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A NEW METHOD FOR DEPOSITION OF CERAMIC COATING ON AL ALLOY USING DUPLEX PROCESSES OF ANODIZING AND Al_2O_3 MODIFIED ELECTROLYTE MICRO -ARC OXIDATION (MAO)

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ABSTRACT

In this work, surfaces of Al 6061 alloy were coated using anodizing and micro–arc oxidation (MAO) duplex processes. MAO electrolyte was modified using (2-6 g/l)Al_2O_3 additives . X-ray diffraction (XRD), scanning electron microscopy (SEM), Vickers indenter, atomic force microscopy (AFM), and Microprocessor coating thickness meter ,were employed for characterization of the deposited coatings .Results showed that the coatings contained porous oxide γ-alumina with morphologies characterized by different levels of porosity non-uniform distribution, and their thickness and hardness increased by the increasing of Al_2O_3 additives. The research demonstrates that a relatively hard (421-490Hv), thick (43-65µm) and uniform coatings, can successfully be deposited on preanodized Al alloy (12-15 µm with hardness of 190Hv) using Al_2O_3 additives containing MAO electrolytes as a new method for more future research on surface improvements of Al alloys

Keywords: Micro arc oxidation, Aluminum alloy, Anodizing, Hardness, Duplex processes, Al_2O_3

طريقة حديثة لترسيب طلاءات سيراميكية على سبائك الالمنيوم باستخدام عمليات ثنائية الا نودة والاكسدة المايكروية (MAO) بمحلول محسن باضافة دقائق الالومينا

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الخلاصة

تم في هذا البحث طلاء سطوح سبيكة الالمنيوم Al 6061 باستخدام عمليات ثنائية تضمنت الانودة والاكسدة المايكروية MAO. محلول MAO تم تحسينه باضافة 6 g/l من دقائق الالومينا Al_2O_3. فحوصات حيود الاشعة السينية XRD, التركيب المجهري SEM , الصلادة , طبوغرافية السطح AFM و سمك الطلاء قد اجريت لتوصيف الطلاءات المرسبة . اثبتت النتائج ترسيب طلاءات تكونت من اوكسيد γ-alumina مسامي البنية وذا توزيع غير منتظم للمسامات , وان سمك وصلادة هذه الطلاءات يزداد بزيادة نسبة دقائق الالومينا المضافة للمحلول. لقد نجح البحث في تقديم طريقة حديثة للبحث في المستقبل في مجال تحسين سطوح سبائك الالمنيوم بترسيب طلاءات منتظمة من الالومينا السيراميكية بصلادة 421-490Hv و سمك 43-65µm باستخدام محلول MAO المحسن باضافة دقائق من الالومينا على سطوح سبائك الالمنيوم المعاملة مسبقا بالانودة (بسمك 12-15 µm وصلادة 190Hv) .

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INTRODUCTION

The micro-arc oxidation (MAO), also called micro plasma oxidation (MPO) in which the metal is oxidized using very high discharge voltages, has been proved as a new effective surface treatment technique to enhance the tribological properties of Al alloys by deposition of hard and thick alumina coatings Soboleva et.al.(2018), Hong and Jin (2017) , Lederer et al. (2017), Clyne and Troughton (2019), Malyshev and Volkhin (2013), Wenbin et al. (2017), Zhang et al. (2018), and Zhang et al. (2017). The high voltage oxidation of the metals results in many sparks ,which in, the original oxide layer is broken and reformed, and porous oxide is deposited with thickness and hardness depend on the type of electrolyte and the applied voltage Laís et al.(2014). The MAO oxidation method is a combination of plasma discharge and anodizing oxidation , and the initially of the MAO method is an anodization method Hussien, and Northwood(2014). Also ,of the most common and widely used surface treatment processes for Al are the durable and porous oxides formed by anodization for protective and decorative purposes of Al surfaces labisz et al. (2018), Ardelean et.al. (2018), Sami et al. (2010),and Teng-Shih et al.(2014). Oxide films can be impregnated with various substances, which are distinctive by the good appearance and lower energy depreciation.However, the anodization films, cannot have cogent anticorrosion and hardness performance Xuping et al.(2017) .Our previous works have proved the superior effectiveness of combination of anodizing and natural additives modified MAO electrolytes in surface modification of Al alloys Samir(2019). In the present study, the pre anodizing and Al_2O_3 modified electrolyte MAO processes were combined for surface of Al 6061alloys to show the effect of pretreatment of anodizing on the properties of MAO coatings as a new method for surface improvement of Al alloys.

EXPERIMENTAL WORK

Samples preparation

The samples of 6061 Al alloys with the dimensions of 25×5 mm^2 and hardness of 75 HV were used . Prior to anodizing they were polished by emery papers followed by buff polishing to a surface roughness of R_a 0.04μm . The nominal composition of 6061 Al alloys is given in table 1 Samir(2019).. Then they were dipped into methanol and ultrasonic vibration, cleaned by distilled water and dried in hot air Samir(2019).

Anodizing and micro arc oxidation process

The anodization was conducted at 15 V constant voltage and 15mA/cm^2 at 15°C for 12 min in a 15 wt% H_2SO_4 solution. The anodized samples were sealed in hot water for15 min at 95°C . A 500V DC-AC homemade MAO deposition unit shown in fig. (1) was used to deposit the ceramic coatings at voltage of 380V . A five litters bath from container was used Samir (2019). . 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. MAO coatings were deposited using different concentrations of Al_2O_3 particles (Ø 40μm) in Na_2SiO_3 electrolytes for 20 minutes at constant current density (6A /dm^2) Samir (2019). . The electrolytic solutions were mixed after preparation for 2 hours before the MAO process. Tables (2) and (3) show the electrolyte composition and Al_2O_3 concentrations Yerokhin(1999).

CHARACTERIZATION

The modified coatings were identified using X-ray Diffractometer (XRD-7000 SHIMADZU) SYSTEM. The microstructure was studied using scanning electron microscope (INSPECT S50,FEI Company). The micorhardness was determined according to ASTM standard using Vickers indenter (HVS-1000,Laryee,digital Micro-hardness tester) under load of 4.9 N and holding time of 15 seconds [S. Hamid Awad, 2019]. 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 were cleaned with alcohol and dried at room temperature.

