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CHARACTERIZATION CORROSION BEHAVIOR OF NANO ALUMINA COATINGS ON $Al_{12}Si$ FABRICATED BY ELECTROPHORETIC DEPOSITION

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ABSTRACT: - This paper compares the corrosion behavior of Al_2O_3 coatings produced by Electrophoretic technique to Nano-sized alumina coatings on aluminum alloy surfaces by using a well dispersed stable suspension produced by addition of Al_2O_3 powder plus a small amount of water and iodine to ethanol. Electrophoretic deposition for (2,3,4 and 5) min at (50-60) V resulted in formation of a uniformly dense film on the top, The maximum defect-free sintered thickness by EPD allowed us to obtain coatings as thick as 7 µm. The protective behavior against corrosion and the corrosion kinetics of the produced films were studied through polarization resistance (PR) measurements in aggressive media (sea water). The corrosion resistance with sintering to 400C° with 2hours holding time has decreased the corrosion current density (about $32\mu Acm^2$) when compared coatings without sintering for coatings produced by EPD. Moreover, alumina coatings present an excellent resistance in sea water. AFM observations suggest that coatings produced by EPD are homogeneous and defect-free. The aim of this work has been to prepare thick Al_2O_3 coatings deposited by EPD in order to increase the corrosion resistance of aluminum substrates. The corrosion resistance of the coatings has been evaluated through electrochemical methods as a function of different processing parameters: final thickness of the coating, applied voltage, and deposition time.

Keywords: polarization resistance; Electrophoretic deposition /coatings; alumina.

1- INTRODUCTION

Electrophoretic deposition (EPD) is a rapid developing technology capable of producing ceramic coatings (1, 2), functionally graded materials, thin and thick layers, porous materials and nanoparticle deposits (3, 4). Various materials including alumina, zirconia, hydroxyapatite and carbon nanotube (5) have previously been deposited by this technique. EPD has received increasing attention because of simplicity, low cost, applicability to different materials, possibility of using complicated substrates and capability of scale-up to large production rates (6, 7). EPD comprises two steps: (i) charged colloidal suspended particles are forced to migrate towards an electrode under the applied electric field and (ii) the particles depositing on the working electrode form a coherent dense layer (5, 7). These processes follow drying and densification by sintering or curing. Although many efforts have been devoted to understand this process, there are still many parameters that must be worked on to control the formation of the EPD layers (8).

Two types of parameters are to be considered to control the morphology and microstructure of the electrophoretically deposited layer (9). (i) physical factors comprising of the applied voltage, deposition time, suspension concentration and substrate specifications and (ii) chemical parameters including zeta potential, liquid-phase dielectric constant, raw materials morphology and their particle size plus conductivity, viscosity and stability of the suspension. Kinetic equations have previously been developed to predict the effect of the influential parameters on the rate of deposition (9, 10).

Packing behavior of the colloidal particles is influenced by particle size, particle concentration, interaction between particles and rheological properties of the mixture. Packing compactness affects shrinkage, density and microstructure of the consolidated ceramic objects (11). A uniform green density has substantial effect on controlling the sintering contraction and microstructural flaws which may cause in-use component fail (12). It is commonly accepted that ceramic compacts having high green density and small uniform pores can most effectively be densified by sintering (13, 14).

Much effort has been devoted to study the corrosion protection of metals (stainless steel, aluminum alloys, copper, carbon steel, galvanized steel, etc.) by coatings, but published results are often contradictory. Some papers have evaluated the protective behavior of the coating considering the variation of corrosion potential, a parameter not relevant for measuring the corrosion behavior (5). Inorganic coatings are adequate barriers against oxidation but show a poor behavior in electrolytic media due to the presence of micro-cracks or defects (6, 7).

Previous works described the use of EPD process to obtain thick Al_2O_3 coatings onto aluminum alloy using either acid-catalysed sols containing colloidal particles, or basic-catalysed particulate sols (9,11).

2. EXPERIMENTAL WORK

In this work, EPD was carried out with electric field applied between an aluminum silicon counter electrode (anode) and a substrate Stainless steel 316L (cathode). The distance between the electrodes was 10 mm, and they were kept in a liquid solvent, which contained a suspension of powders of the materials to be deposited. EPD was carried out at room temperature using applied voltages 50 V and deposition times of (2, 3, 4 and 5) minutes. The substrate sample was of dimensions 15 mm x 20 mm x 1.6 mm. The bath consisted of 5g/L alumina (Al_2O_3) aqueous dispersion of nano sized particles type MKN- A040 USA, suspended in Ethanol with distilled water. The electrolyte was charged by a suitable additive (0.5g/L Iodine) as shown in Table (1). Powder suspension was prepared by magnetic stirring of the mixture of ceramic powders in ethanol for 30 min. It was followed by a high-energy sonicator after deposition; the coatings were dried at room temperature prior to sintering. Vacuum sintering involved heating at 400 °C for 120 minutes. Heating and cooling rates were (6 °C/min and 30° C/min) as shown in Figure (1). The microstructures of coatings were examined using optical microscopy, scanning electron microscopy and atomic force Microscopy.

