

Double- layer coatings for surface improvement of Al 6061 alloys by anodizing and micro plasma oxidation process MPO using new hydroxyapatite and rock additives modified electrolytes

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Abstract: In this work, duplex ceramic coatings were deposited on Al 6061 alloy, using anodizing and micro plasma process (MPO) . MPO electrolyte was modified using hydroxyapatite and 15g/l rock additives rich with Calcium Carbonate (CaCO_3).Phase composition of the coatings, microstructure, micro-hardness, topography, thickness, roughness, and wear resistance were evaluated by X-ray diffraction (XRD), (SEM), a Vickers indenter, AFM, and Microprocessor coating thickness meter, roughness test, and Microtest, respectively. Results showed that the samples coatings contained γ -alumina, and their thickness and hardness increased by the increasing of deposition time. The research demonstrates that a relatively hard, thick and uniform coatings with good wear resistance, can successfully be deposited on Al alloy using hydroxyapatite and 15g/l CaCO_3 rock additives containing electrolytes as an natural rock additives.

Key Words: Micro arc oxidation, Aluminium alloy, Rock additive, Hardness, wear resistance

1. INTRODUCTION

The treatments for surface improvement of Al Alloys such as chemical conversion coatings , anodic oxidation, laser processing and ion implantation ,are increasingly used to modify their surface for heavy load bearing applications [1]. MAO process, is a new effective surface treatment technique to enhance the tribological properties of Al alloys by deposition of hard and thick alumina coatings [2-9]. Many studies have been done on the modification of the electrolytes by using multiple additives (micro & nano additive), to improve the coatings mechanical and tribological properties [10- 14]. The MAO oxidation method is a combination of plasma discharge and anodizing oxidation , and the initially of the MAO method is an anodization method[15]. In anodizing , durable and porous coatings are formed by oxidation and durable surface coating to improve the corrosion resistance of Al surfaces [16-18]. Anodizing is a widely used process, which is distinctive by the good appearance and lower energy depreciation . However, the anodization porous oxide films, cannot have satisfied hardness and anticorrosion performance [1] .

In our study, anodic and MAO duplex coatings were combined to get their advantages .Also, this study is an attempt in using of Iraqi rock additives rich with Calcium Carbonate (CaCO_3) with nano hydroxyapatite in modification the MAO electrolyte as an assistant additives for surface modification of pre- anodized Al alloys. Iraqi land is rich of rock materials that contain natural materials like CaCO_3 . CaCO_3 is white , fine, and odourless powder. CaCO_3 is one of the most plentiful materials found in earth's crust and forms the rock sorts like chalk and limestone [19].

2. Experimental:

2.1 Powder preparation:

2.1.1 Preparation of nano HA powder

The wet chemical precipitation process was used for preparation of nano HA powder using chemical precipitation process using precursors of $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and NH_4OH as the precipitant. XRD and particle size tests were conducted to identify the powder and to characterize particle size. The test results proved pure hexagonal Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ powder with particle size of 250 nm, because of the high agglomerations occur due to the surface area of the particles.

2.1.2 Preparation of calcite powder

In this process, a suitable amount of calcium carbonate rocks was selected from (lime factory, Karbala/Iraq) and manually kibbled using mortar to get the quasi-finished powder. Then the powder was milled for 5 hours by using ball mill at speed 350 rpm. After milling, powder was tested by laser particle size analyzer (Type Better size 2000), and XRD. The test results proved pure CaCO_3 powder with particle size of about (3 μm).

2.2 Samples preparation:

Samples from Al 6063 alloy with hardness of 75 HV were cut into dimensions of ($\phi 25 \times 5 \text{mm}^2$). The chemical composition of Al substrates is given in table 1. All samples were polished to get surface roughness $R_a = 0.1 \mu\text{m}$, before anodization, then they were dipped into methanol and ultrasonic vibration. After that the samples were immersed in 5 mass% NaOH alkaline solution at 60°C for 45 s for degreasing, and water rinsed for 15 min. In the pickling process, samples were submerged for 60 s at room temperature in 30 vol % HNO_3 aqueous solution followed by water rinsing 15 min.

Table -1: Al 6063 alloy chemical composition.

Element	Content (wt. %)	Element	Content (wt. %)
Si	0.5	Zn	0.1
Fe	0.3	Cr	0.2
Cu	0.1	Other	0.12
Mn	0.1	Al	Bal.
Mg	0.79		

2.3 Anodizing and micro arc oxidation process:

The anodization was conducted at 15 V constant voltage and $15 \text{mA}/\text{cm}^2$ at 15°C for 12 min in a 15 wt% H_2SO_4 solution. The anodized samples were sealed in hot water for 15 min at 95°C . A 500V DC-AC homemade MAO deposition unit shown in fig. (1) was used to deposit the ceramic coatings at fixed current density of $(5) \text{A}/\text{dm}^2$ and voltage of 380V. A five liters bath from container was used. In the plastic container, the electrolyte was agitated and cooled using a mechanical stirrer and cooling system, respectively. Also, the plastic container was equipped with a sample holder as the anode and a st st

316L plate serving as the cathode. The cooling unit connected to the MAO unit works to prevent electrolyte solution heating over to 30 C. It provides the cooled water to a big plastic container surrounded the electrolyte solution container. Then, all samples were rinsed in distilled water and, dried in air.

The electrolytic solutions were mixed after preparation for 2 hours before the MAO process. Tables (2) and (3) show the electrolyte composition & deposition parameters.

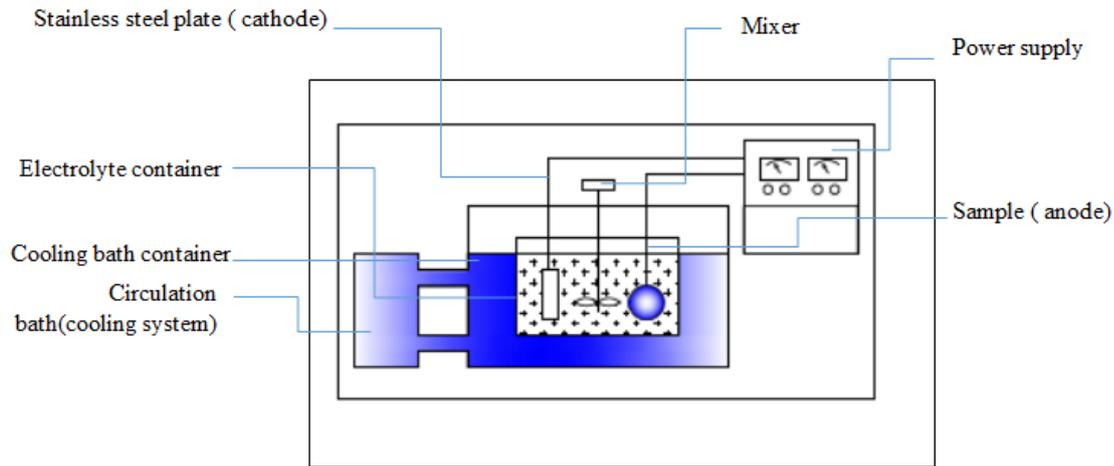


Fig.1: MAO coating equipment

Table- 2: Composition of modified electrolytes

Table- 3: Deposition parameters

Component	Concentration	Specification
KOH	3g/l	Electrolyte conductivity increasing
KH ₂ PO ₄	15g/l	Property modification
HA	20g/l	Assistance
CaCO ₃	15g/l	Assistance

