Int. J. Electrochem. Sci., 11 **(2016)** 1355 - 1369

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Corrosion Behavior in Highly Concentrated Sodium Chloride Solutions of Nanocrystalline Aluminum Processed by High Energy Ball Mill

El-Sayed M. Sherif[1,2,*], *Jabair Ali Mohammed*[1] *and Hany S. Abdo*[1,3]*and Abdulhakim A. Almajid*[1,4]

[1]Center of Excellence for Research in Engineering Materials (CEREM), Advanced Manufacturing Institute, King Saud University, P. O. Box 800, Al-Riyadh 11421, Saudi Arabia
[2]Electrochemistry and Corrosion Laboratory, Department of Physical Chemistry, National Research Centre (NRC), Dokki, 12622 Cairo, Egypt
[3]Mechanical Design and Materials Department, Faculty of Energy Engineering, Aswan University, Aswan 81521, Egypt
[4] Mechanical Engineering Department, King Saud University, P.D. Box 800, Riyadh 11421, Saudi Arabia
[*]E-mail: esherif@ksu.edu.sa, emsherif@gmail.com

Received: 9 November 2015 / *Accepted:* 26 November 2015 / *Published:* 1 January 2016

The manufacturing of nanocrystalline aluminum using mechanical alloying technique after different ball milling times, namely 1, 3, and 5 h was reported. The effect of milling period on the corrosion behavior of the manufactured aluminum in 4.0 wt.% sodium chloride (NaCl) solutions was carried out. The corrosion measurements were studied using potentiodynamic polarization (PP), chronoamperometric current-time at constant potential value (CCT), and electrochemical impedance spectroscopy (EIS) techniques. It has been found that the increase of milling time from 1 h to 5 h refines the grain size of the aluminum as was confirmed by the X-ray diffraction investigations. The corrosion tests indicated that the increase of milling time increases the reactivity of the aluminum surface and thus increases its corrosion. This was confirmed by the data obtained from polarization measurements, where the corrosion current density, the corrosion rate, the anodic current and cathodic current were increased with increasing the milling time. This effect was also noticed to increase the values of the absolute currents for aluminum with time when applying an anodic potential value. EIS measurements also confirmed the data obtained by PP and CCT that refining the grain size of the aluminum increases the corrosion of aluminum in the sodium chloride solutions.

Keywords: corrosion resistance; high energy ball mill; nanocrystalline aluminum; polarization; EIS; SEM

1. INTRODUCTION

Aluminum and its alloys have been widely used in many applications in industry for their thermal and electrical conductivities, workability, density, and good corrosion resistance [1-4]. Aluminum alloys with its varied compositions have been greatly used in transportation such as in cars, aircrafts and aerospace, and in other applications like in household appliances, electrical engineering, building, and containers [3-8]. When these metallic materials are exposed to corrosive media, it corrodes and their applications become limited. Although, most aluminum alloys develop an oxide film on their surfaces upon exposing to air, its corrosion takes place in chloride containing solution [9-12]. This is because the formed oxide layer does not have enough ability to prevent the attack of the high concentration of chloride ions towards the aluminum surface. Here, the breakdown of the formed aluminum oxide occurs via localized and/or uniform corrosion [9-13].

There have been many trails to increase the corrosion resistance of metals and alloys including aluminum ones against corrosion in aggressive environments. These include; the addition of minor percentages of more passive alloying metals [14]; painting the surface with protective coatings [15]; the use corrosion inhibitors to decrease the severity of the corrosive media; decreasing the grain size of the employed metals to the range of nanoscale [16,17]; etc. Changing the size of the grain of metals from the micro to nanocrystalline microstructure (< 100 nm) in addition to increasing the volume fraction of grain boundaries have been found to improve the physical, chemical, and mechanical properties of these materials [18,19]. High energy ball milling (HEBM) is a handy, effective and economical processing technique that continues to draw researcher's attention. It is a process wherein powder particles are continuously deformed, repeatedly welded, fractured and re-welded to produce fine particles. The major attributes of HEBM process are the grain refinement, reduction in particle size and homogeneous blending of particles into new phases [16,17,20-22]. Under safe and controlled atmosphere, this processing technique is also suitable for hazardous or inflammable materials.

In the present study, we report the fabrication of a series of nanocrystalline aluminum metal as well as investigating their hardness and corrosion resistance in 4.0% NaCl solutions. The fabrication of the nanocrystalline aluminum was carried out using mechanical alloying method. The crystallite size of the fabricated aluminum was evaluated using X-ray diffraction and Vickers hardness was measured to express the strength of aluminum. The corrosion was tested by measuring the potentiodynamic polarization, electrochemical impedance spectroscopy, and chronoamperometric current-time at -0.6 V vs. Ag/AgCl. The surface of the corroded aluminum electrodes was investigated using scanning electron microscope. All measurements were carried out after 1 h and 24 h immersion in the chloride solution and at room temperature.

