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Effects of Natural Rock and Nano-TiO_2 Additives on Al_2O_3 Layer Deposited on Al Alloys by Micro-Arc Oxidation (MAO)

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Abstract: Ceramic coatings on Al alloys were prepared via. micro arc oxidation process using natural rock (10 g/L fired and unfired porcelanite) and (2.4 g/L) nano-TiO_2 additives. The phase composition, microstructure (SEM and EDX), micro hardness, thickness, roughness and wear resistance of the coatings were studied. The results showed that the thick and hard γ-Al_2O_3 ceramic coatings can be deposited by MAO process on Al alloys using electrolytes contained fired porcelanite with modified tribological properties and less porosity and its non-uniform distribution in the structure. The addition of nano-TiO_2 recorded the highest hardness and reduced the pore size and tunnels in coatings structure.

Key words: Aluminium alloy, micro arc oxidation, hardness, rock additive and wear resistance, structure, Iraq

INTRODUCTION

Aluminum and its alloys are broadly utilized in automotive and aerospace industry owe to their excellent properties such as low density, high strength, good non-magnetic properties and good formability properties. However, the poor surface wear resistance and hardness inhibit their application in various ways (Xiang *et al*., 2015).

Ceramic coatings are very effective in producing wear-resistant and hard layers on the surface of aluminum alloys. Recently, different surface treatments such as Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD) and thermal spraying have been applied to improve the poor tribological properties of metallic substrates (Wang *et al*., 2010).

Micro-Arc Oxidation process (MAO) has gained much interest as an effective plasma electrolytic surface process to form a hard and thick alumina Al_2O_3 coating on Al alloys components through high voltage plasma discharging to improve their hardness and tribological properties (Li *et al*., 2013; Jin *et al*., 2006). MAO can be economically and quickly produced with wide coating composition and thickness range on components of any size and shape, depending on the treatment conditions (Kumruoglu *et al*., 2011).

MAO technique involves electro-chemical/thermal oxidation in alkaline electrolytes through DC and AC high voltage surface multiple discharges (Huang *et al*., 2008). Many works have focused on the effect of composition and concentration of electrolytes, oxidation time, current density and duty cycle on MAO coating (Al-Dulamy and Rubay, 2017; Ma *et al*., 2014). Recently, in order to change the composition of MAO coating and further improve its performance, some researchers, therefore have tried to add different nano-particles into the electrolyte to obtain ceramic coating with complex composition and thus to further improve its property (Wang *et al*., 2014). The results proved that the additives doping affected the morphological feature of the coating while it had little effects on the elemental composition (Li *et al*., 2013). The present study is an attempt in using of natural rock additives of porcelanite and nano-TiO_2 additives to modify the MAO electrolyte and coatings deposited on Al alloy.

MATERIALS AND METHODS

Micro arc oxidation: Commercially, 1105-GOST4784 Al alloy (0.145 Si, 0.317 Fe, 5.21 Cu, 0.692 Mn, 1.37 Mg, 0.007 Cr, 0.006 Ni, 0.003 Zn, 0.023 Ti, 0.020 Pb, 0.006 V and Al Ball) with (Ø25×5) mm^2 were used as the substrates for MAO process. All samples were ground utilizing SiC papers, cleaned by acetone, rinsed by distilled water and air-dried. The surface roughness and hardness of the alloy were 0.254 μm and 183.3 HV, respectively.

Porcelanite powder, collected from Iraqi porcelanite rock was washed, dried at 100°C for 5 h. Then, fired at 900°C for 3 to convert all the carbonate content into oxides. Then, the powder was milled for 8 h to obtain a fine-size powder. Nano-TiO_2 powder (Ø10 nm) (purity 99%) was used in the electrolyte. In the MAO process, a homemade high voltage AC-DC power supply (Fig. 1) was