RESULTS AND DISCUSSIONS

MAO spark conditions

It could be observed that when the sample is placed in the electrolyte ,the sparking and terminal deposition voltages gradually decreased with the increasing of Al_2O_3 concentration, but the sparking voltage begins to increase when the Al_2O_3 concentration is more than 4 g/ L. Experimental results show that the arcing voltage is 280 V, the arcing current is 0.7 A, in the electrolyte system. However, the recorded values for the voltage –current during the MAO treatment using the modified electrolytes could clearly show the normal and continuous sparks movement at 380 V .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. Generally, raising the voltage above 280V could start the dielectric breakdown and it varied with the anode material, and the electrolyte temperature and composition.

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 mean peaks were γ- Al_2O_3 according to the standard cards (JCPDS No. 010-0425). The dominated peaks of γ-Al2O3 were existed at 2θ of 19.7731°,44.7000°, and 44.8000° for sample ME2,and at 19.4676°, 37.4676°, 44.7729°, and 45.8987° for sample ME5 . The peaks intensities of samples ME5 were higher than those of ME2 due to increasing of Al_2O_3 additives in the electrolytes. The Al peaks were observed according to the standard cards (JCPDS No. 004-0787) .These peaks were existed at 2θ of 38.7970°,45.0114°, and 45.2000° for sample ME2,and at 38.5781°, 39.0196°, and 43.6851° for sample ME5.

The Al peaks 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. In comparison of Al_2O diffraction at different 2θ obtained in the present study with those of standard specification, there were little differences. Probably, such difference can be attributed to the differences in the preparation conditions of Al_2O , and the conditions of obtaining of diffractions data and its accuracy.

Results of SEM

Figures (8-11) show the different magnifications for the coatings surface morphology resulted from SEM. The morphologies can be observed are characterized by different sizes of pan-like or sphere-like geometry pores in the structure, which are resulted from the molten liquid that quickly solidified leaving distinct boundaries around the pores .As shown in figure (11) , such rapid solidification induced the microcracks appearance on the morphology due to molten oxide continuous exposing to cold electrolyte.

Furthermore, at the sparking 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 .It can be observed that such melted oxide which is denoted by the white particles in the SEM results increase with increasing of Al_2O_3 addition, thereby, increasing the micorhardness. In general, sample ME_3 showed structure characterized by pores non-uniform distribution. Considering such non-uniform distribution of porosity, it could have its effects in lowering the hardness of sample ME_2 in comparison with other samples. In general, the hardness differences is strongly affected by the non-uniform distribution of pores in coatings , and the presence of Al_2O_3 in the their distinct boundaries. .The structure of ME_5 was characterized by, relatively low pores with uniform distribution, which has its effects on the increasing hardness values.

Thickness and Hardness results of coatings

The anodized aluminum oxide coating is very hard, and the preanodized treatment could provide 12-15 µm ceramic coatings with hardness of 190 Hv. The unmodified MAO coatings showed hardness measurements in the rang (417-419 Hv) .Table (4) presents the results from thickness and hardness .Figures (12) and (13) give the effect of Al_2O_3 additives on the resulted hardness and coatings thickness with and without pretreatment. In general, duplex coatings deposited by anodizing and process MPO processes using Al_2O_3 modified electrolytes could improve the Al substrates with thick and hard ceramic alumina in comparison to untreated coatings . Furthermore ,the MAO ceramic coatings could enhance the Al hardness from (75HV) to (421-490) Hv. The porous nature of the 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 increasing of Al_2O_3 additives can be attributed to the broken of weak oxide layer by strong spark during growth, thereby, any modifying elements in the electrolytes can be incorporated into oxide films by the discharge to form highly thick and porous films. It can be concluded that the thickness values were (43-65) µm, and the sample ME_5 exhibited the highest value (65 µm) in comparison with the other coatings. While sample ME_2 recorded the lowest (43µm) thickness. Generally, the increasing of coating thickness can be observed with increasing of alumina additives. 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 ME_3 recorded the lowest (421- 435 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 (8.61-15.3) µm. Generally, the coating roughness decreased with increasing of alumina additives, while after that the increasing of additives to 6 g exhibited the highest roughness (15.30 µm).

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 (15).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 (15) 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 (8.61-15.3) µm. Generally, the coating roughness decreased with increasing of Al_2O_3 additives to 5 g, then the coatings of sample ME_5 have surface roughness higher those of other samples due to incorporating of more of Al_2O_3 as modifying elements in the coatings , and due to the highest 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.

CONCLUSIONS

1. The using of duplex processes of anodizing as a pretreatment and MAO electrolytes modified by Al_2O_3 additives can be used to deposit hard and thick γ-Al_2O_3 coatings on Al alloy substrates .
2. The hardness values of pretreated coatings were higher than those of non-pretreated .
3. The XRD and EDS results proved the deposition of γ-Al_2O_3 coatings by the duplex processes.
4. The MAO ceramic coatings with thicknesses (43 -65) µm can enhance the Al hardness from (75HV) to (421-490) HV. Hardness differences were strongly affected by the non-uniform distribution of pores and increased with increasing Al_2O_3 additives.
5. The microstructure of coatings was characterized by different sizes of pores and distributions

Table -1: Al 6061 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		

Table- 2: Composition of modified electrolytes.

Component	Concentration	Specification
NaOH	1g/l	Electrolyte conductivity increasing
Na_2SiO_3	10g/l	Property modification
Al_2O_3	1-6g/l	Assistance
$NaCO_3$	10g/l	Assistance

Table- 3: Al_2O_3 concentrations.

Sample Code	**Al_2O_3 concentration g/l**
ME_1	0
ME_2	2
ME_3	4
ME_4	5
ME_5	6

Table (4): Results of coatings thickness and hardness, and roughness.