Sample code	Deposition time (min)
ME ₁	10
ME ₂	20
ME ₃	40
ME ₄	60

2.4 Characterization

The powders and substrates were identified using X-ray Diffractometer (XRD-6000SHIMADZU, Japan, Cu K α radiation, 40Kv, 30MA, 6/min scanning speed). The coatings were tested with XRD- 7000 SHIMADZU system. The microstructure was studied using scanning electron microscope (INSPECT S50,FEI Company). Micro-hardness was measured by a Vickers indenter (HVS-1000,Laryee,digital Micro-hardness tester) with load of 4.9 N and holding time of 15 seconds. Microprocessor CM-8822, coating thickness, was employed to measure thickness coatings. All experimental measurements of 3D surface topography and roughness parameters were obtained using Atomic Force Microscopy (AFM, contact mode, spm AA3000 Angstrom advanced Inc., USA) ,prior to AFM analysis the surface of the samples was cleaned with alcohol, and

dried at room temperature. The wear resistance was tested using (Microtest-28021) and ϕ 6mm carbide pin at load 10N, sliding speed 200rpm, sliding distance 75 mm, and time 15min.

3. Results and discussions:

3.1 MAO spark conditions:

The recorded values for the voltage –current during the MAO treatment using the natural additives containing electrolytes could clearly show the normal & continuous sparks movement at 380 V and 5 A/dm² current density. The spark movement can be attributed to the deposition of substrate, and spot localized healing with the subsequent sparking at weak spots in the coating. Anyhow, raising the voltage above 280V could start the dielectric breakdown and it varied with the anode material, and the electrolyte temperature and composition.

3.2 XRD results

Figs. (2) and (3), display the XRD results of the coated samples. XRD patterns proved the deposition of aluminum oxide on the surface of substrates. The main peaks were γ - Al₂O₃ (JCPDS No. 010-0425). The Al peaks (JCPDS No. 004-0787) observed in XRD results can be attributed to the thicknesses and Al peaks coming from the underlying substrate were detected due to the X-rays penetration into the Al substrates. Typically, it could be observed that at high Bragg angles the thin films have low intensities [12].