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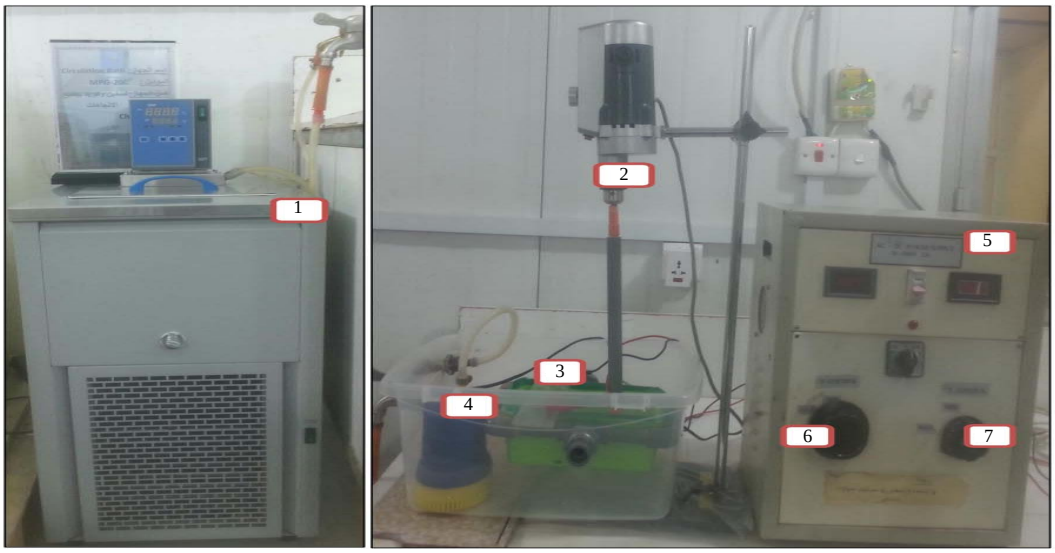

Fig. 1: Photographs of MAO coating unit: 1) Circulation bath (cooling system); 2) Mixer; 3) Coating container; 4) Cooling container; 5) Power supply; 6) Voltage gauge and 7) Current gauge

Table 1: Composition of basic materials and porcelanite containing electrolytes

Electrolyte	Composition	Time (min)
A_1	(20 g) KH_2PO_4 (8 mL)	15
A_2	H_3PO_4 (12 g)	30
A_3	$(NH_3)_2MO_7O_{24}$	45
A_4	(10 g) Na_2CO_3	60
B_1	(20 g) KH_2PO_4 (8 mL)	15
B_2	H_3PO_4 (12 g)	30
B_3	$(NH_3)_2MO_7O_{24}$ (10 g)	45
B_4	Unfired porcelanite	60
C_1	(20 g) KH_2PO_4 (8 mL)	15
C_2	H_3PO_4 (12 g)	30
C_3	$(NH_3)_2$ MO_7O_{24} (10 g)	45
C_4	Fired porcelanite	60
D	(20 g) KH_2PO_4 (8 mL) H_3PO_4 (12 g) $(NH_3)_2MO_7O_{24}$ (10 g) fired porcelanite (2.4 g) nano-TiO_2	45

used and the aluminium sample was used as anode whereas the cathode was a stainless steel in an electrolyte bath. MAO was applied at a voltage 270-360 V, 10-25°C for 15-60 min. The basic (Awad and Qian, 2006) and modified electrolytes were prepared with one liter of distilled water as illustrated in Table 1. Eventually, the coated samples rinsed using distilled water and then dried by air.

Apparatuses and characterization: The composition of the coatings were examined using X-Ray Diffractometer (XRD-6000 Shimadzu, Japan, Cu Kα radiation, 40 kV, 30 MA, 6°/min scanning speed). The elemental analyses were completed with Energy Dispersive X-Ray Spectroscopy (EDS). The microstructure of coatings were studied using Scanning Electron Microscope (SEM, TESCAN/ VEGA 2 Series/USA). Micro-hardness, surface roughness and thickness of the coatings were identified using (HVS-1000, Laryee, digital micro-hardness tester) at 9.8 N load, surface roughness test) and microprocessor CM-8822 and SRT-6210, respectively. Pin on disc wear test (Micro test-28021) using alumina pin at load (10 g) for 15 min, the weight losses were recorded after 5 min was applied to the coated and uncoated substrates in order to evaluate the friction coefficient and wear resistance.

RESULTS AND DISCUSSION

XRD and EDS results: Figure 2-5 show the XRD results of the coated samples using rock and nano-TiO_2 containing electrolytes. Figure 6-8 show the EDS results. XRD results of MAO coatings showed the aluminium peaks (JCPDS No. 004-0787) which come from the underlying substrate were detected due the X-rays penetration into the Al alloy substrates and γ-Al_2O_3 (JCPDS No. 010-0425) phase. The Al_2O_3 is created by plasma chemical thermal reactions in the discharging channels. Also, the appearance of Al in the coatings patterns can be attributed to the presence of porosity in MAO coatings. EDS Analysis proved the existence of Al and O element in the coatings, thereby denoted to the formation of Al_2O_3 ceramic layers modified with another elements of C and Si at different weight of these modification elements.

