for use in such circumstance that need corrosion resistance.

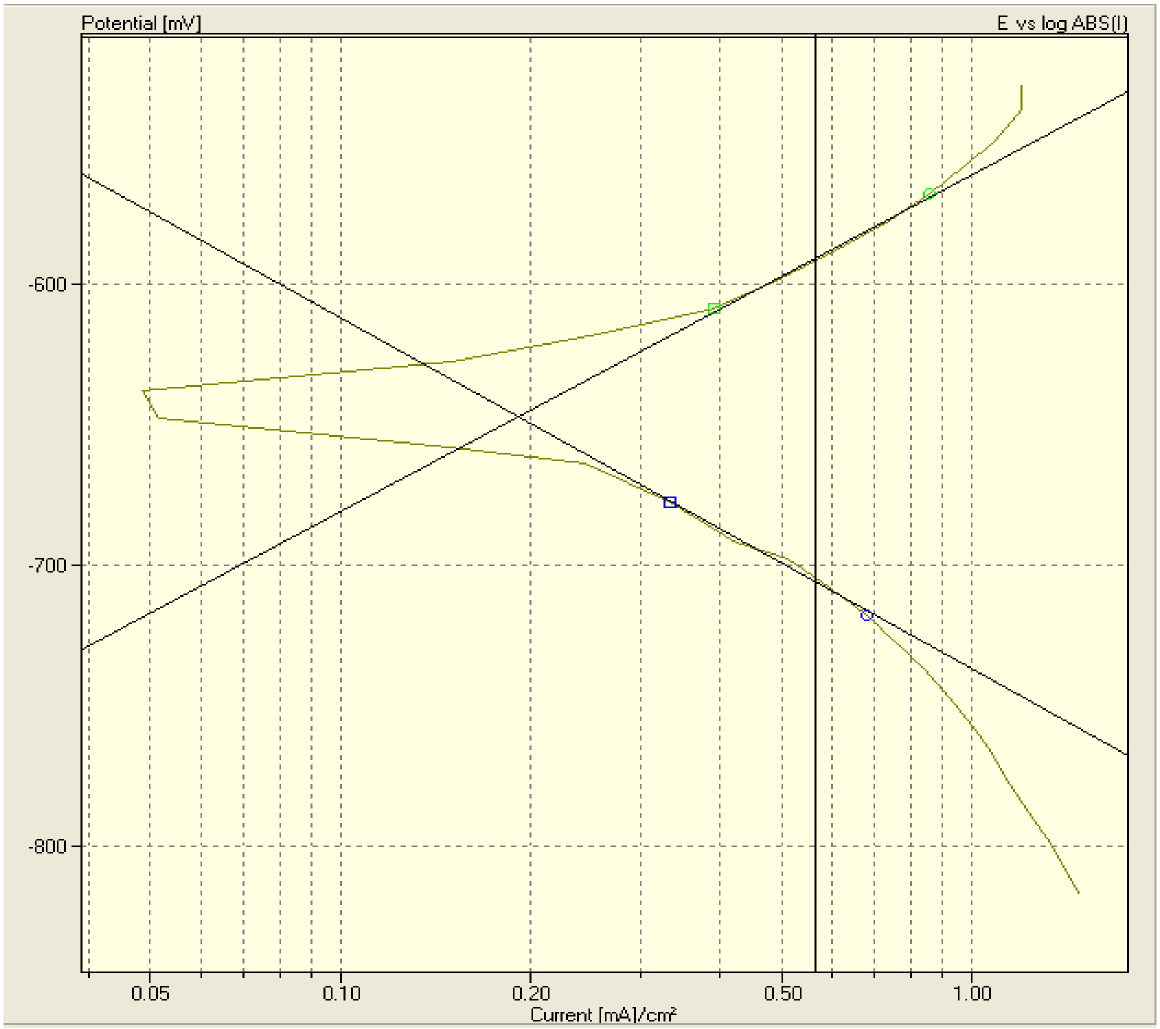


Fig.12, Tafel extrapolation of aluminum (A1) without Nano additives

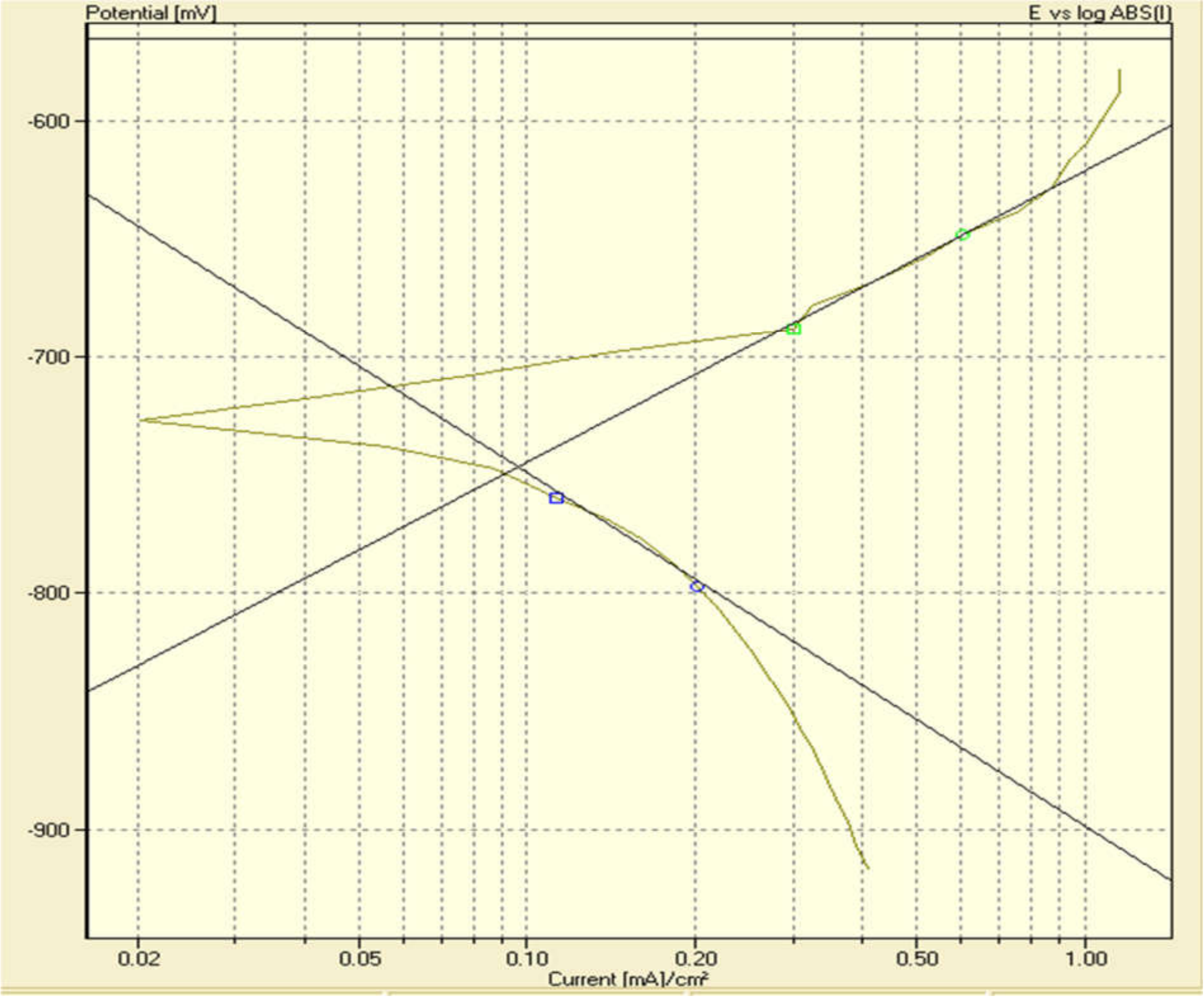


Fig.13, Tafel extrapolation of aluminum (A2) with Nano powder TiO_2 additives

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تحسين الطبقة الانودية لسبيكة الالمنيوم AA6061T6 باستخدام دقائق اوكسيد التيتانيوم – روتايل النانوي

د صفاء محمد حسوني ، د مصطفى خليل اسماعيل

الخلاصة: -

في هذا البحث تمت دراسة انودة الألمنيوم لسبيكة (AA6061T6) في حامض الكبريتيك (200g/l) في حمام من الثلج. حيث تم الحصول على الطبقة الأنوديه للألمنيوم ضمن كثافات تيار مختلفة ومن خلال الفحوصات تم اختيار افضل طبقه انوديه. ان تحسين افضل طبقه انوديه كان باستخدام ماده نانوية هي اوكسيد التيتانيوم روتايل (nano-TiO_2 Rutile) عن طريق عملية التشبيع (impregnation) والتي تم اضافتها على شكل صبغة وكعامل ختم (sealing) لطبقة الانودة وبالتالي تم الحصول على طبقه انودية مركبة. أن التوصيف للطبقة الأنودية المركبة تم باستخدام المجهر الضوئي، المجهر الماسح الإلكتروني، قياس الصلادة المايكروية وحيود الأشعة السينية وكذلك تم اجراء فحص التاكل حيث كانت مقاومة التاكل للالمنيوم مع المادة النانوية اكثر من مقاومة التاكل للطبقة الانودية بدون مادة نانوية.وايضا لوحظ زيادة في مقاومة البلى وزيادة بصلادة روكول المباشرة نوع HRF بمقدار 12%.

الكلمات المفتاحية: انودة, المنيوم, نانو, اوكسيد التيتانيوم, روتايل, حامض الكبريتيك