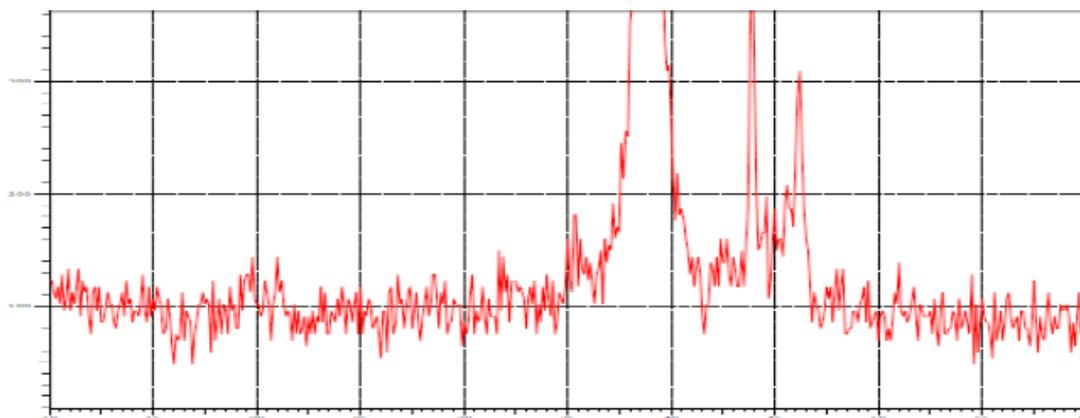


Figure (2): XRD patterns of sample ME₁

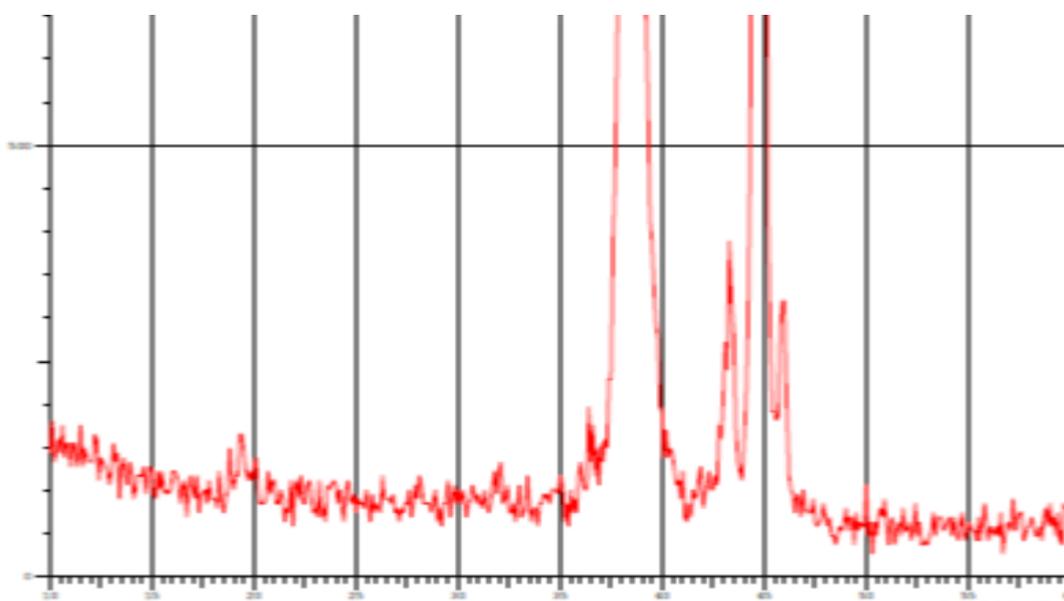
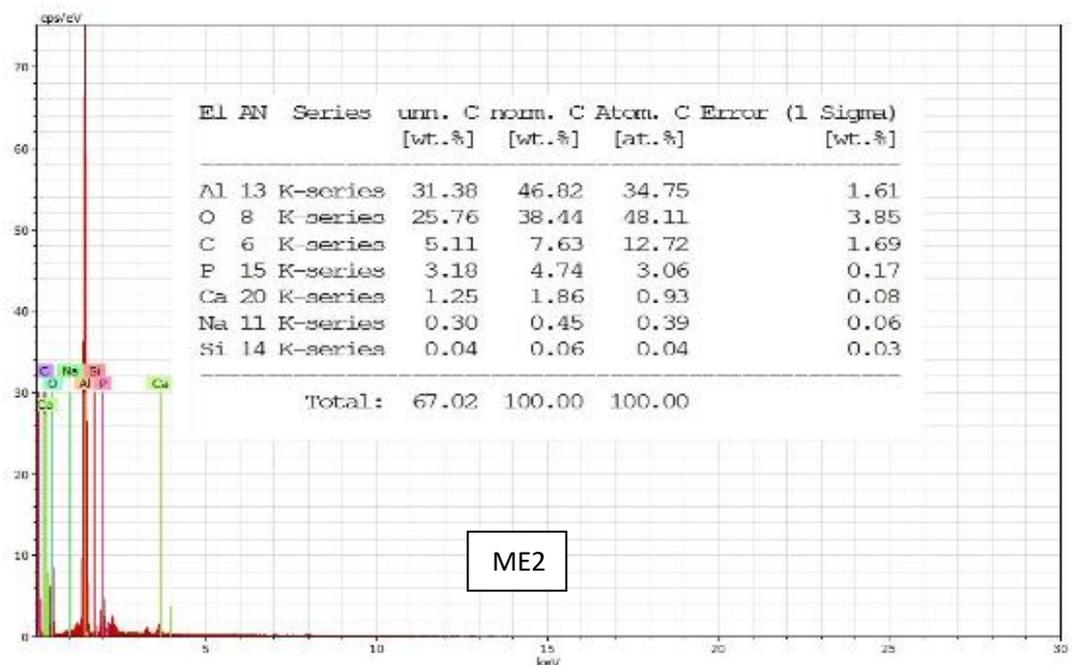
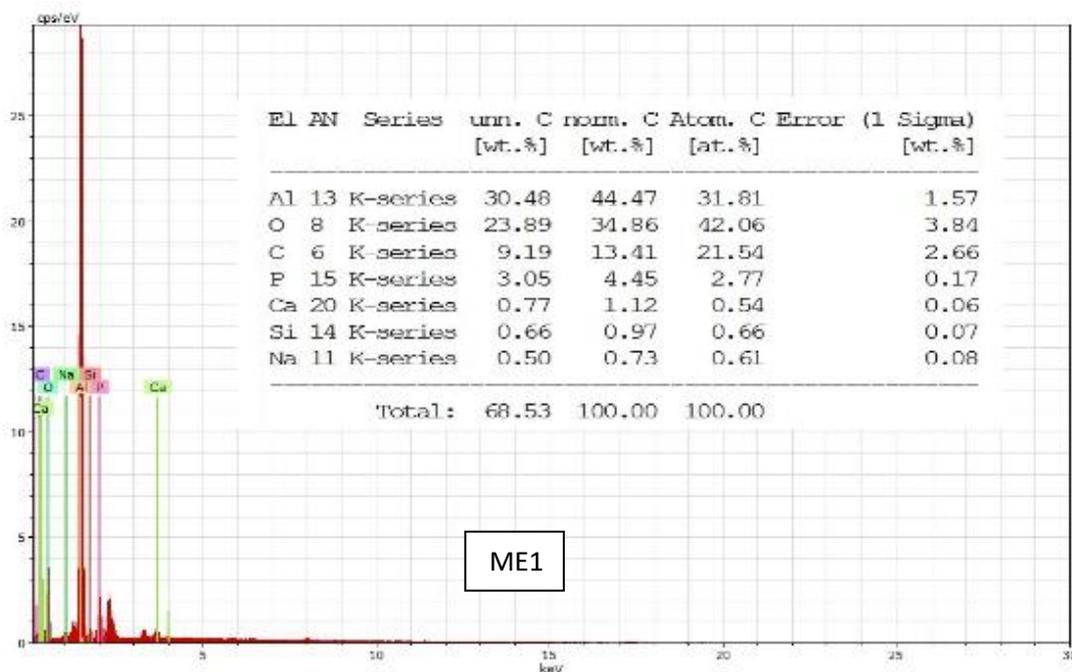
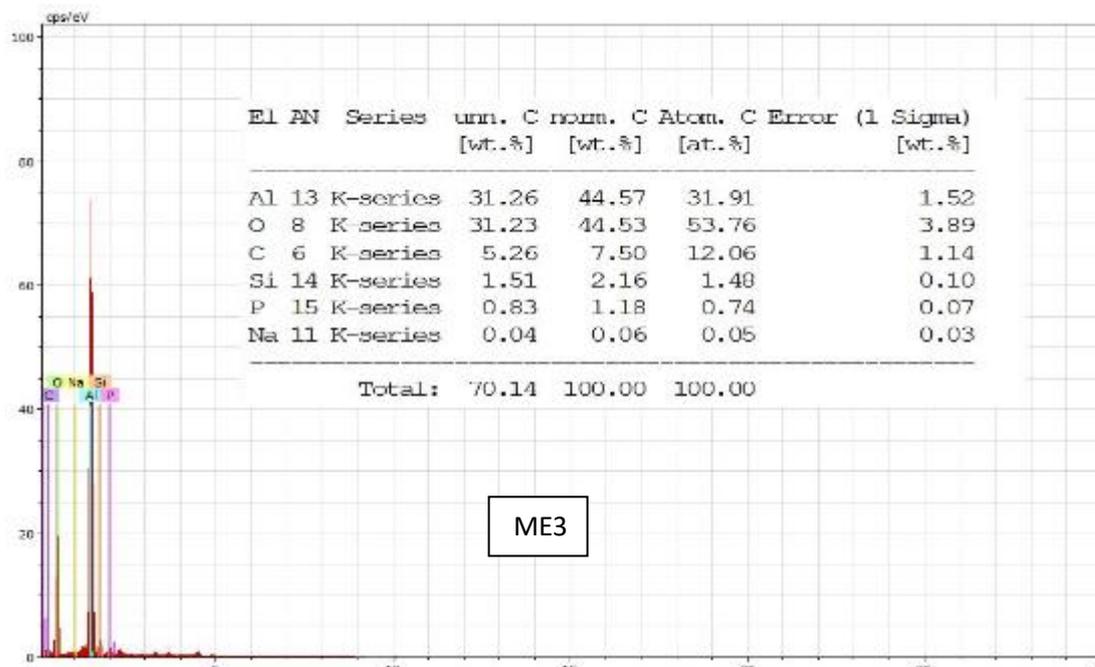