SEM results: Figure 9-12 illustrate the surface morphology of ceramic coatings (samples A_3-C_3 and

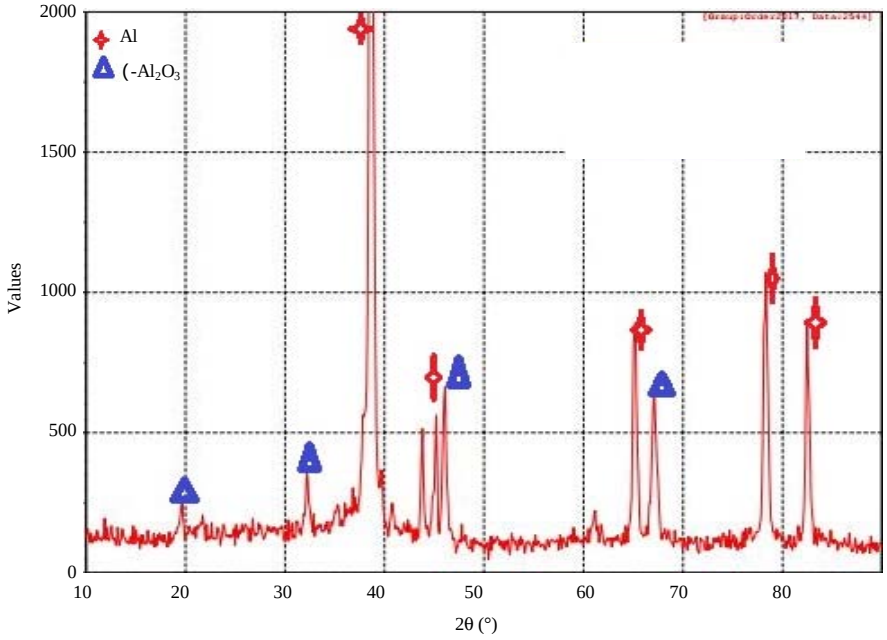

Fig. 2: XRD patterns of sample A_3

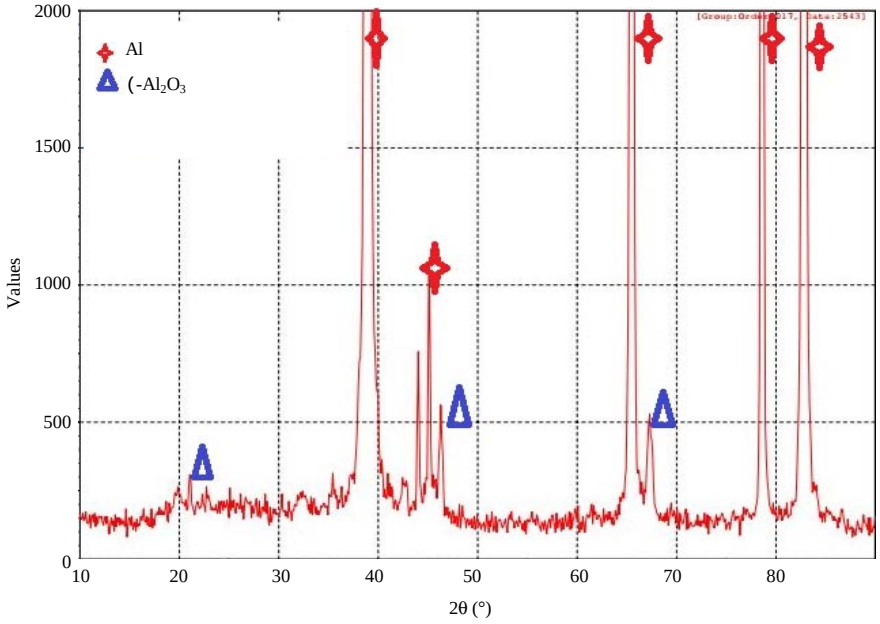

Fig. 3: XRD patterns of sample B_3

D at different magnifications) which were formed by the molten Al_2O_3 flow out of the discharge channels rapidly solidified after the quenching effect by the surrounding electrolyte (Wang *et al*., 2010). The coatings surfaces are characterized by island-like structures have the features of porosity and roughness. It can be observed that the sample A_3 showed the highest porosity and non-uniform distribution. For coatings of sample B_3 shown in Fig. 10, it can be observed that the porosity decreased with the addition of (10 g porcelanite) to the electrolyte it may attributed to incorporation of porcelanite components into the micro-pores which leads to reduce the amount of pores in the structure. Such behavior can be also noticed at MAO coatings modified with fired porcelanite (sample