Sample	**Thickness (µm)**	**Hardness (HV)**		**Roughness (µm)**
		Un pretreated	**Preanodized**	
ME_2	43	427	444	8.61
ME_3	50	421	435	5.94
ME_4	57	460	490	3.48
ME_5	65	485	520	15.30

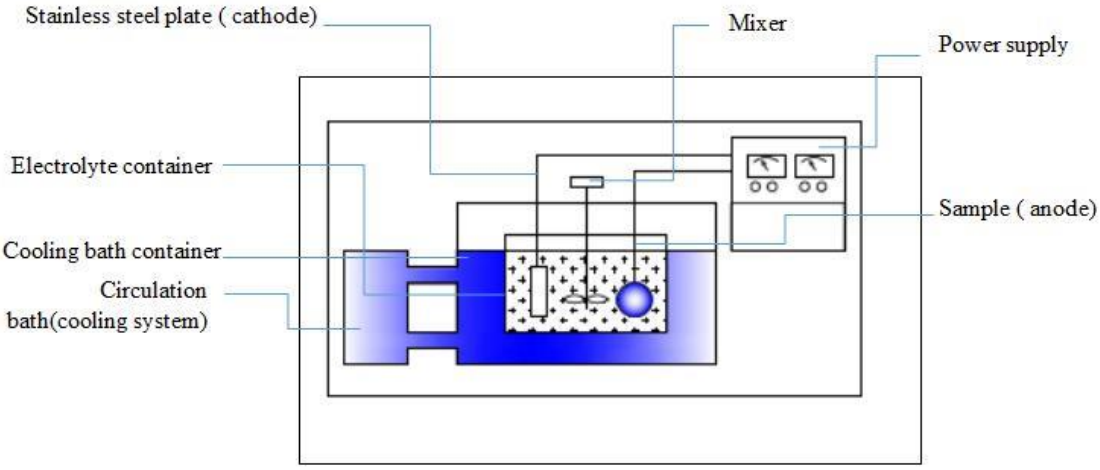


Fig.(1): MAO coating equipment

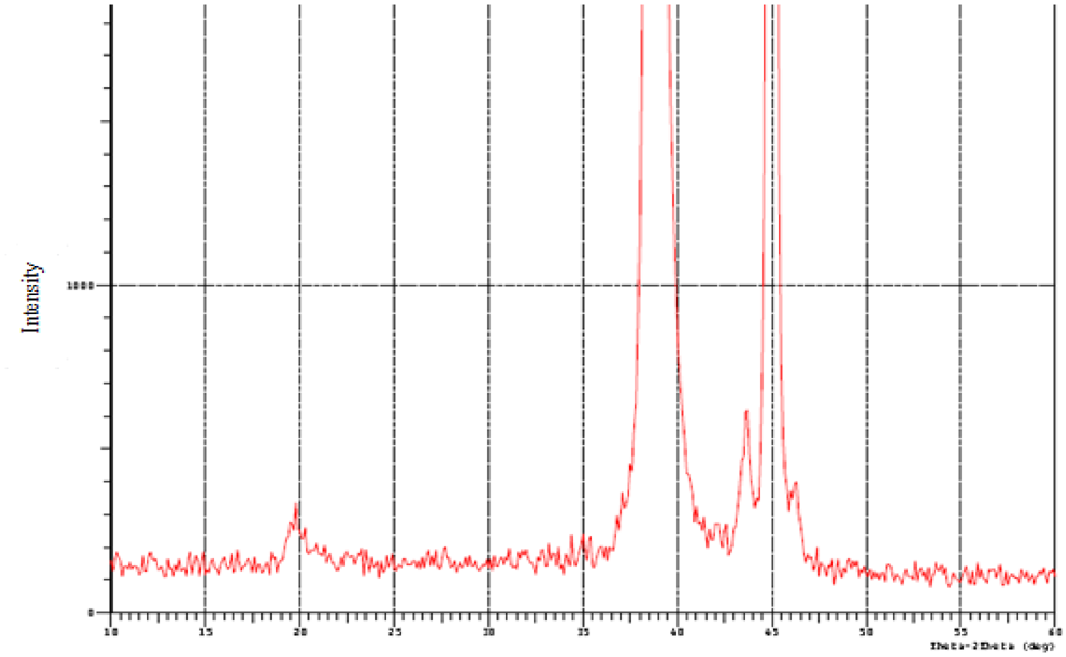


Fig. (2): XRD patterns of sample ME_2

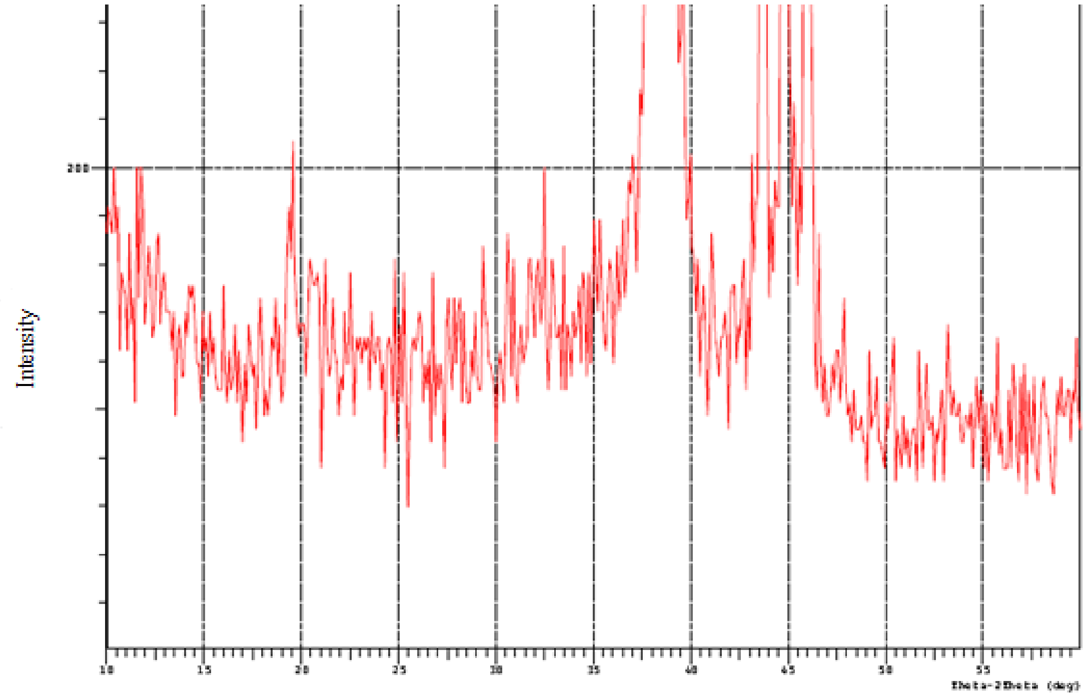
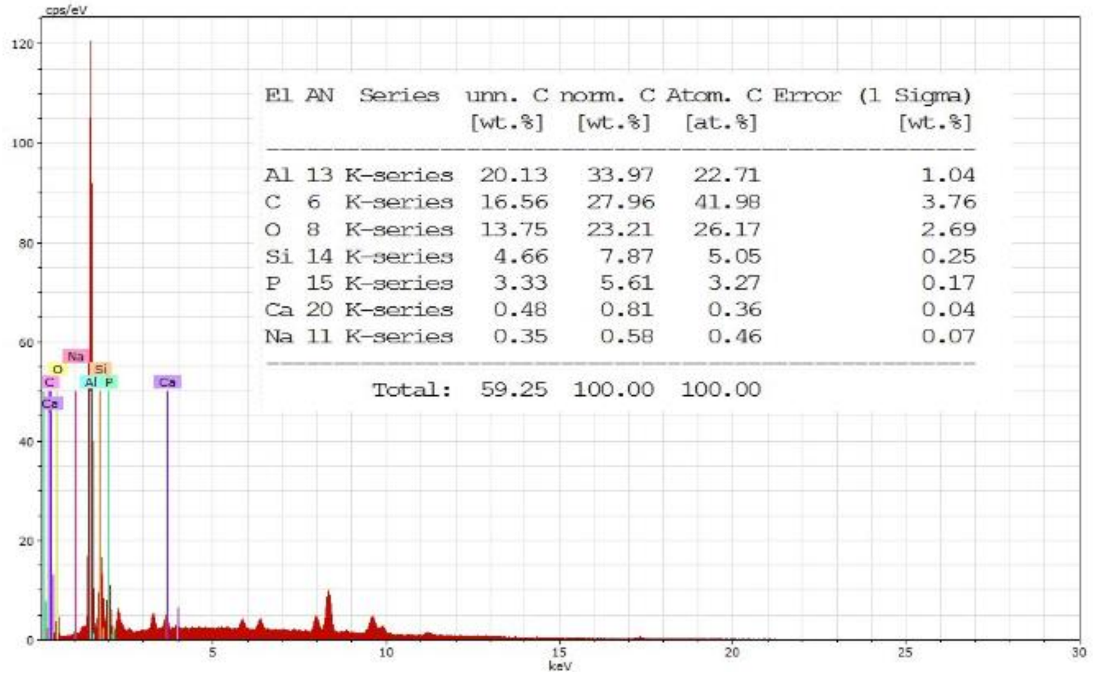


Fig. (3): XRD patterns of sample ME_5



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
Al 13 K-series  20.13   33.97   22.71            1.04