Figure (3): XRD patterns of sample ME₄

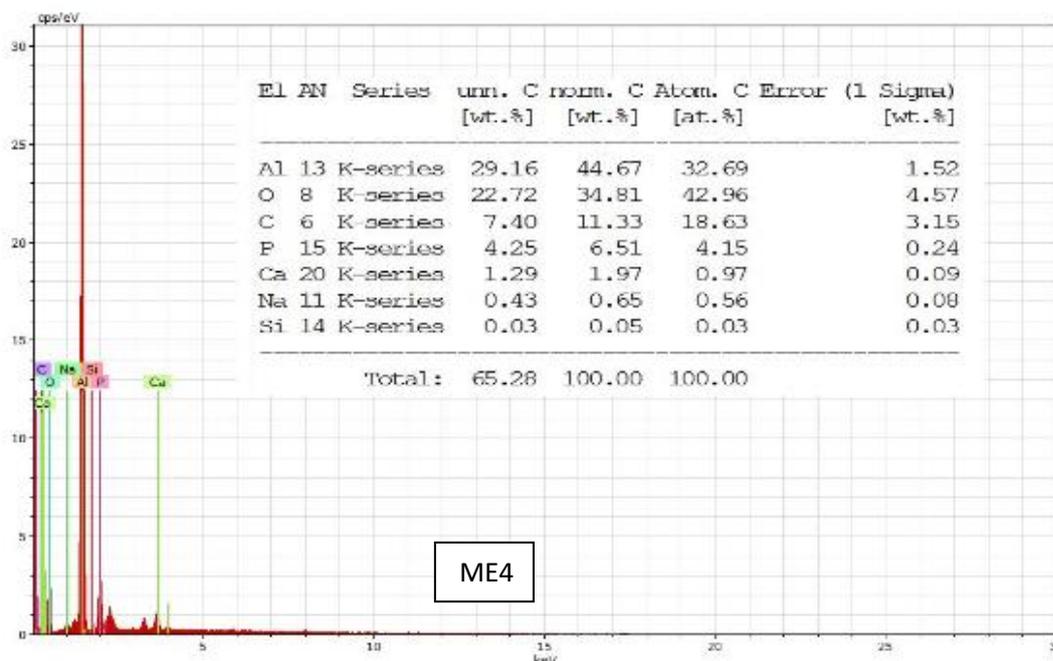
3.3 EDS results

Figures (4 – 7) show the results of EDS. The EDS results could indicate the deposition of aluminum oxide. The existence of Aluminum (Al) and Oxygen (O) elements in the coatings, referred to the Al_2O_3 layers formation with different weights of modification elements of C, P, Ca, Si and Na. Generally, C element is always precipitated in the MAO electrolytes, deposited as contaminate, and detected on the unpolished coatings. Furthermore, other elements may be resulted from the contaminates in hydroxyapatite and $CaCO_3$. Also, P is belonged to the chemical compounds used in preparation of the electrolytes. Generally, different elements used in preparation of electrolytes could react with Al of substrate to produce complex compounds, may also be alloyed within the MAO sparks, leading to the high content of such elements on the deposited coatings.





ME3



ME4

3.3 Results of SEM for samples:

Figures (8- 11) show the surface morphology results from SEM for the coated sample at different magnifications. The morphologies can be observed are characterized by different sizes of sphere-like geometry pores in the structure. These coatings have a pan-like structures with a nonuniformly distributed porous structures. At the discharge spots sites, the metal from substrate and its oxide are melted and projectile over from discharge tunnels due to the very high temperatures at those sites. The observed pan-cake-like morphology is resulted from the molten liquid that quickly solidified leaving distinct boundaries around the pores. Also, such rapid solidification induced the microcracks appearance on the morphology due to molten oxide continuous exposing to cold electrolyte.

In general, sample ME₂ (at 20 min) showed structure characterized by pores non-uniform distribution and their different sizes. Considering such non-uniform distribution of porosity, it could have its effects in lowering the hardness of sample ME₂ in comparison with other samples. In general, the hardness differences is strongly attributed to the non-

uniform distribution of pores in coatings. The MAO discharge canals can result in a highly thick and porous films, and the components and any modifying elements in the electrolytes can be incorporated into oxide films by the discharge. The structure of ME₄ was characterized by, relatively low pores with uniform distribution, which has its effects on the increasing hardness values.