2. EXPERIMENTAL DETAILS

2.1. High Energy Ball Milling (HEBM)

Aluminum (Al, 98% purity) fine powder with micro particle size was obtained from Loba Chemie, India and was used as received. The HEBM of high purity aluminium powder was carried out in an attritor ball mill. In the attritor, steel balls were fed into a cylindrical steel container followed by adding the aluminum fine powder. The ball to powder ratio (BPR) was 30:1 with a fixed speed of 250 rotations per minute (rpm). In order to avoid any agglomeration of the powder and to have a proper balance between cold welding and fracturing of the powder, 1.0 % of stearic acid was used as process control agent (PCA). The milling time was varied from 0.0 to 5.0 hours. To prevent any oxidation of the powder, the milling process was done under inert atmosphere using argon gas. The proper cooling of the system was done to evade any temperature build up inside the container.

The sintering of the powder was done in a 10 mm graphite die whose was placed in a high-frequency induction heat sintering (*see our previous work [23]*). The low pressure sintering process was conducted under 10 MPa pressure for 3 min at 600 °C. The compaction and sintering processes were done simultaneously at vacuum level of 1×10^{-3} Torr for avoiding the grain growth and the aluminum surface oxidation. The specimens were then left to cool down to reach room temperature and were finally extracted out of the die.

2.2. X-ray diffraction (XRD) and Vickers hardness measurements

The processed metal powder and final samples obtained before and after milling for desired duration of time were characterized using X-ray diffractometer (XRD, BRUKER, D8_Discover, Japan). The Vickers hardness measurements of bulk samples were done using Buehler 5100 series Micro Hardness Measuring Machine. The load was 100 gm/f and the dwell time was 10 seconds. The obtained hardness values were the average of five readings on each bulk sample.

2.3. Test Solution and Electrochemical Cell

Sodium chloride salt (NaCl, Merck, 99%) was used as received to prepare the 4.0% NaCl solution. A three electrode configuration electrochemical cell, which accommodates for 250 cm^3 was used to perform all electrochemical measurements. The Al, an Ag/AgCl electrode (in 3 M potassium chloride (KCl) solution), and a platinum sheet were used as working, reference, and counter electrodes, respectively. The Al electrode was prepared, polished, and ground to be employed in the performance of the electrochemical measurements as has been previously reported [23].

2.4. Electrochemical measurement methods

For carrying out the electrochemical measurements, an Autolab Potentiostat-Galvanostat that was purchased from Metrohm was employed. The potentiodynamic polarization curves were measured after 1.0 h and 24 h immersion in the chloride test solution by scanning the potential from −1600 mV in the positive direction to -400 mV at a scan rate of 1 mV per second in regard to the Ag/AgCl reference electrode. The electrochemical impedance spectroscopy (EIS) data were obtained after 1 and 24 h immersion in 4% NaCl solution from the free corrosion potential (E_{OCP}) value. The frequency of the EIS was in the range of 100,000 Hz to 0.1 Hz using an AC wave of ±5 mV peak-to-peak overlaid on a DC bias potential. The EIS data were collected using Powersine software at a rate of 10 points per decade change in frequency. For the chronoamperometric current-time curves, a constant value of potential at -600 mV vs. Ag/AgCl was applied for 1 h after the aluminum electrodes were immersed in the chloride solution for 1 h and 24 h. All electrochemical experiments were carried out on a fresh surface of aluminum electrodes. Also, all tests were performed using a new portion of stagnant and freely aerated 4.0% NaCl solution at room temperature.

2.5. Surface Characterization

A scanning electron microscope from JEOL (Japan) was used to obtain the SEM micrographs. The images were collected on Al electrodes that were immersed in 4.0% NaCl solution for one hour after which a constant potential value of −600 mV was applied for another one hour.