The EPD cell used in this study consists of a beaker and two electrodes suspended in the suspension. Figure. 2**.** Is shown the schematic EPD system used in this study.

Analytical balance with accuracy 0.0001gm (Scaltec instruments) was used to weight the specimens after each steps of this work. Specimens weighting was considered as an essential procedure to determine the amount of weight gain after coating of specimens , this gives a primarily indication for forming a surface coating layer which would be subsequently confirmed by other method of surface analysis. The value of weight of the coated film (weight gain) was obtained from the difference between the weight of the specimen before and after the coating process.

The thickness of coatings increases linearly with processing time, while within the standard range (<100 µm). For more precise and accurate measurements, the thickness was measured non-destructively using eddy current thickness gauge *Instruments CMI 100, Italy.*

To verify the accuracy of the eddy current thickness gauge, mounted cross-sections were prepared and examined by optical microscopy as shown in Fig. (4) These served to confirm that the measurements were accurate, these also indicate that in most cases the surface roughness of the coating and the waviness of the coating/substrate interface place a greater limit on the precision of thickness measurements than the techniques themselves.

Coated specimen was examined by using optical microscope (Nikon Type 120, Japan optical microscope) to show the appearance of the coated surface layer of the specimen.

This procedure is repeated for the other coated specimens with different times and different applied voltage. The microscope provided with digital camera type DXM 1200 F. The micrographs were analyzed through Nikon ACT- version 2.62, 2000 software.

Atomic Force Microscopy (AFM) was used for studying the surface morphology and roughness of YSZ coated samples. For this, CSPM-AA3000 AFM instrument was used for non-contact mode scan of the samples. For analysis of the AFM data and to get the roughness values, analysis software was used.

The protective behavior against corrosion was studied by potentiostatic polarization in sea water with a testing area of 1 cm^2, without stirring. Before starting the measurement, the potential of open circuit was measured until no changes were registered (approximately 15 min). The corrosion kinetics was studied through polarization resistance in sea water Figure (3). Show the electrochemical corrosion unit.

3. RESULTS AND DISCUSSION

3.1. Optical microscope observations

Al-12Si alloy specimens coated with a layer of alumina shows Figure (4) rough surface with number of porosity and micro cracks. And the surfaces appear more homogenous with sintering; cracks appear on the surface of all specimens (c and d).

3.2. Characterization of particulate sols and coatings

From the discussion in previous sections, it is found that the deposition rate of charged particles would be mainly influenced by applying voltage and polyelectrolyte value. Furthermore, the microstructure of deposit, e.g., densification and grain size would also be affected by sintering and these factors. The effects of such factors on microstructure of deposits would be further discussed in this section (8,16).

The deposition characteristics of EPD are influenced by several factors mentioned, such as pH value, solid loading, percentage of water and applied voltage. Fig 4 represents cases of constant pH6.5 for the deposition rate of Al_2O_3 deposit with different time. It was found that the deposition rate for constant solid loading would also increase abruptly with increasing time. This also means that the amount of iodine adsorbed on particle surface would increase with increasing pH value (11).

EPD tests were performed on aluminum alloy substrates using 60 volt for deposition times (2, 3, 4 and 5) min, using the diluted sols. Since cathodic deposition takes place, no H_2 bubbling is observed. A critical thickness, defined as the maximum crack-free sintered thickness attainable, was reached after deposition times of 2, 3 min (9,11). Figure (4) plots the variation of weight per unit area with deposition time. Table (2) shows summaries of the Coating thickness (µm) and deposition time.

3.3. Electrochemical characterization of an EPD coating without sintering compared with the uncoated aluminum

The corrosion kinetics was evaluated through the measurement of the polarization resistance (PR) evolution in aggressive electrolytic media: simulating the sea water (35% NaCl) conditions. Figure. (6a and b) shows the evolution of the PR with time in electrolytic media for an EPD coating without sintering compared with the uncoated aluminum.

The protective character of the alumina coatings was determined by electrochemical measurements. The polarization curves of coatings of different thickness, (1.8, 2.6, 4.7 and 6.4 µm) prepared by EPD from Al_2O_3 2g/l without sintering, compared with the uncoated aluminum. Table (3) summaries the parameters extracted from polarization curves: breakdown potential (E_{corr}), passive region (DE) and passive current density (i_{corr}). These characteristic parameters are indicated for the uncoated aluminum.

All the coating without sintering shows a cathodic current density lower than that of the uncoated aluminum; This behavior is associated to the presence of defects such as micro-pores Figure (7), The poorer protecting behavior with ageing is directly related to the porosity increase. Indeed, it has been reported that ageing promotes growth and agglomeration of particles in the sol leading to porous films (17).

The effect of sintering on the protective behavior of the EPD coatings was also evaluated. Figure (8) shows the polarization curves for coatings of different thickness prepared with different time, compared with the uncoated aluminum.