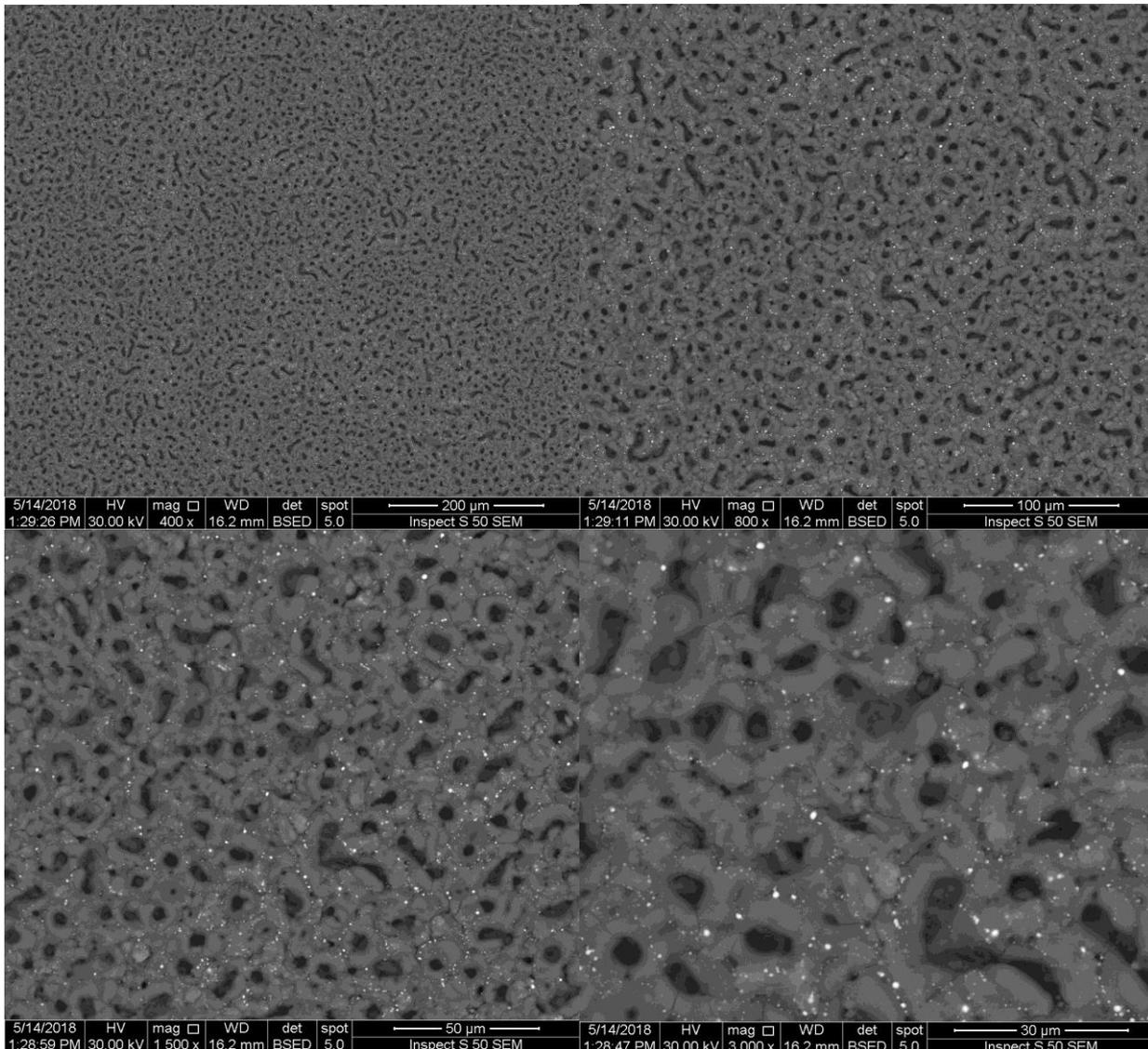
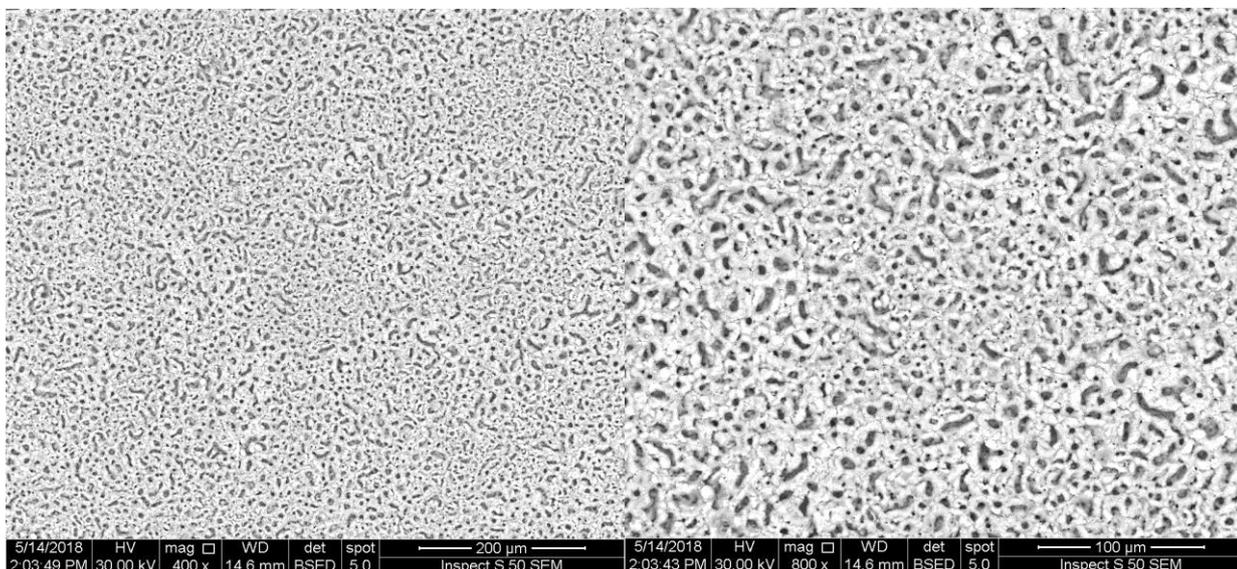


Figure (8): Surface morphology results from SEM observation of sample ME₁ at different magnifications.



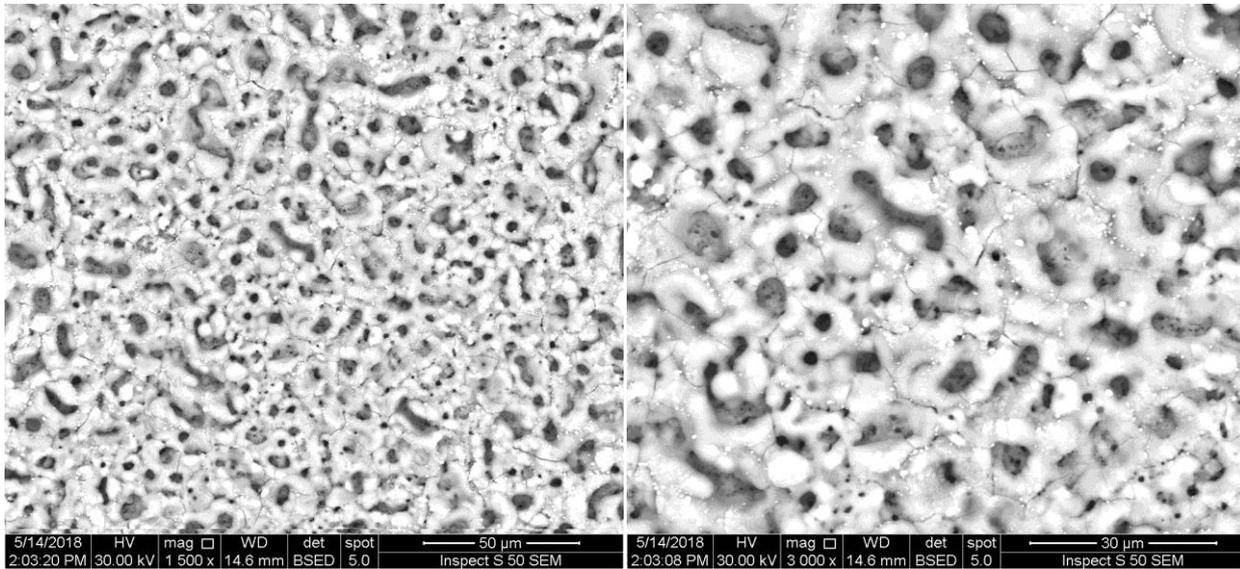


Figure (9): Surface morphology results from SEM observation of sample ME₂ at different magnifications