C   6 K-series  16.56   27.96   41.98            3.76
O   8 K-series  13.75   23.21   26.17            2.69
Si 14 K-series   4.66    7.87    5.05            0.25
P  15 K-series   3.33    5.61    3.27            0.17
Ca 20 K-series   0.48    0.81    0.36            0.04
Na 11 K-series   0.35    0.58    0.46            0.07
------------------------------------------------------
        Total:  59.25  100.00  100.00
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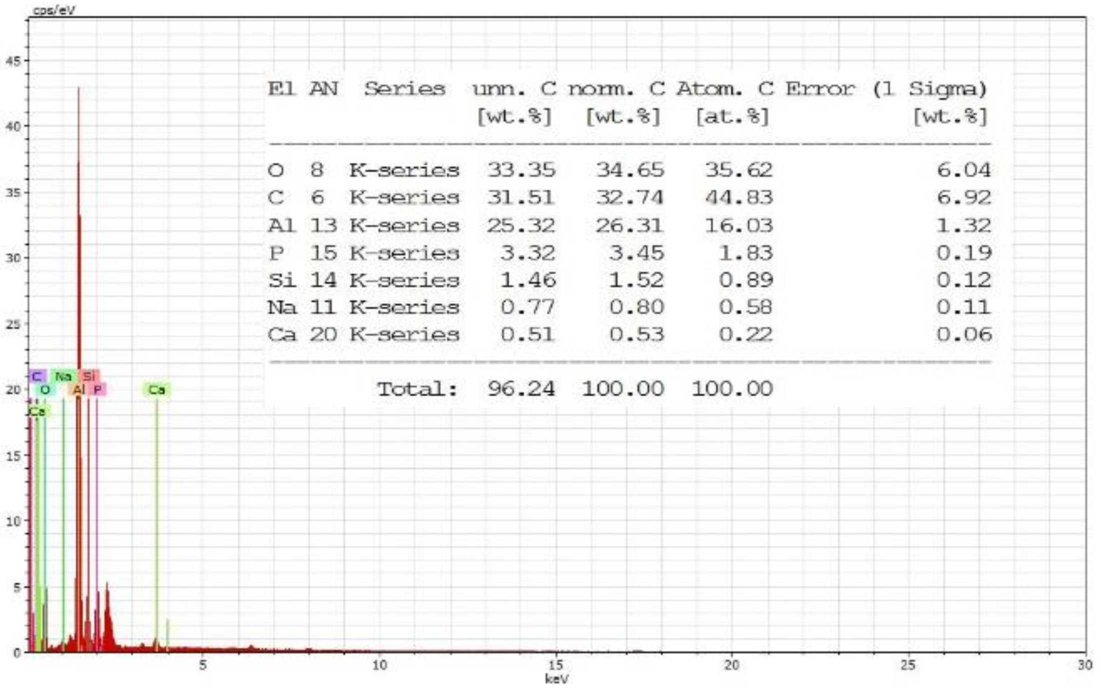
Fig. (4) EDS results of sample ME2