3. RESULTS AND DISCUSSION

3.1. XRD and Vickers hardness data

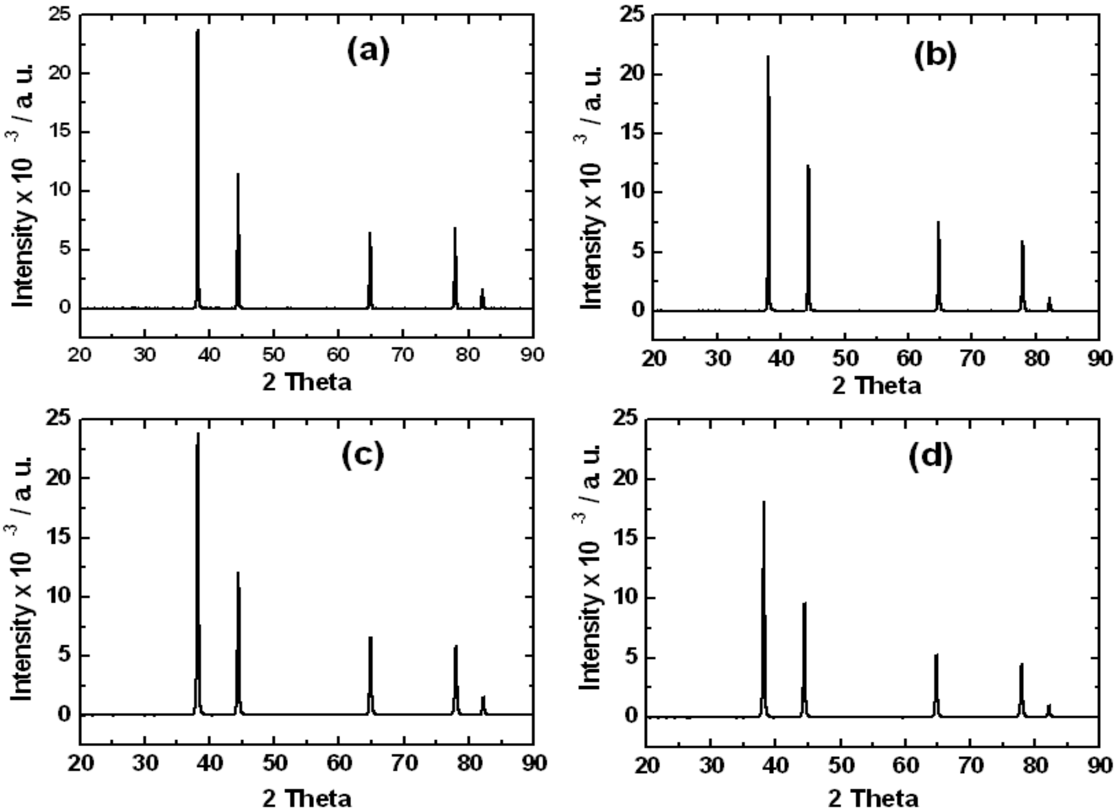

Figure 1. XRD patterns of aluminum powders after different ball milling time; (a) 0.0 h, (b) 1.0 h, (c) 3.0 h and (d) 5.0 h, respectively.

Figure 1 shows the XRD patterns of pure aluminum powders after different ball milling times; (a) 0.0 h, (b) 1.0 h, (c) 3.0 h and (d) 5.0 h, respectively. It is seen from the XRD patterns that the aluminum peaks get broader with the increase of the ball milling time. This is due to the increase of milling time reduces the crystallite size of aluminum as previously reported [16,17,22]. The crystallite size obtained from the XRD data for aluminum that was ball milled for 1.0, 3.0 and 5.0 h recorded 54, 51, and 38 nm, respectively.

The readings of the Vickers hardness measurements (HV) of bulk consolidated sintered samples were measured along the surface at regular intervals, the average of five readings on each sample were considered. Those five readings are tabulated as shown in Table 1 and the average values were taken and plotted against milling time varied from 0.0 to 5.0 h, as seen in Figure 2. It is seen From Table 1 that the hardness values increased gradually with an increase in the milling time. Where, the Vickers hardness value before milling recorded only 37.12 HV, whereas after milling for 5 hours, it increased to 119.84 HV. The increase of milling time of the Al samples to 5 h thus increased the hardness to be more than threefold increment compared to the sample of without milling. Figure 2 also shows an almost linear relationship between the milling times of Al consolidated samples and its hardness. The increase of hardness with milling time is most probably due the increase of compactness of aluminum, which is in turn due to the decreased crystallite size of aluminum with the increase of milling time [22].

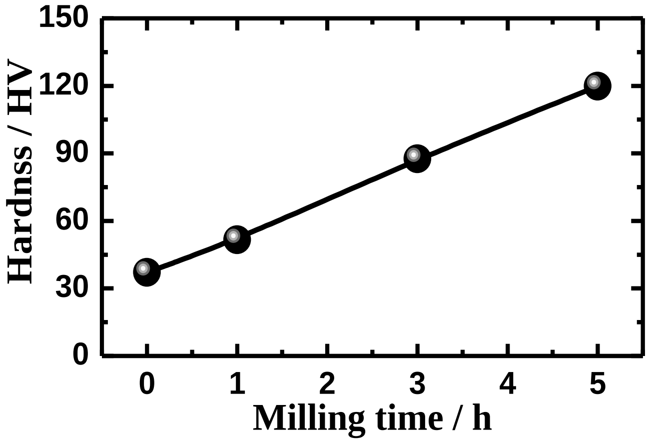

Figure 2. Vickers hardness for aluminum that was processed for 0.0, 1.0, 3.0, and 5.0 h ball milling time.