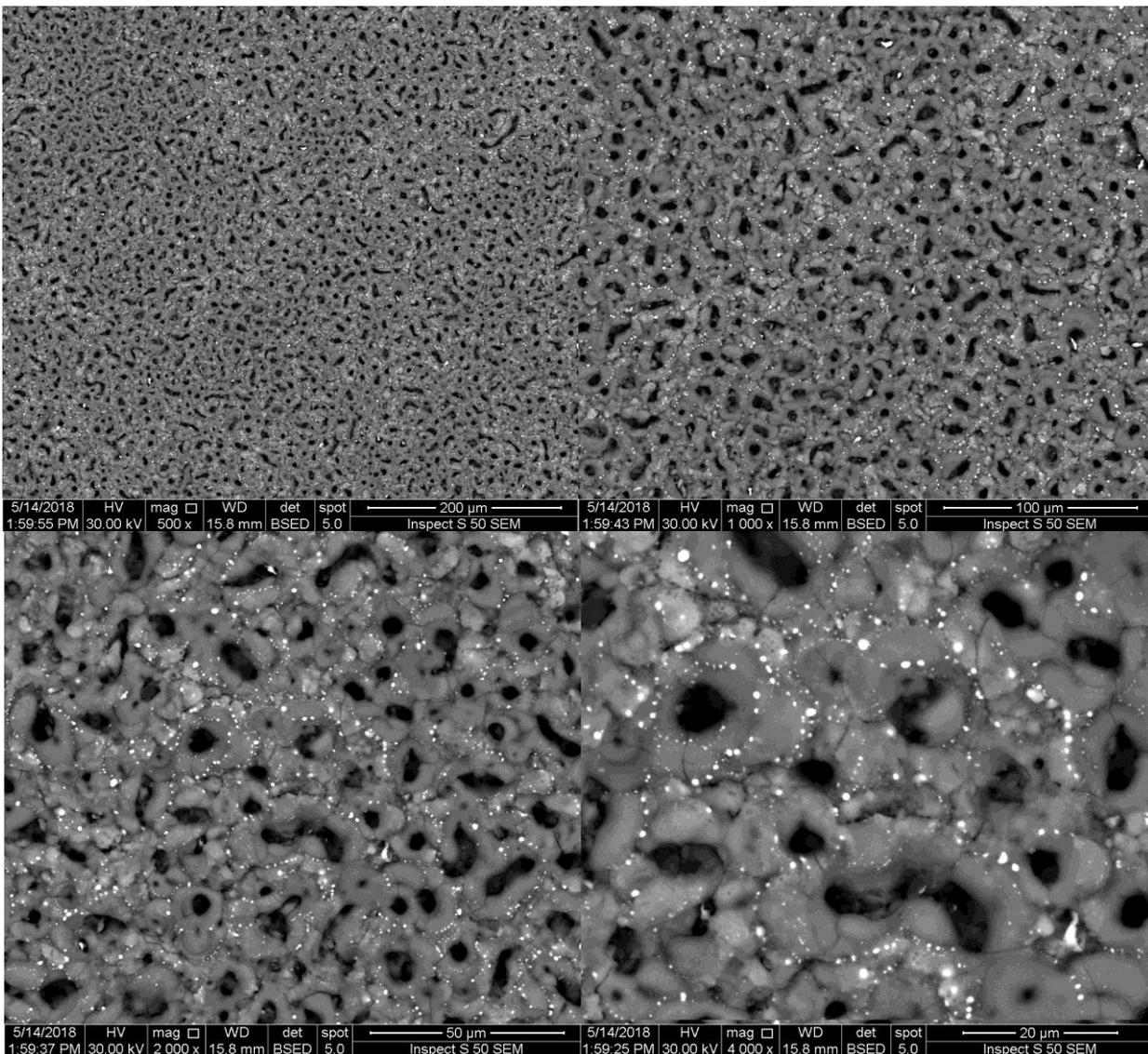


Figure (7): Surface morphology results from SEM observation of sample ME₃ at different magnifications

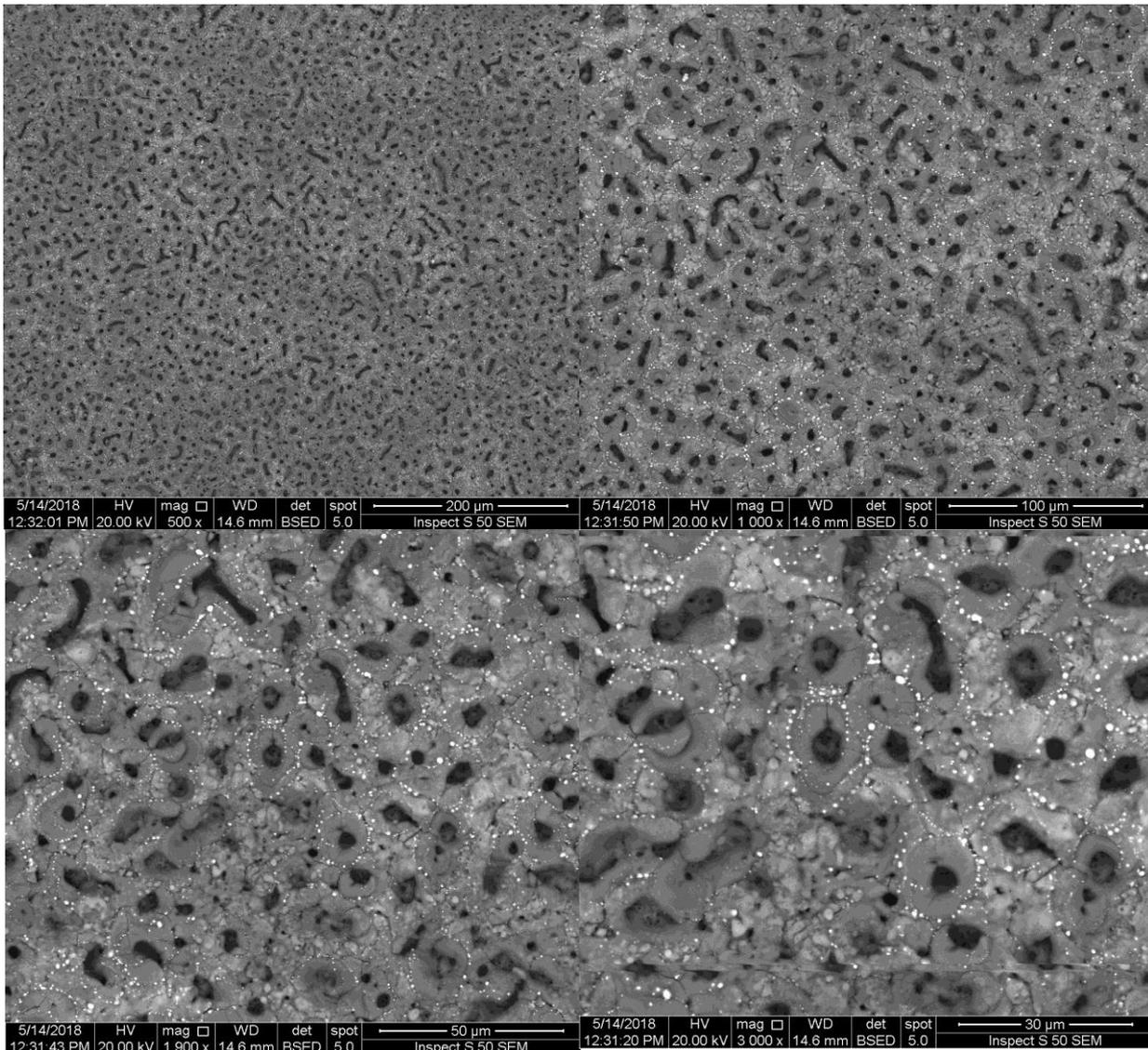


Figure (10): Surface morphology results from SEM observation of sample ME₄ at different magnifications

3.4 Thickness and Hardness results of coatings:

The preanodized treatment could provide 10-13 μm ceramic coatings with hardness of 200 Hv. Table (4) presents the results from thickness and hardness. Figures (12) and (13) give the effect of deposition time on the resulted hardness and coatings thickness with and without pre treatment. In general, double-layer coatings deposited by anodizing and process MPO processes using new hydroxyapatite and CaCO_3 rock additives modified electrolytes could improve the Al substrates with thick and hard ceramic alumina in comparison to untreated coatings. Anodizing permanently changes the outer structure of the oxidized surface, and make it much thicker, up to several micrometers. The anodized aluminum oxide coating is very hard, The porous nature of oxidized surface makes it possible to impregnate such pores with the number of discrete short-lived micro discharges moving across the Al surface during the subsequent MAO process. The variation of coatings thickness with deposition time can be attributed to the broken of weak oxide layer by strong spark during growth, thereby, forms different thickness values. It can be concluded that the thickness values were (55-85) μm , and the sample ME₄ exhibited the highest value (85 μm) at 60 min in comparison with the other coatings.