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
------------------------------------------------------
O   8 K-series  33.35   34.65   35.62            6.04
C   6 K-series  31.51   32.74   44.83            6.92
Al 13 K-series  25.32   26.31   16.03            1.32
P  15 K-series   3.32    3.45    1.83            0.19
Si 14 K-series   1.46    1.52    0.89            0.12
Na 11 K-series   0.77    0.80    0.58            0.11
Ca 20 K-series   0.51    0.53    0.22            0.06
------------------------------------------------------
        Total:  96.24  100.00  100.00
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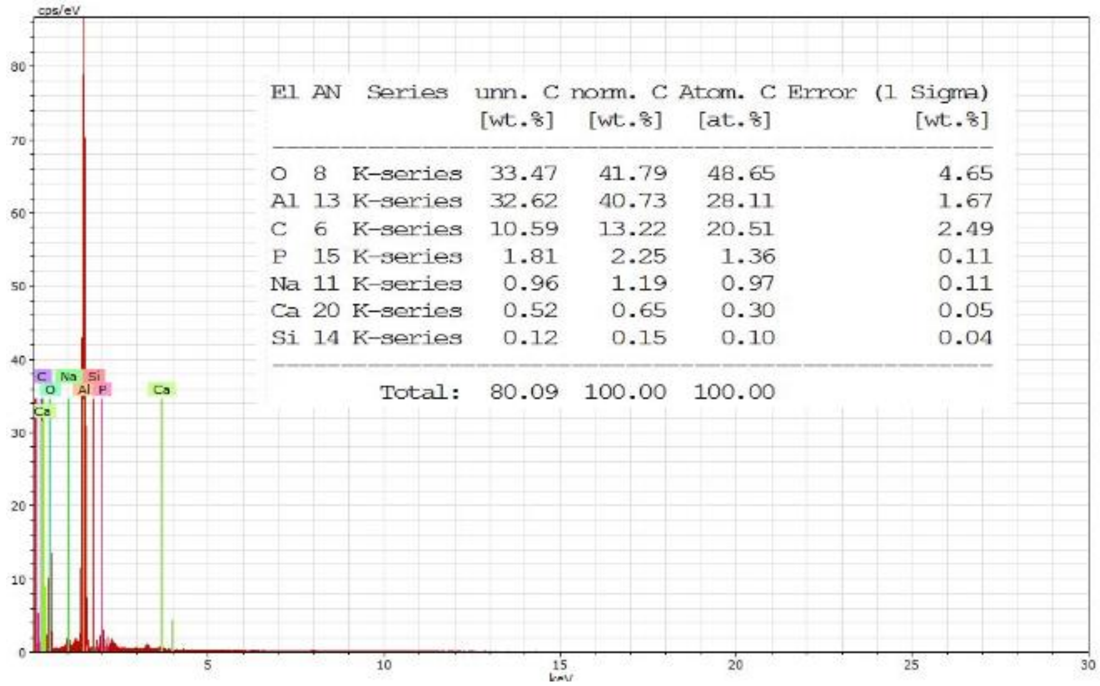
Fig. (5) EDS results of sample ME3



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
O  8  K-series  33.47   41.79   48.65            4.65
Al 13 K-series  32.62   40.73   28.11            1.67
C  6  K-series  10.59   13.22   20.51            2.49
P  15 K-series   1.81    2.25    1.36            0.11
Na 11 K-series   0.96    1.19    0.97            0.11
Ca 20 K-series   0.52    0.65    0.30            0.05
Si 14 K-series   0.12    0.15    0.10            0.04
-------------------------------------------------------
        Total:  80.09  100.00  100.00
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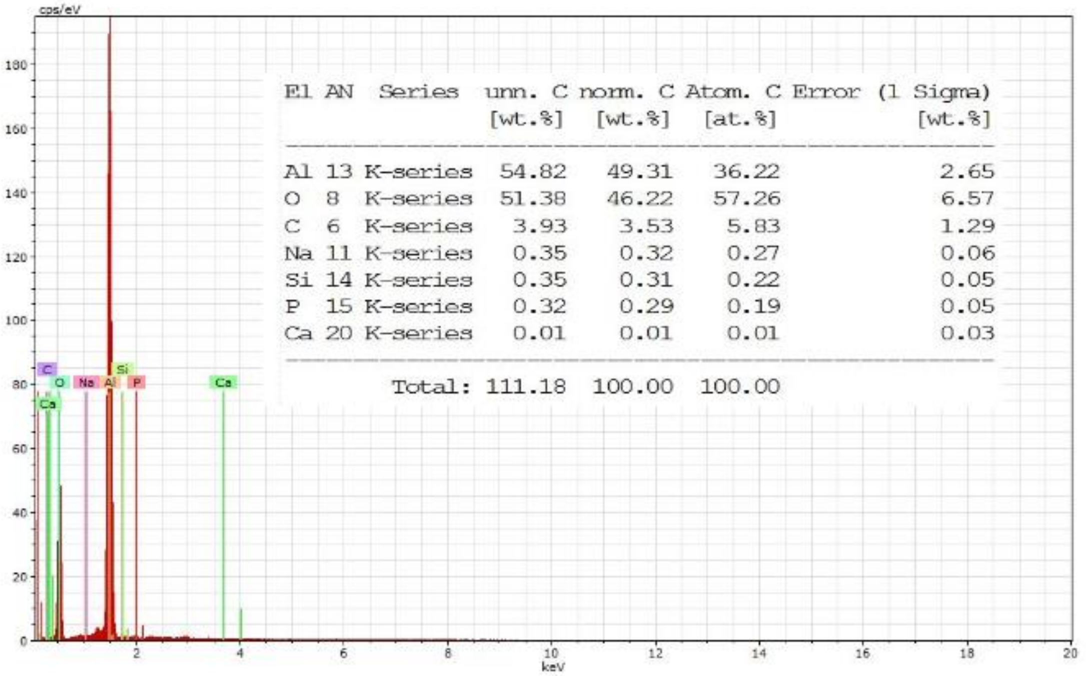
Fig. (6) EDS results of sample ME4