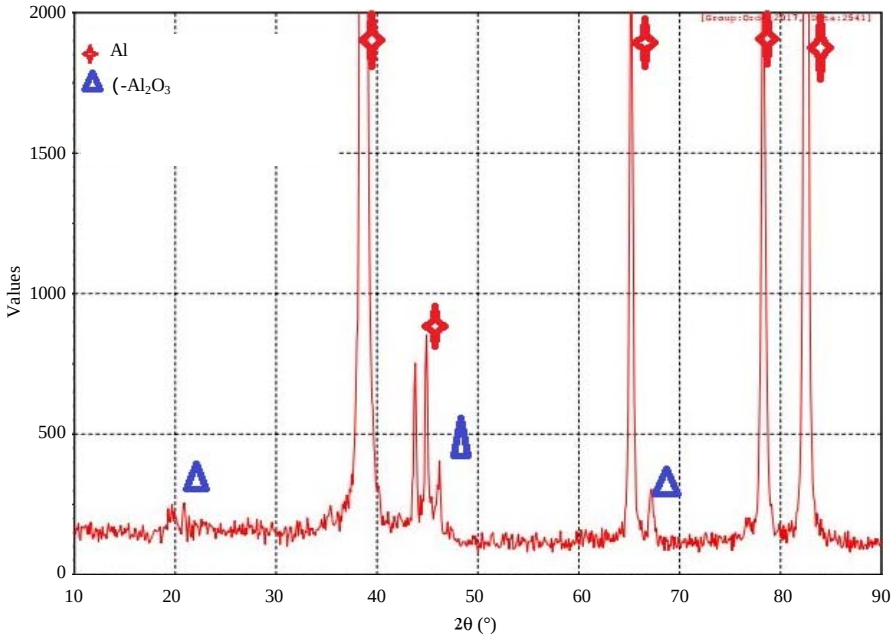

Fig. 4: XRD patterns of sample C_3

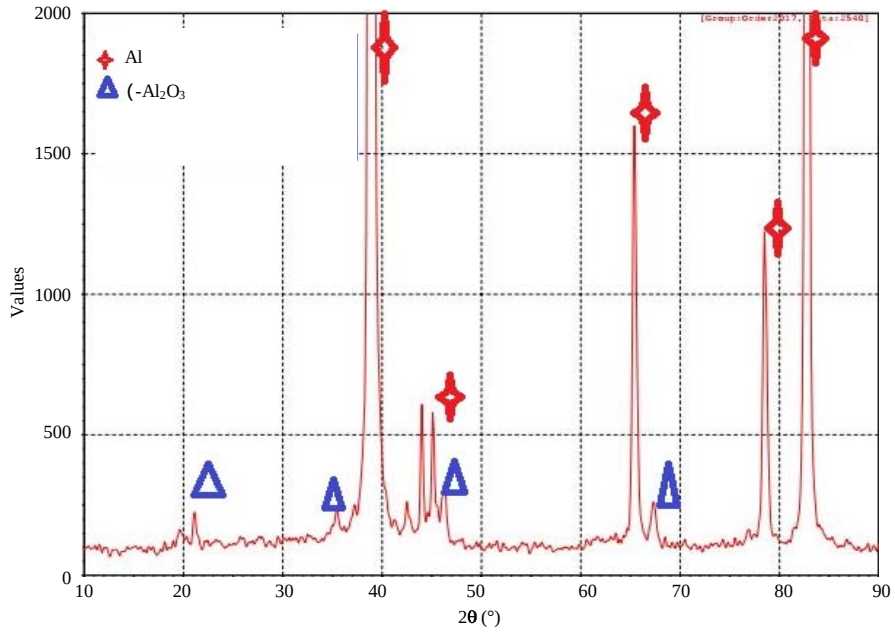

Fig. 5: XRD patterns of sample D

C_3) that has its effect on the hardness improvement. With adding (2.4 g), nano-TiO_2 the structure characterized with less pores and uniform distribution which leads to the improvement of the coatings hardness.

Micro hardness, thickness and surface roughness results: Figure 13-15 show the results of micro hardness, thickness and roughness of the coated samples. In general, it can be observed that the coatings hardness values were in the range (167.7- 400.5 HV) and the highest hardness value could be recorded after the addition of (10 g) of fired porcelanite to the electrolyte at time 45 min. Also, the addition of nano-TiO_2 to the fired porcelanite provided a higher hardness (400.5 HV). For the samples A_1-A_4, the hardness increased with increasing deposition time and the thicker coating (A_3)