While sample ME₁ recorded the lowest (55µm) thickness at 10min. Generally, the increasing of coating thickness can be observed with deposition time increasing. It is interested to mention that, only the micro-hardness test at 4.9 N and holding time (15sec) could evaluated the coating hardness. In general using loads of (50, 100, 150, 250, 350,400) g could not show any track in the coating surface. The dense layer exhibited the higher value of hardness, while the hardness of porous layer was rather low. It can be observed that the sample ME₂ recorded the lowest (230- 280 HV) hardness because of their porous structures characterized by more nonuniform pores distribution in ceramic oxide pointed in SEM results. The ceramic coatings showed surface roughness in the range (1.72-16.5) µm. Generally, the coating roughness decreased with deposition time increasing.

Table (5): Results of coatings thickness and hardness, and roughness

Sample	Thickness (µm)	Hardness (HV)		Roughness (µm)
		Un pretreated	Preanodized	
ME ₁	55	239	300	11.6
ME ₂	63	230	280	6.8
ME ₃	73	329	360	1.72
ME ₄	85	350	400	16.5

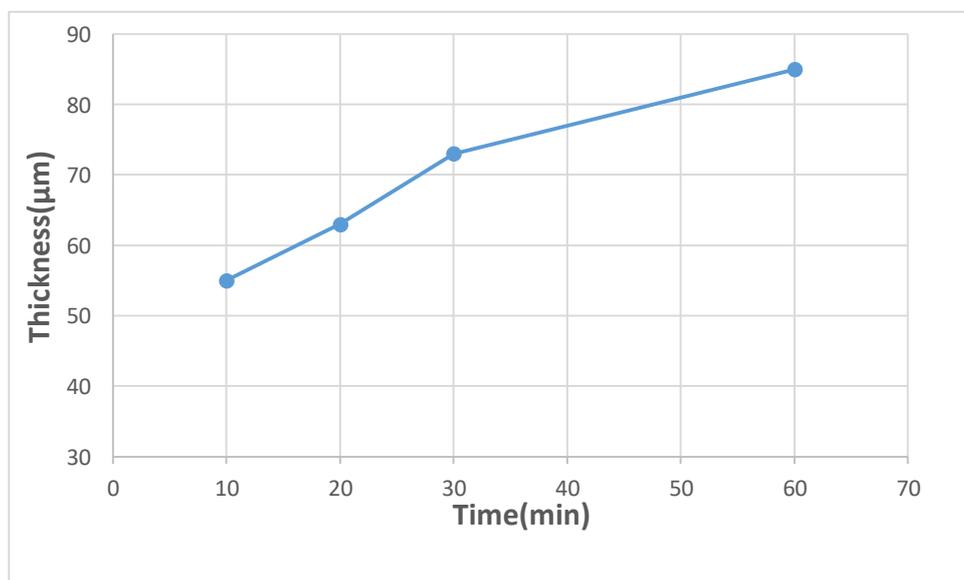


Figure (7): Effect of deposition time on coatings thickness

3.5 AFM results:

The surface roughness of each sample is measured along the same reference length, what can be seen on the 2D view of figure (14). The obtained results of the coatings, are presented in the form of high resolution 3D images. The measurement range on all samples is 4000X4000nm. Figure (14) shows 3D topographies and roughness profiles of the coatings. From presented results of AFM, it can be said that the ceramic coatings showed surface roughness in the range (1.72-16.5) µm. Generally, the coating roughness decreased with deposition time increasing to 30 min, then the coatings of sample ME₄