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]          [wt.%]
-------------------------------------------------------
Al 13 K-series  54.82   49.31   36.22            2.65
O  8  K-series  51.38   46.22   57.26            6.57
C  6  K-series   3.93    3.53    5.83            1.29
Na 11 K-series   0.35    0.32    0.27            0.06
Si 14 K-series   0.35    0.31    0.22            0.05
P  15 K-series   0.32    0.29    0.19            0.05
Ca 20 K-series   0.01    0.01    0.01            0.03
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        Total: 111.18  100.00  100.00
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Fig. (7) EDS results of sample ME5

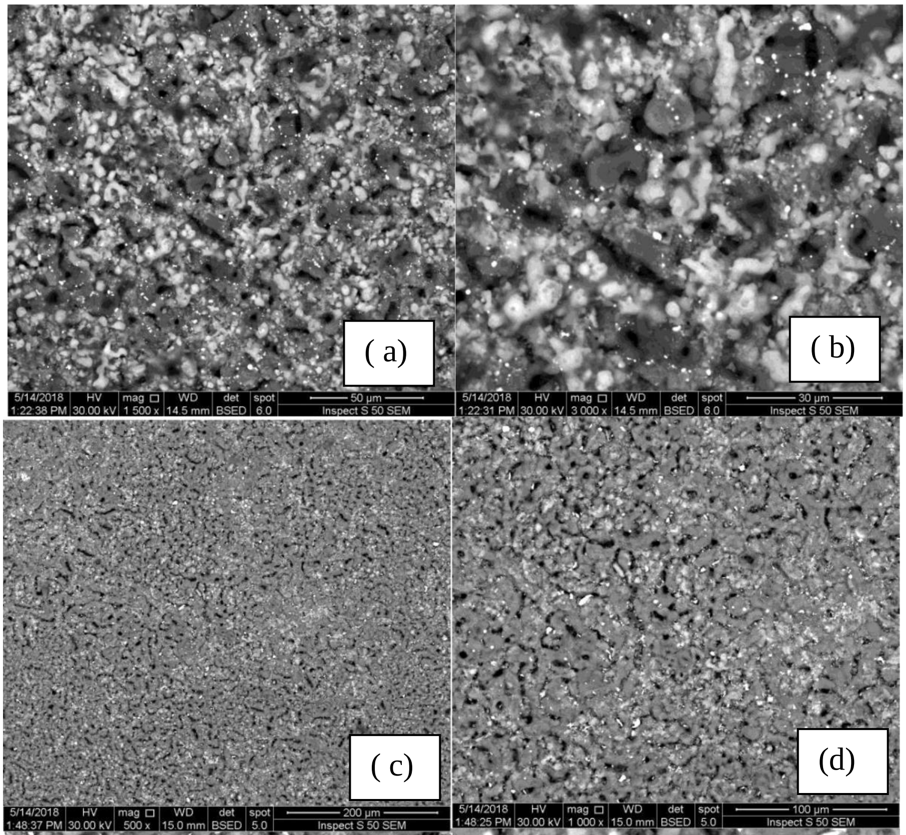


Fig. (8): Surface morphology results from SEM observation of sample ME_2 at different magnifications:(a)500X,(b) 1000X,(c) 1500X,and (d) 3000X.

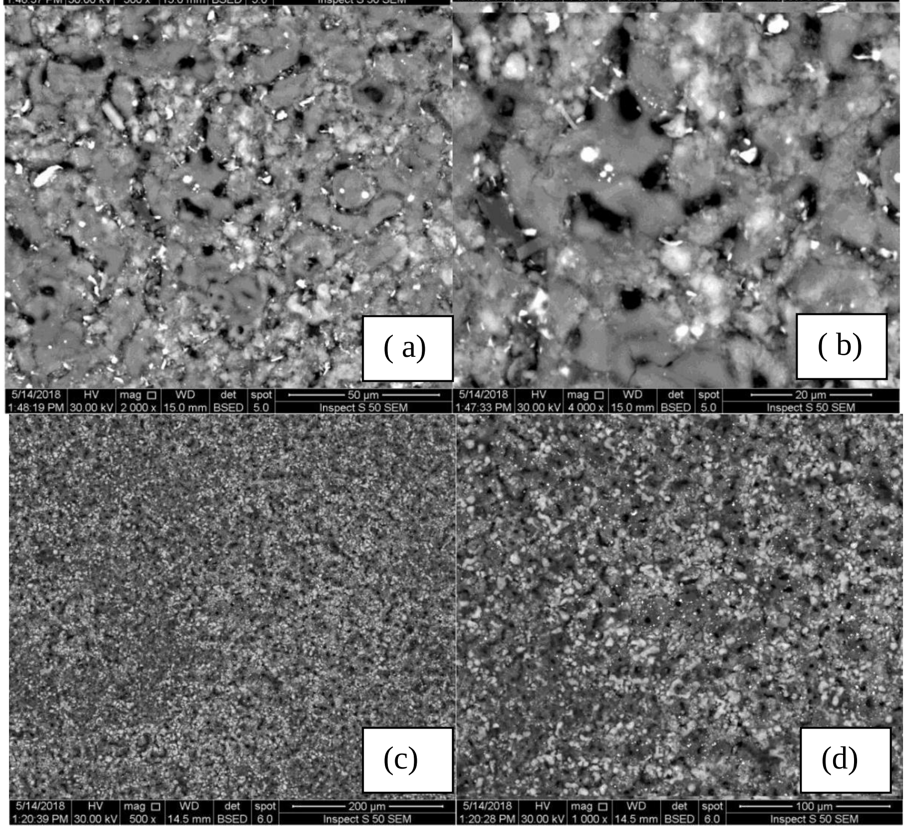


Fig. (9): SEM results of sample ME_3 at different magnifications :(a)500X,(b) 1000X,(c) 2000X,and (d) 4000X.