The presence of the coating improves the corrosion resistance of the aluminum for EPD current densities. Table (2) summaries the parameters extracted from polarization curves: The current density falls down in nearly three orders of magnitude, and E_{corr} for coated samples much higher than E_{corr} of the uncoated aluminum, suggesting a high coating density and the absence of defects in coatings thickness, (1.8, 2.6, 4.7) µm Figure (9a), but coatings thickness 6.6µm is suffering from porous and micro cracking after sintering because of shrinkage Figure (9b).

Atomic force microscopy was used to characterize the surface texture of the coatings, since it was not possible to detect neither defects nor pores in the coatings by scanning electron microscopy. Figure (10) shows the AFM images of the topography of the coatings obtained AFM indicates that the coating presents a homogeneous, pore-free and dense surface, while without sintering coatings a less smooth surface with apparent porosity regions Figure (10a). On the other hand, the topographic analysis of the sintering coatings illustrate a dense and homogeneous texture Figure (10b).

4. CONCLUSIONS

1. Homogeneous defect-free and thicker coatings have been obtained by EPD, where a critical thickness around 6 µm was reached after sintering at 400 °C.
2. EPD allows producing thicker coatings with enhanced corrosion resistance, even when the sol is previously diluted. This facilitates processing and extends the stability of the sol over much longer times.
3. The protective character of EPD coatings depends on the pore-free and dense surface. The measurement of corrosion kinetics from polarization resistance tests demonstrates that a (3-5) µm-thick.
4. The surface texture and the packing density of EPD coatings appear uniform even after dilution. Due to the throwing power of ethanol-based suspensions original surface roughness is leveled out resulting in a smooth surface.

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Table (1): The bath composition and deposition conditions.

Electrolyte	Ethanol +5% water			
Surfactant	Iodine			
pH	6.5			
Applying voltage DC	50			
Temperature	At room temperature (≈ 25±2 C°)			
Dispersion time/min	2	3	4	5
Dispersion	Al_2O_3			

Table (2): Summaries the Coating thickness (µm) and deposition time.

Coating thickness (µm)	deposition time (min)
1.8	2
2.6	3
4.7	4
6.4	5

Table (3): Summaries the parameters extracted from polarization curves: The i_{corr} (mA/cm^2), and E_{corr} for coated samples without sintering.

Coating thickness (µm)	E_{corr} (mV)	i_{corr} (mA/cm^2)
1.8	-723.3	66.63
2.6	-675.42	72.4
4.7	-638.2	92.82
6.4	-620.6	107.56
Uncoated aluminum	-719.1	33.2

Table (4): The parameters extracted from polarization curves: The i_{corr} (mA/cm^2), and E_{corr} for coated samples after sintering.

Coating thickness (µm)	E_{corr} (mV)	i_{corr} (mA/cm^2)
2.1	-403.1	23.65
2.8	-440	27.61
5	-225.6	28.8
6.6	-685.5	14.14
Uncoated aluminum	-719.1	33.2

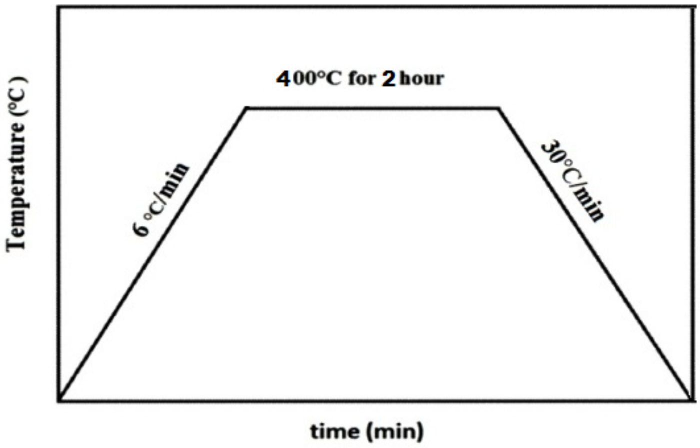


Fig. (1): The sintering profile of the green deposits after drying at room temperature for 24 hr.