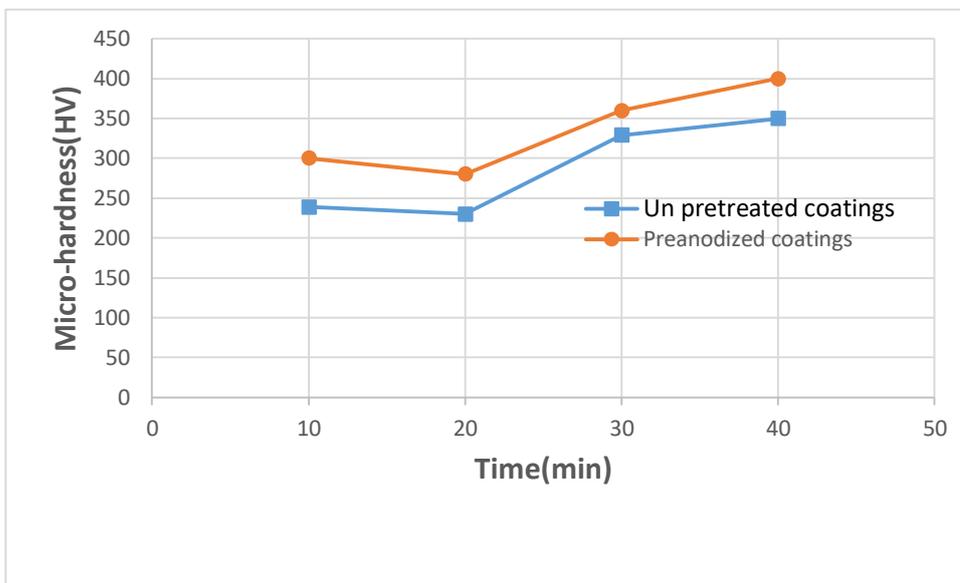


Figure (8): Effect of deposition time on coatings hardness

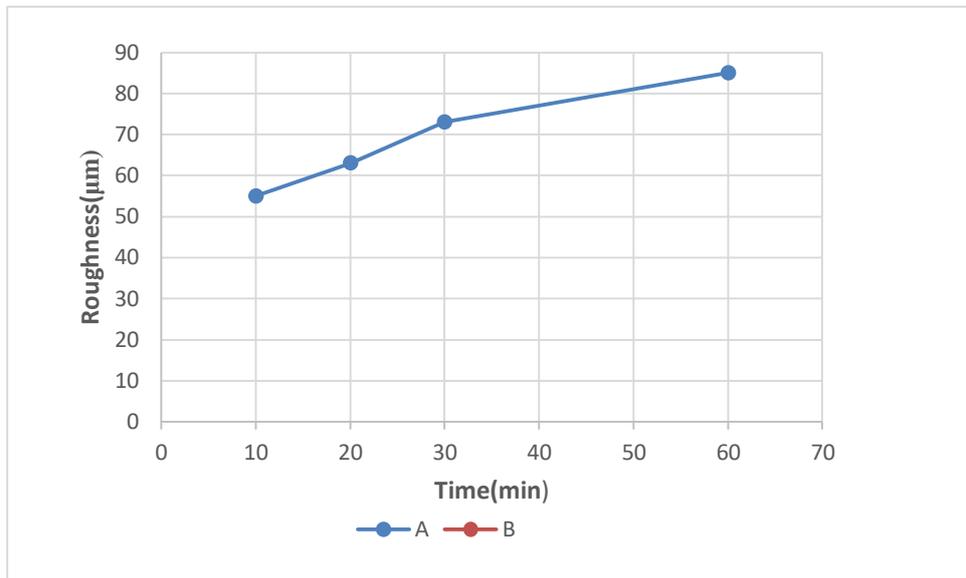
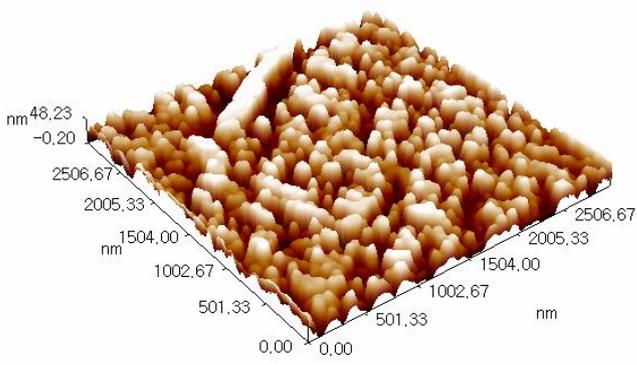


Figure (9): Effect of deposition time on coatings roughness

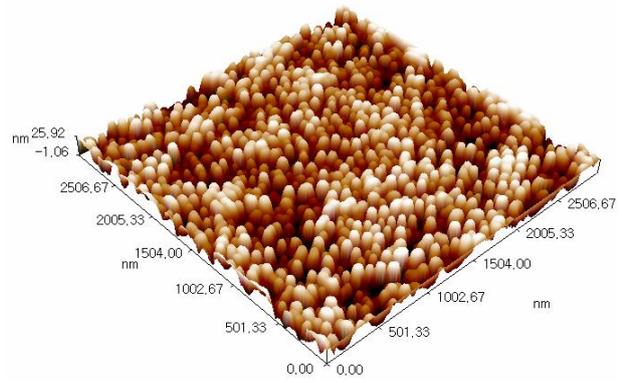
have surface roughness higher those of other samples due to increasing of coating thickness. Anyhow, AFM results showed cluster of particles with highly dense structure, the particles were closely bonded, and no voids were observed in samples. While the voids were, appeared in sample ME₄, which indicated that the surface roughness increased with the increasing of deposition time to 60 min.

3.5 Wear results:

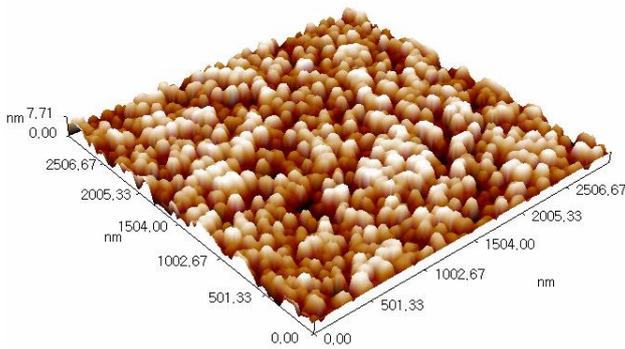
The wear mass loss of test samples weighted to an accuracy of 0.1mg produced by pin-on disc sliding wear test were used to evaluate the wear rate. The values of weight loss are shown in table (4).The Al substrate had a higher weight loss of (42×10^{-4}) g while, samples coated using modified electrolytes had weight loss of $(5 \times 10^{-4} - 10 \times 10^{-4})$ g .Such results could prove the successes of the pretreatment of anodizing and the using of new hydroxyapatite and rock additives modified electrolytes for surface improvement of Al alloys to deposit oxide layers with good wear resistance.



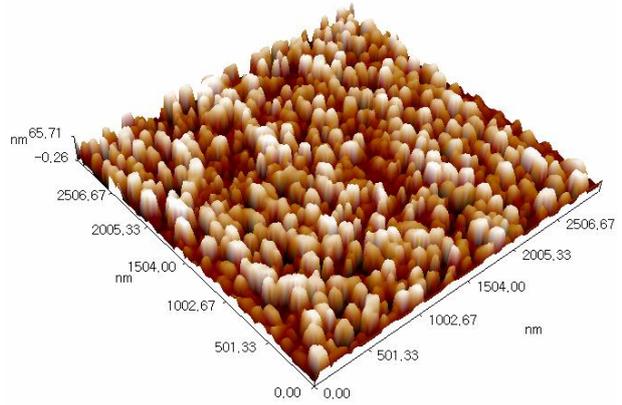
(a): Ra=11.6



(b): Ra=6.8



(c): Ra=1.72



(d): Ra=16.5

Figure (11): AFM Results of Samples ME: (a) 10min ,(b) 20min ,(c) 40min ,and (d) 60min

Table- 4: Wear results

Samples	Weight loss (g)
Substrate	42×10^{-4}
ME ₁	10×10^{-4}
ME ₂	8×10^{-4}
ME ₃	7×10^{-4}
ME ₄	5×10^{-4}

Conclusion:

1. The pretreatment of anodizing and using of new MAO electrolytes modified by nano hydroxyapatite and CaCO₃ natural rock additives can be used to deposit hard and thick γ -Al₂O₃ coatings on Al alloy substrates .
2. The MAO ceramic coatings with thicknesses (55 -85) μ m can enhance the Al hardness from (75HV) to (280-400) HV. Hardness differences were strongly

affected by the non-uniform distribution of pores and increased with increasing of deposition time..

3. The microstructure of coatings was characterized by different size of pores and distributions.
4. The AFM results showed an average roughness in the range (1.72-16.5 μm) which decreased with increasing of deposition time to 40 min , then showed maximum value at 60 min due to the highest coating thickness .
5. The wear resistance improved by MAO coatings using the modified electrolyte, and the weight loss decreased from (42×10^{-4}) for Al alloy to (5×10^{-4}) for thick ceramic coatings deposited for 60 min.

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