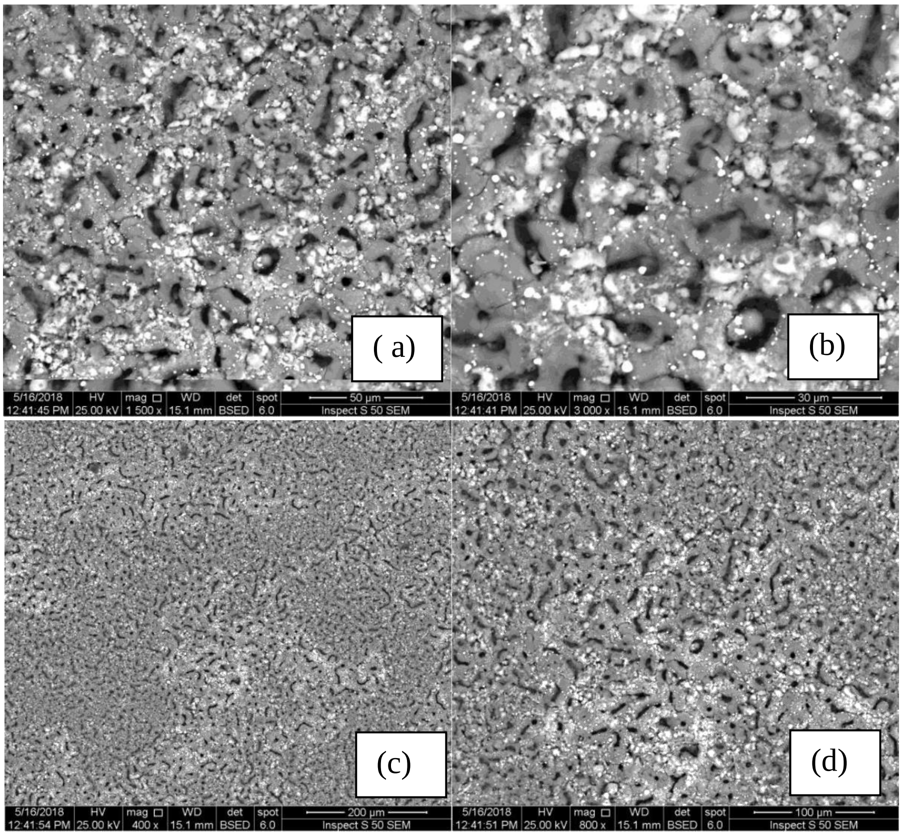


Fig. (10): SEM results of sample ME_4 at different magnifications :(a)400X,(b) 800X,(c) 1500X,and (d) 3000X.

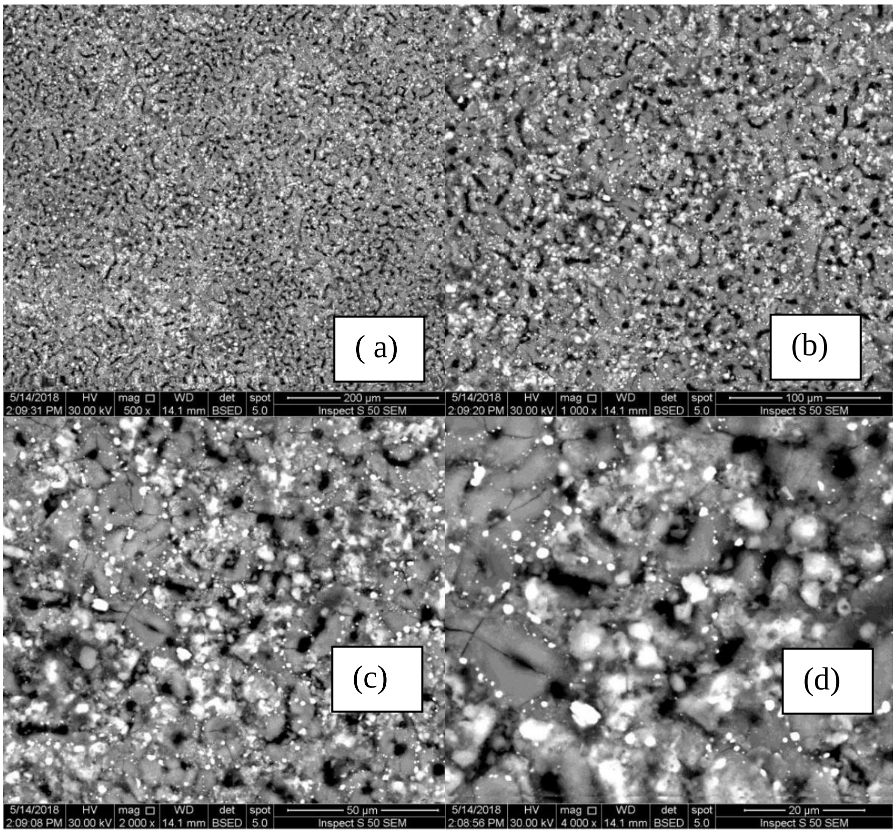


Fig. (11): SEM results of sample ME_5 at different magnifications:(a)500X,(b) 1000X,(c) 2000X,and (d) 4000X