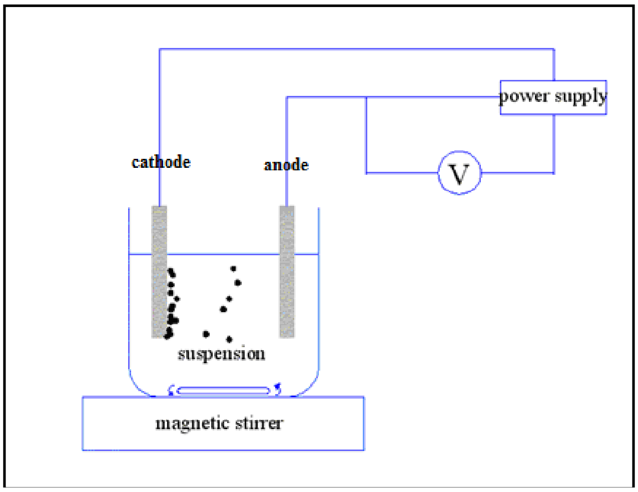
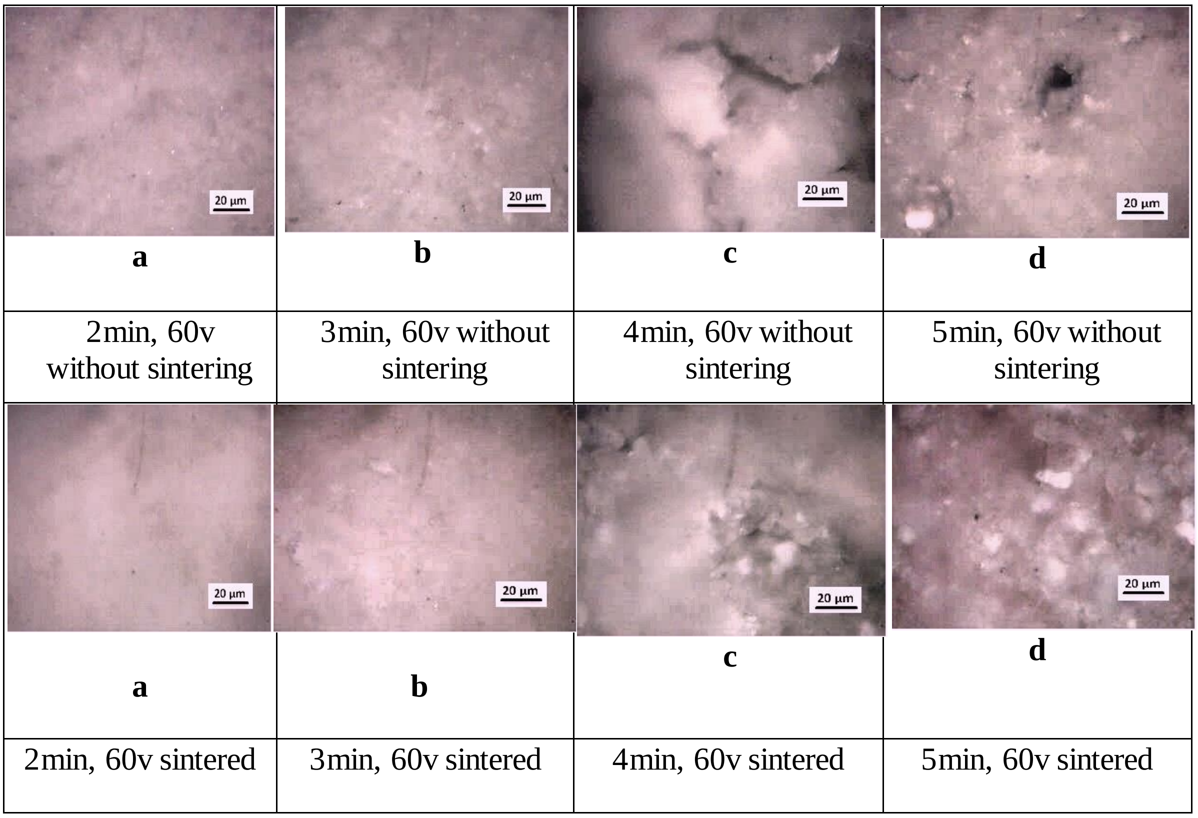


Fig. (2): Schematic representation of EPD system.

Fig. (3): The electrochemical corrosion unit.



a	b	c	d
2min, 60v without sintering	3min, 60v without sintering	4min, 60v without sintering	5min, 60v without sintering
a	b	c	d
2min, 60v sintered	3min, 60v sintered	4min, 60v sintered	5min, 60v sintered

Fig. (4): Optical micrograph view of specimens coated with alumina for different times.