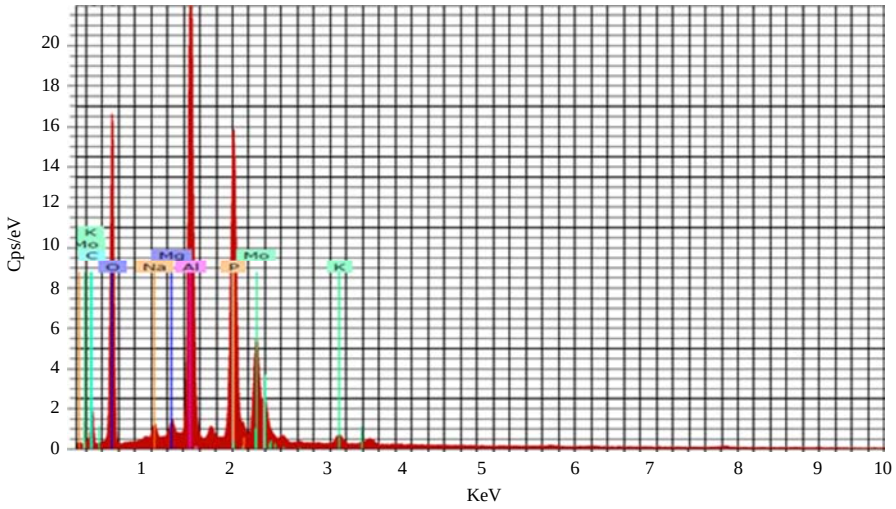

Fig. 6: EDS of sample A_3

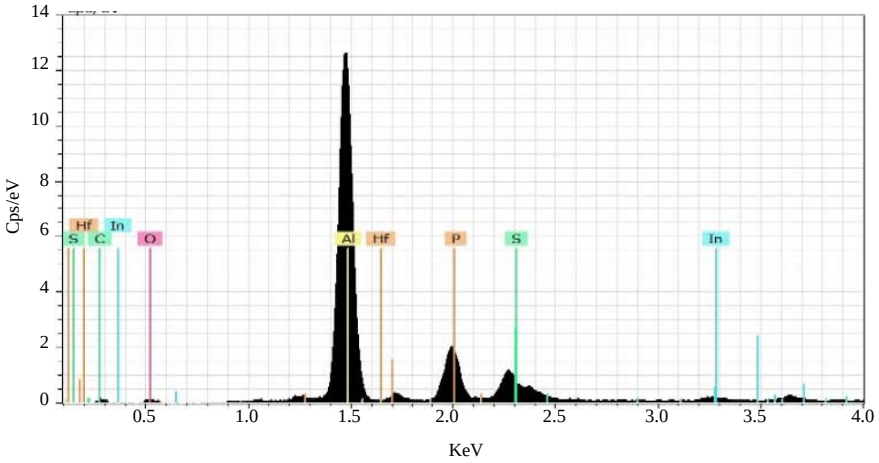

Fig. 7: EDS of sample B_3

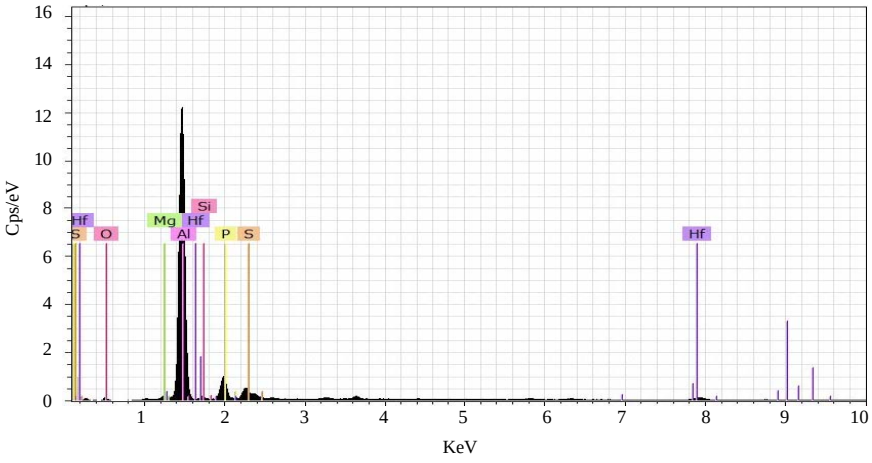

Fig. 8: EDS of sample C_3

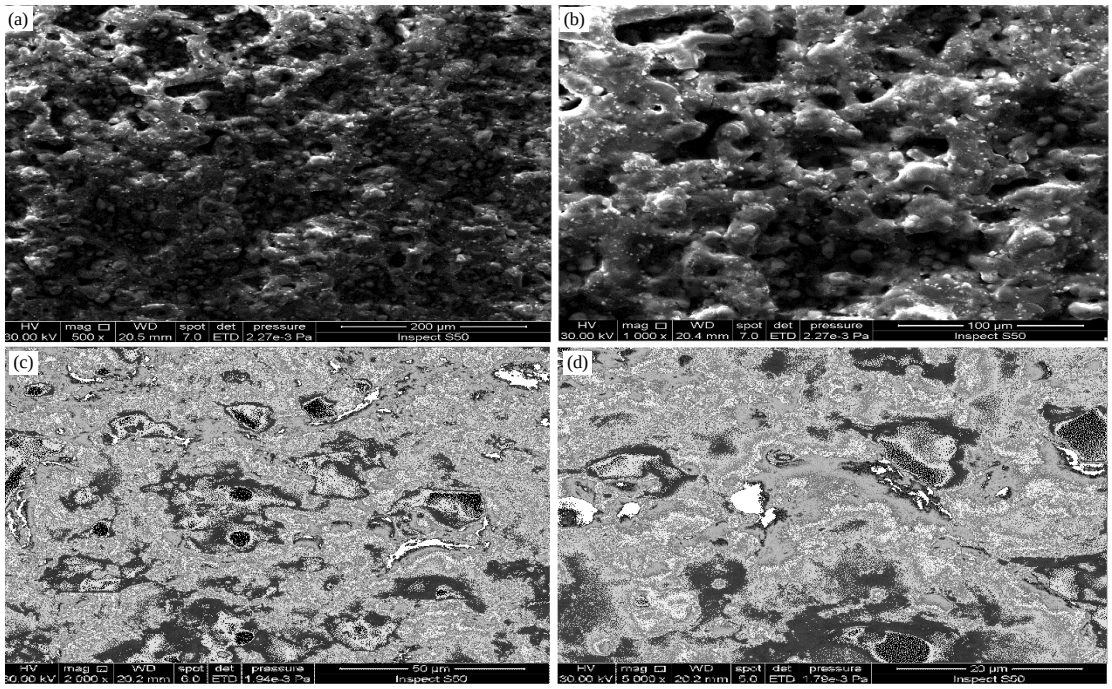

Fig. 9: a-d) SEM images of sample A_3 at different magnification

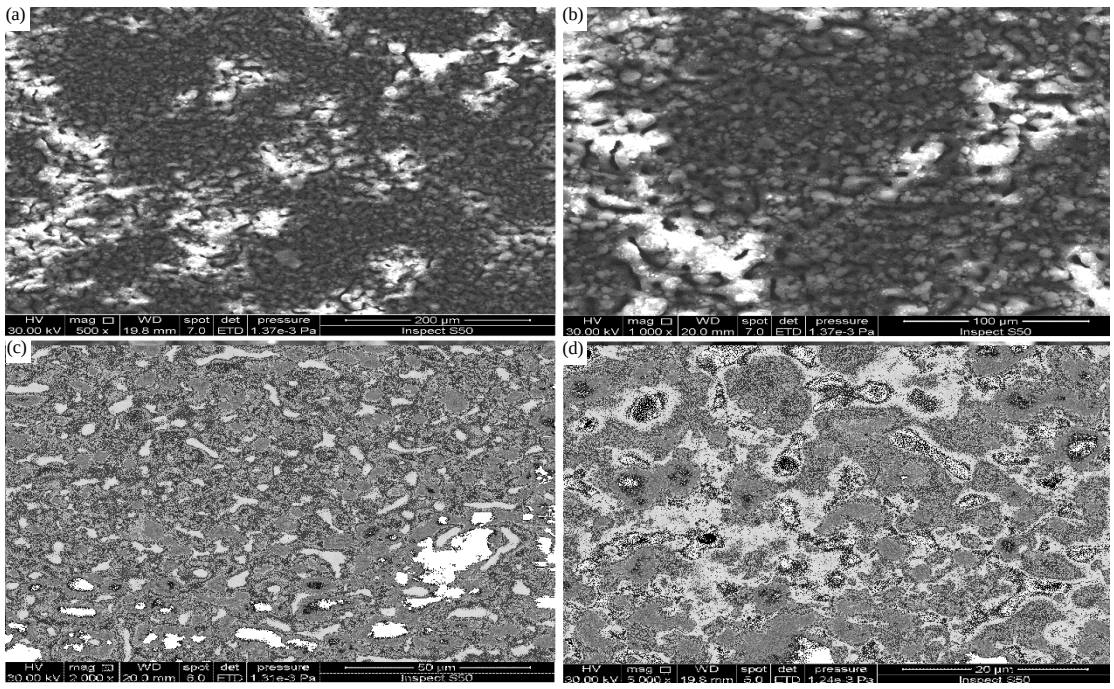

Fig. 10: a-d) SEM images of sample B_3 at different magnification

has the higher value of hardness (303.7 HV) among the other A samples. The addition of fired porcelanite recorded a higher hardness than the unfired porcelanite. The coatings thickness varied with the deposition time in the range (38-78.1 μm) and the highest thickness value could be recorded after the addition of the fired