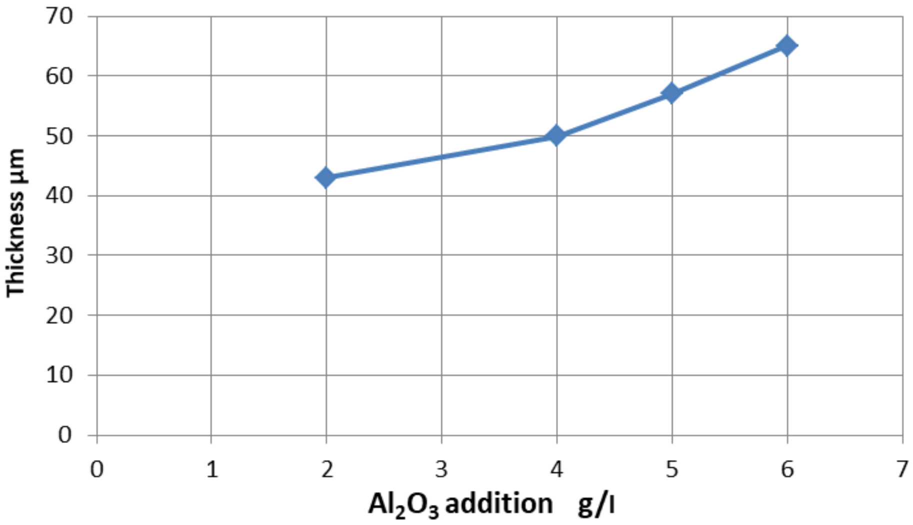


Fig. (12): Effect of Al_2O_3 addition on coatings thickness

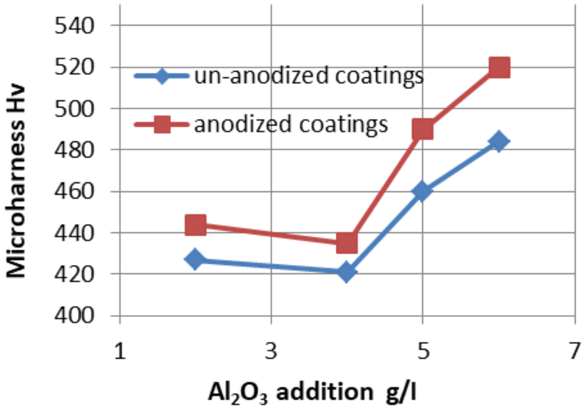


Fig. (13): Effect of Al_2O_3 addition on coatings hardness

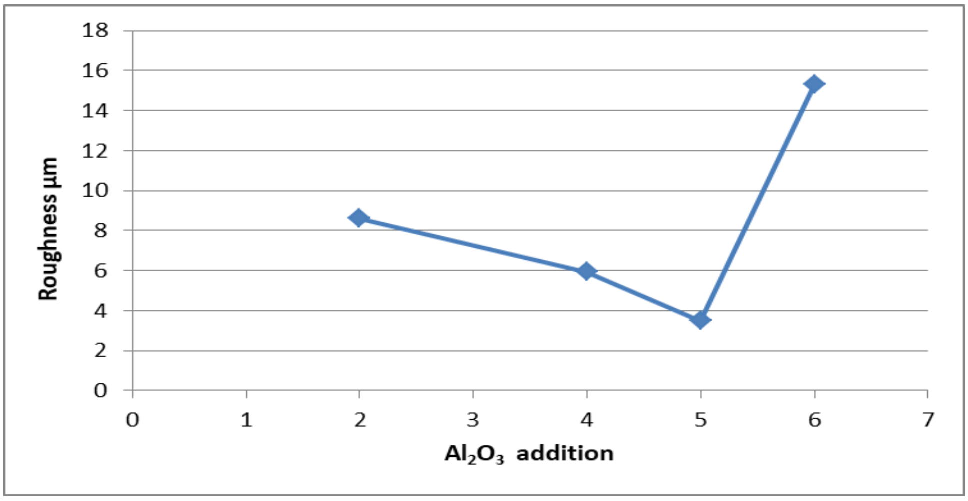
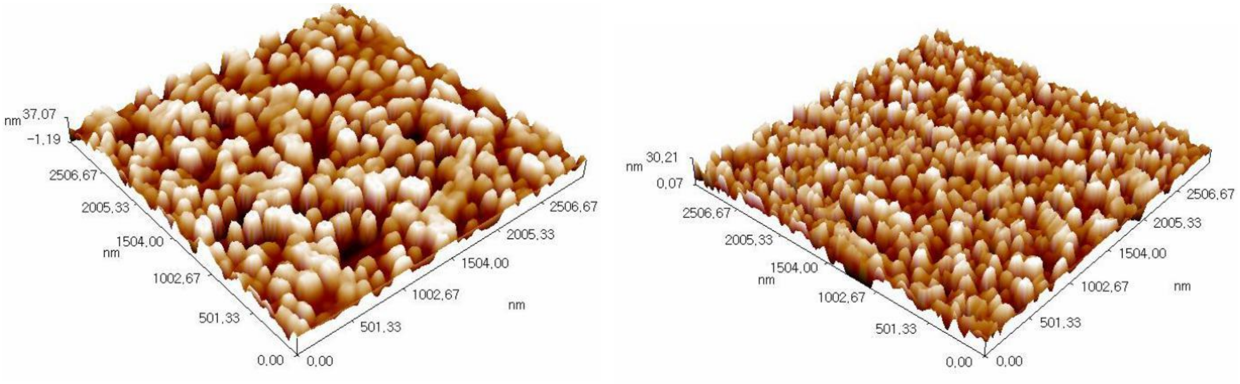
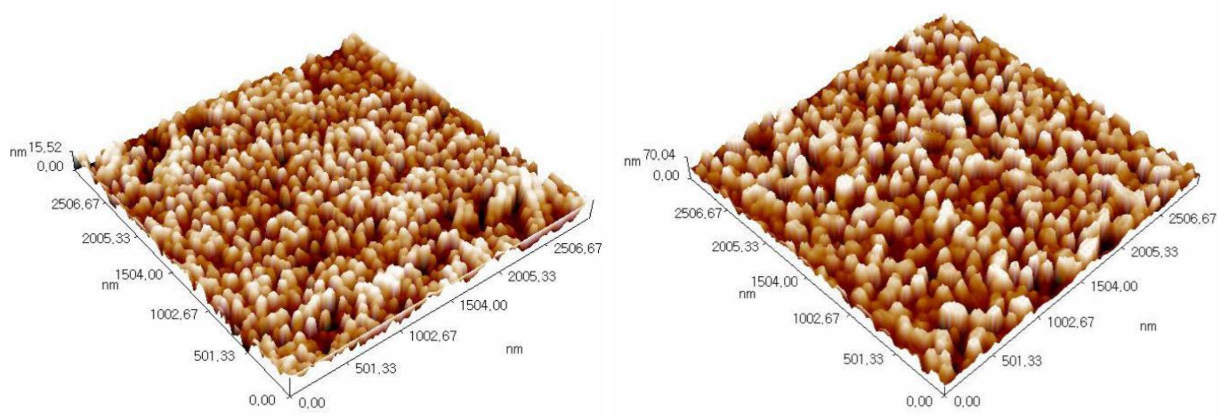


Fig. (14): Effect of Al_2O_3 additives on coatings roughness



(a): Ra=8.61µm

(b): Ra=5.94 µm



(c): Ra=3.48 µm

(d): Ra=15.30 µm

Fig. (15): AFM Results of Samples: (a) ME_2 ,(b ME_3 ,(c) ME_4 and (d) ME_5

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