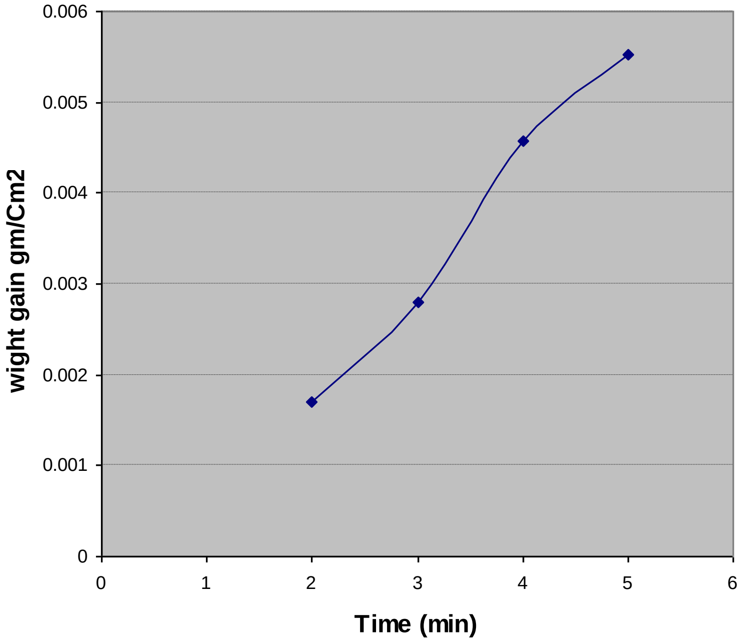
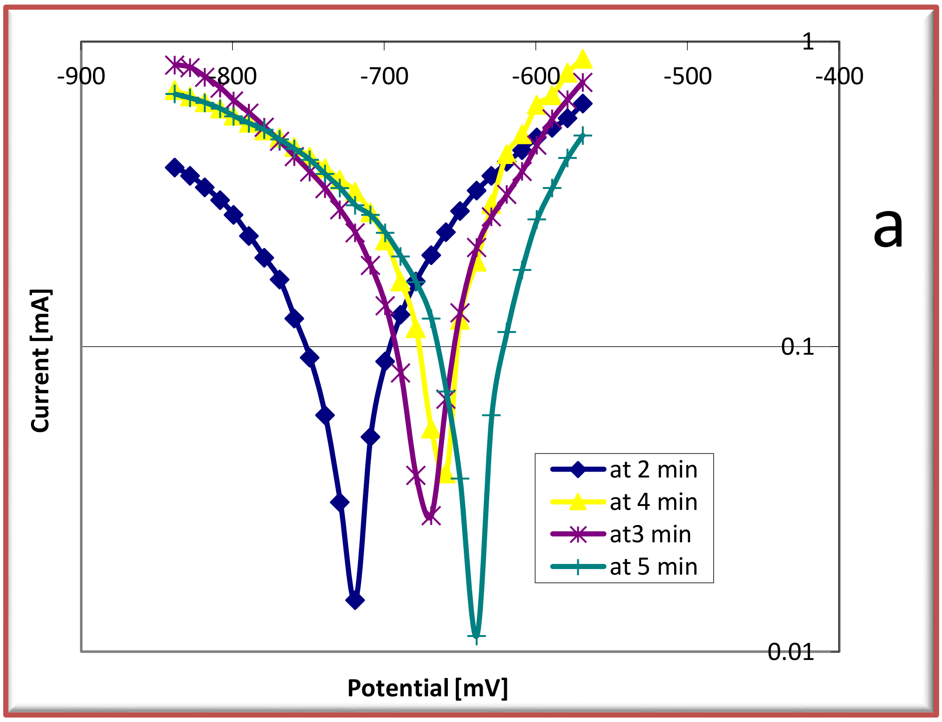


Fig. (5): EPD Evolution of the weight per unit area with deposition time for pH6.5 solution with different time electrophoresis cells at room temperature.



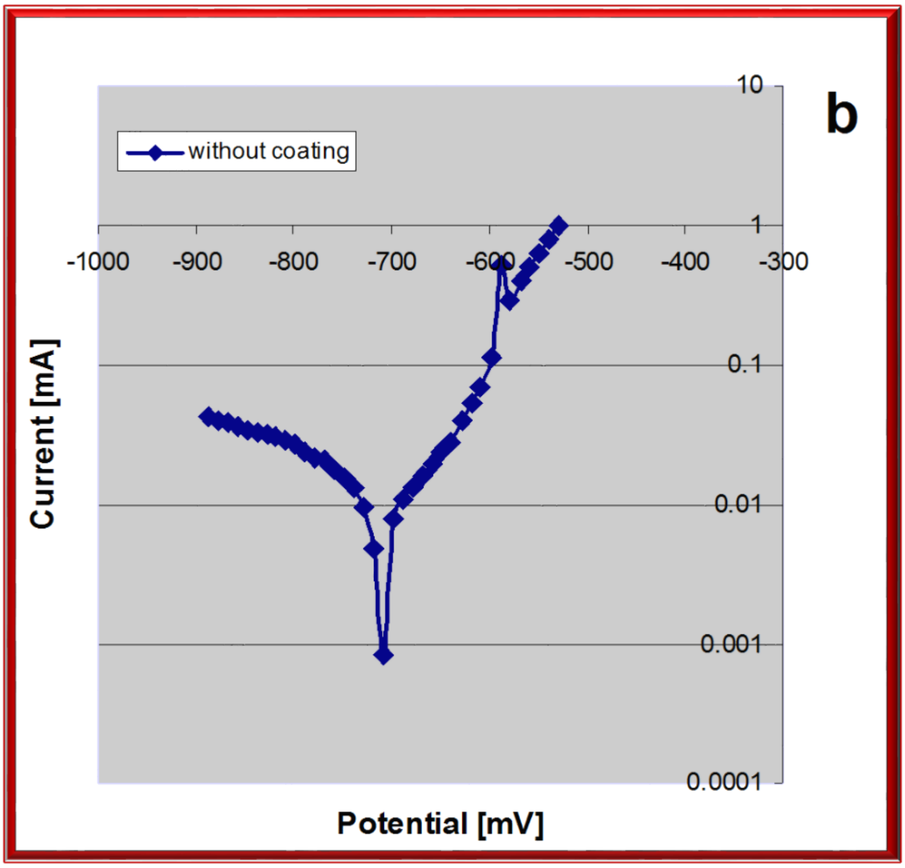


Fig. (6): shows the evolution of the PR with time in electrolytic media for an EPD coating. a) Without sintering. b) uncoated aluminum