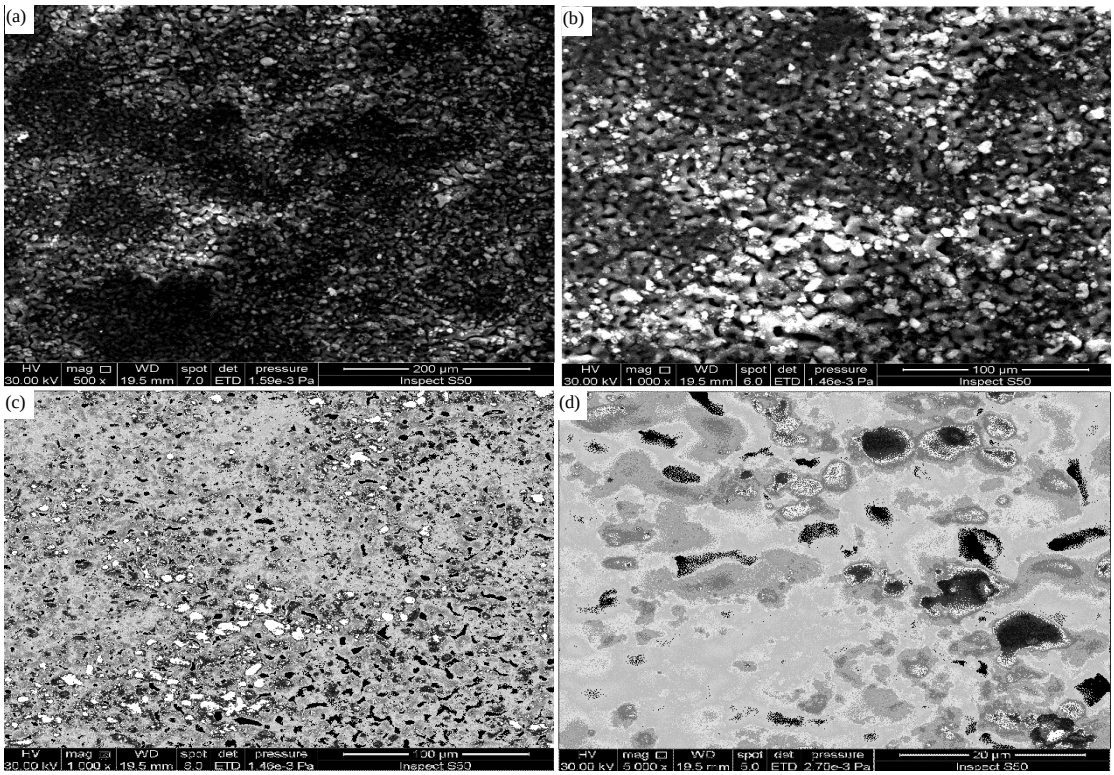

Fig. 11: a-d) SEM images of sample C_3 at different magnification

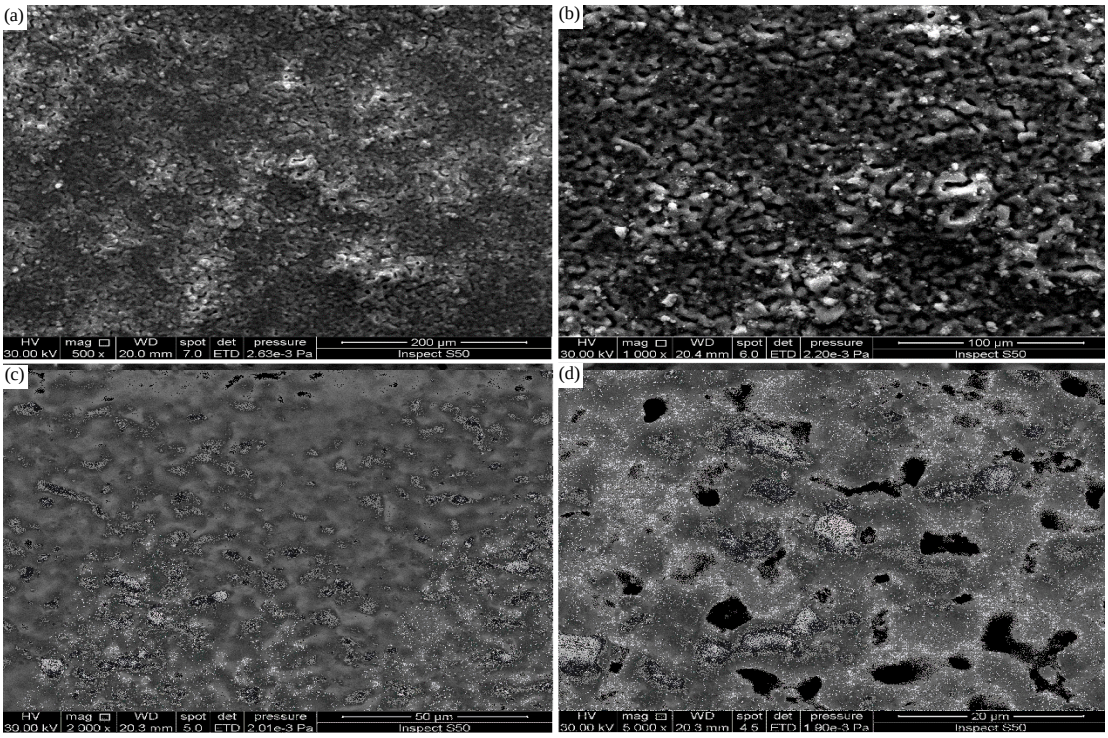

Fig. 12: a-d) SEM images of sample D at different magnification

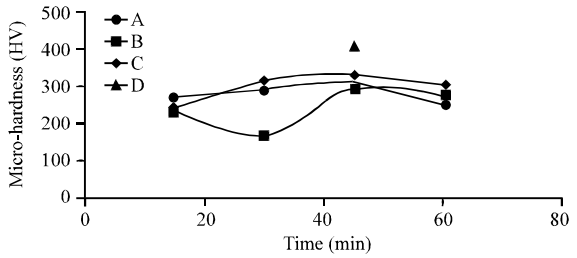

Fig. 13: Relationship between the micro-hardness and deposition time

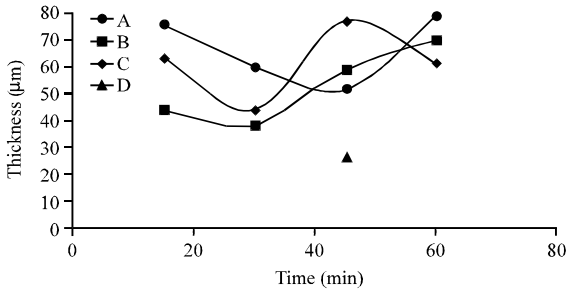

Fig. 14: Relationship between coatings thickness and deposition time

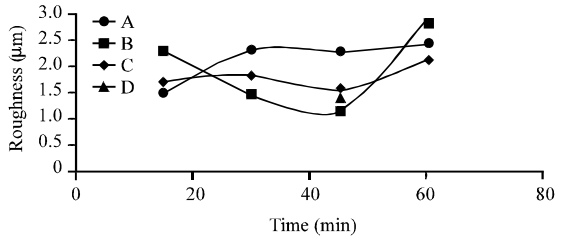

Fig. 15: Relationship between surface roughness and deposition time

porcelanite (78.1 µm for sample C_4). The addition of nano-TiO_2 to the rock additives could not has the noticeable effect on increasing the coatings thickness in comparison with its effect on improving the hardness.

Wear results: Table 2 shows the weight losses and friction coefficient for the coated and the uncoated samples. It can be observed that the weight losses of coated samples with different additives were lower than those of uncoated samples. Also, samples A_3 and D recorded the lowest weight loss among the others samples. The friction coefficient decreased for the MAO coated samples and the lowest friction coefficient was recorded with the using of (2.4 g) nano TiO_2. These results could prove the success of using the rock additives in improve the wear resistance of aluminium alloys.

Table 2: Results of weight loss and friction coefficient

Samples/Weight loss (g)	µ
Uncoated samples	
0.0006	~0.072
0.0008	
0.00024	
A_3	
0.0003	~0.021
0.0001	
0.0001	
B_3	
0.0001	~0.053
0.0001	
0.0003	
C_3	
0.0002	~0.047
0.0001	
0.0004	
D	
0.0003	~ 0.015
0.0002	
0.0001	

CONCLUSION

In summary, the γ-Al_2O_3 ceramic coatings were successfully deposited on the aluminium alloy using modified electrolytes contained natural rock additives of porcelanite. The deposited coatings with 167.7- 400.5 HV micro hardness and 26- 78.1 µm thickness could enhance the wear resistance and friction coefficient of the aluminium surfaces. The addition of nano-TiO_2 with the fired porcelanite recorded the highest hardness where the hardness increased with deposition time increasing. The porosity and its non-uniform distribution decreased after using of fired porcelanite and the addition of nano TiO_2 could decrease the pores size and tunnels in the coating structure.

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