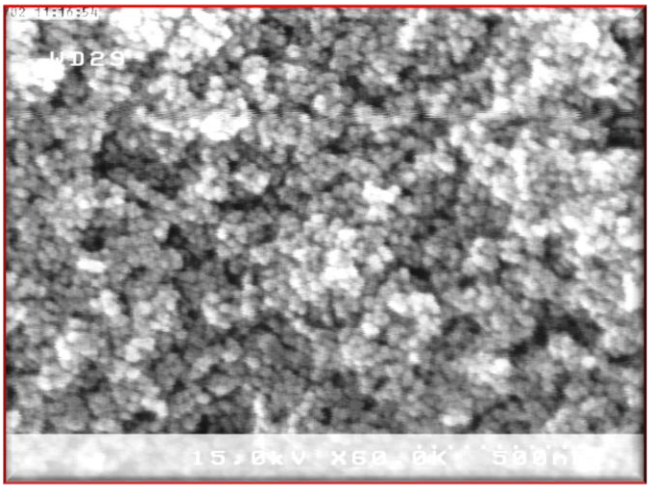


Figure (7): SEM micrographs illustrating the surface morphology of Al_2O_3 green compact without sintering.

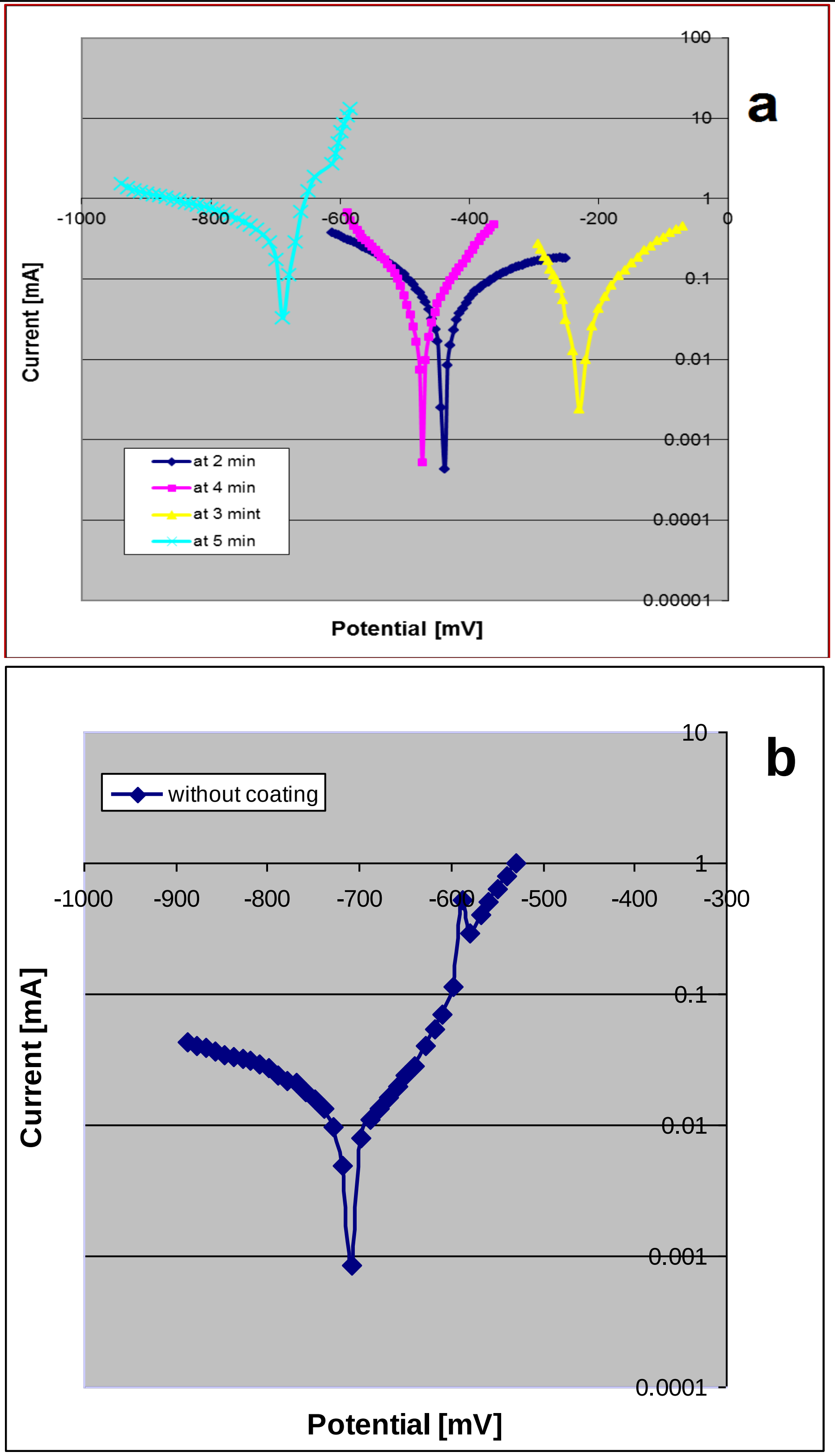


Figure (8): The evolution of the PR with time in electrolytic media for an EPD coating a) after sintering. b) Uncoated aluminum.

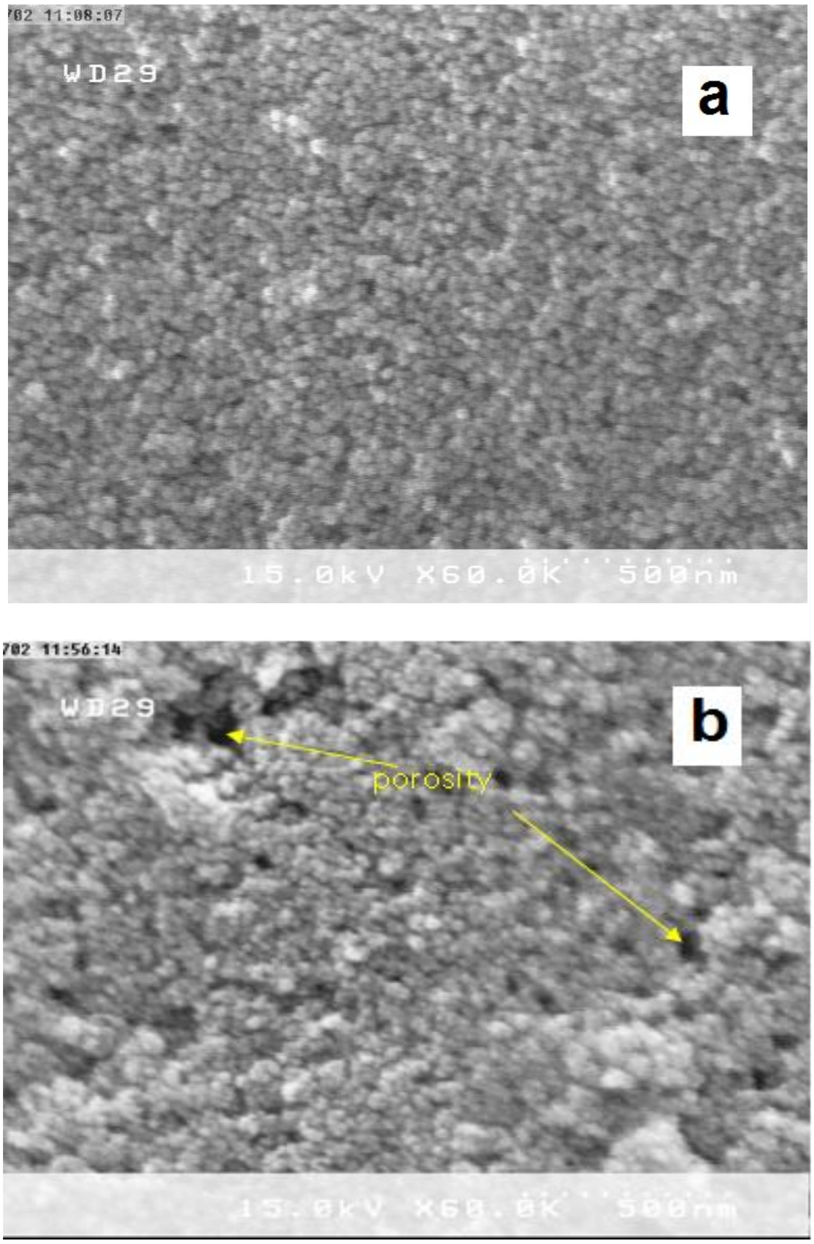


Fig. (9): SEM micrographs illustrating the surface morphology of Al_2O_3 after sintering. a) Without defect. b) Porous and micro cracking.

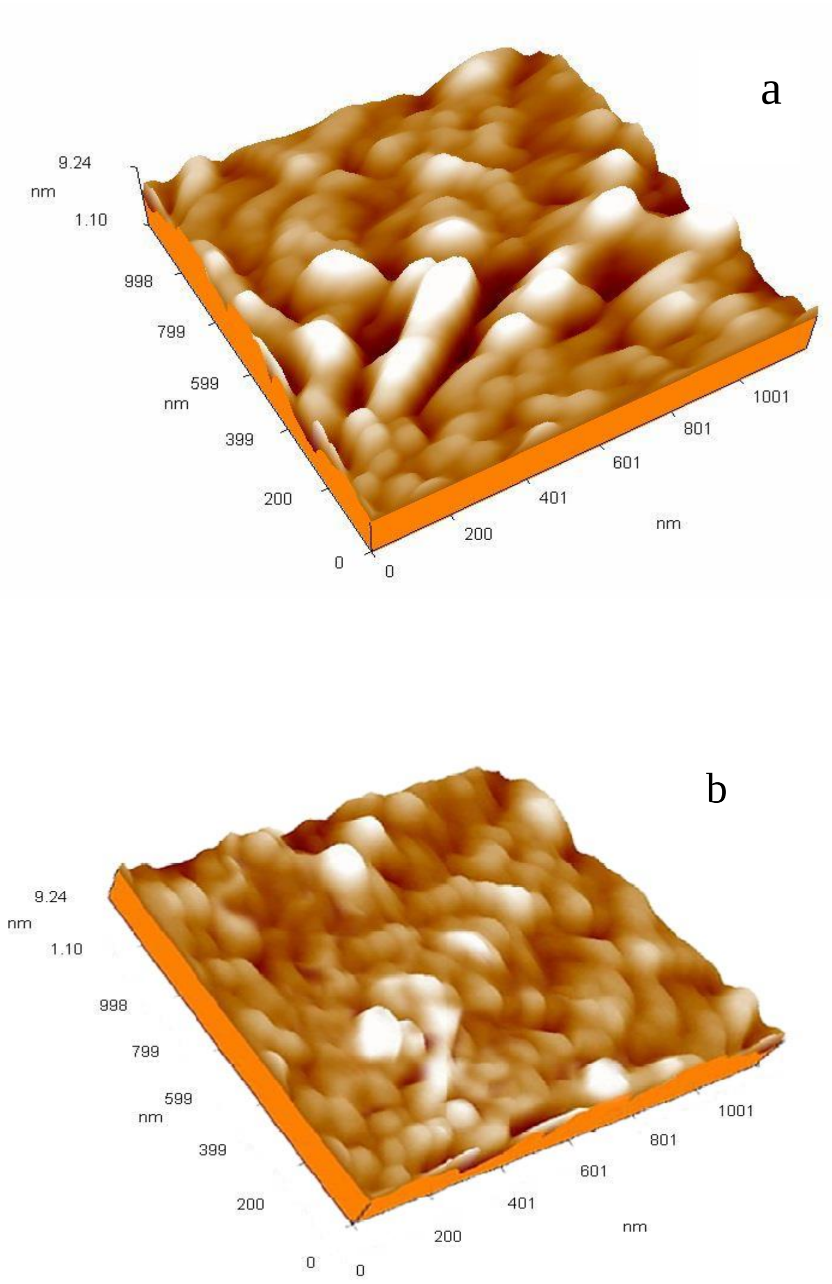


Fig. (10): AFM showing surface roughness of EPD YPSZ overlay coatings. a) Deposited without sintering, Roughness average = 1.299 nm. b) deposited with sintering. Roughness average = 3.113 nm.

وصف سلوك التآكل لطلاء النانوالومينا المصنع بالترسيب الكهربي

عبد الجبار سعد جمعة
مدرس مساعد / كلية الهندسة / جامعة ديالى

الخلاصة

في هذا البحث تم مقارنة سلوك تآكل طلاء الألومينا Al_2O_3 نانوي الحجم المنتج باستخدام تقنية الطلاء الكهربي للالومينا على الأسطح لسبائك الألمنيوم باستخدام عالق مستقر تم انتاجه بإضافة مسحوق الألومينا Al_2O_3 بالإضافة الى كمية صغيرة من الماء و اليود إلى الإيثانول. أدى الترسيب الكهربي الى تشكيل فيلم كثيف بشكل موحد على السطح لزمن (2،3،4 و5) دقائق في (50−60) V ، والحد الأقصى هو انتاج سمك متماسك خالي من العيوب بواسطة عملية (EPD) سمحت لنا الحصول على طلاء بسمك 7 ميكرون. تمت دراسة السلوك الوقائي ضد التآكل و حركية التآكل للطبقة المنتجة من خلال مقاومة الاستقطاب (PR) القياسات تمت في وسط عدائي (مياه البحر). مقاومة التآكل للطلاء المنتج سمح لعملية(EPD) إنتاج طلاءات واقية باستخدام محلول مخفف ومستقر مع مرور الوقت. مقاومة التاكل لطبقة طلاء الالومينا مع التلبيد هي اكثر بثلاثة مرات من الطبقة الغير ملبدة للطلاء المنتج بواسطة عملية (EPD). علاوة على ذلك ، طلاء الألومينا يقدم مقاومة ممتازة في مياه البحر .من خلال مشاهدات مجهر (AFM) تشير إلى أن الطلاءات المنتجة بعملية(EPD) متجانسة و خالية من العيوب.كان الهدف من هذا العمل اعداد طلاءات سميكة بالألومينا Al_2O_3 باستخدام محلول الجسيمات الأساسية المحفزة تم ترسيبها بعملية (EPD) من أجل زيادة مقاومة التآكل لسبائك الألمنيوم. تمت دراسة استقرار المحلول ومتغيرات عملية(EPD). وقد تم تقييم مقاومة للتآكل من خلال طلاء الطرق الكهروكيميائية (voltammetry الخطية و مقاومة الاستقطاب) بوصفها من معاير المعالجة المختلفة: السمك النهائي للطلاء، تطبيق الجهد، ووقت الترسيب.

الكلمات المفتاحية: مقاومة الاستقطاب، الترسيب الكهربائي، الطلاء، الالومينا.