Table 1. Change of Vickers hardness for the sintered aluminum that was processed after different ball milling periods of time.

Reading number	Milling time			
	0.0 h	1.0 h	3.0 h	5.0 h
1	37.8	49.8	88.1	124.1
2	36.7	53.7	86.7	119.2
3	35.7	52	85.8	118.4
4	37.3	50.2	87.8	122
5	38.1	52.2	89.4	115.5

3.2. Potentiodynamic polarization measurements

Figure 3 depicted the potentiodynamic polarization curves obtained for aluminum electrode that was processed after (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4) 5.0 h milling time respectively, after (a) 1.0 h and (b) 24 h of their immersions in 4.0% NaCl solutions. The values of the cathodic Tafel (β_c) and anodic Tafel (β_a) slopes, corrosion potential (E_{Corr}), corrosion current density (j_{Corr}) and polarization resistance (R_p) that were obtained from the polarization curves shown in Figure 3 are listed in listed in Table 2. These values of E_{Corr} and j_{Corr} were obtained as previously reported in our earlier studies [24-27]. Besides, the values of Rp were calculated using the following equation [27]:

$$\mathrm{Rp} = \frac{1}{\mathrm{j}_{\mathrm{Corr}}}\left(\frac{\beta_c \beta_a}{2.3\,(\beta_c \beta_a)}\right) \qquad (1)$$

The values of the corrosion rate were calculated according to this equation [26,27]:

$$\mathrm{R}_{\mathrm{Corr}} = \mathrm{j}_{\mathrm{Corr}}\left(\frac{k\,E_W}{d\,A}\right) \qquad (2)$$

Where, k is a constant that defines the units for the corrosion rate (k = 128,800 milli inches (amp cm year)), E_W the equivalent weight in grams/equivalent of, d the density in gcm^{-3}, and A the area of electrode in cm^2.

It is obvious from Figure 3a, curve 1 that the current rapidly decreases with increasing the applied potential in the cathodic side until the current reaches a region that its value does not change before reaching the value of j_{Corr}. The cathodic reaction at this condition is the oxygen reduction as follows [23-27]:

$$\mathrm{O_2 + 2H_2O + 4}e^- = \mathrm{4OH^-} \qquad (3)$$

After reaching the value of j_{Corr} and E_{Corr}, the current in the anodic side dramatically increases with potential due to the dissolution of aluminum under the effect of potential and the aggressiveness action of the chloride ions. This can be expressed by the following dissolution reactions:

$$\mathrm{Al = Al^{3+} + 3}e^- \qquad (4)$$

$$\mathrm{Al^{3+} + 3Cl^- = AlCl_3 + 3}e^- \qquad (5)$$

$$\mathrm{AlCl_3 + Cl^- = AlCl_4^-} \qquad (6)$$

In the case of 1.0 h milling time (Figure 3a, curve 2), the anodic current decreased and the corrosion potential (E_{Corr}) shifted to the more negative value. This effect also decreased the region of the unchanged cathodic current, decreased the value of j_{Corr} and a little passive region in the anodic branch was appeared. Prolonging the milling time to 3.0 h (Figure 3a, curve 3) led to a great shift in the value of E_{Corr} to the more negative direction and the curve showed a large passive region in the anodic branch of the polarization curve. The appearance of this large passive region was most probably due to the formation of aluminum oxide (Al_2O_3) layer on the aluminum surface according to the following reactions [24-27];

$$\mathrm{Al + 3OH^- = Al(OH) + 3}e^- \qquad (7)$$

$$\mathrm{2Al(OH)_3 = Al_2O_3.3H2O} \qquad (8)$$

Increasing the applied potential in the less positive direction led to an abrupt increase in the anodic current as result of the breakdown of the formed oxide layer and the occurrence of pitting corrosion. Where, the chloride ions target the aluminum surface and dissolve it to form aluminum chloride compounds according to equation (4) and equation (5) [24]. The polarization curve for the aluminum that was ball milled for 5.0 h, Figure 3a (curve 4) showed the lowest cathodic, anodic and j_{Corr} currents. Table 2 also confirmed that the highest corrosion resistance and lowest R_{Corr} were recorded for the aluminum that was milled for 5.0 h. This is because the increase of milling time refines the aluminum particles and allows better consolidation, which reflects on its better corrosion resistance [16,17,22].

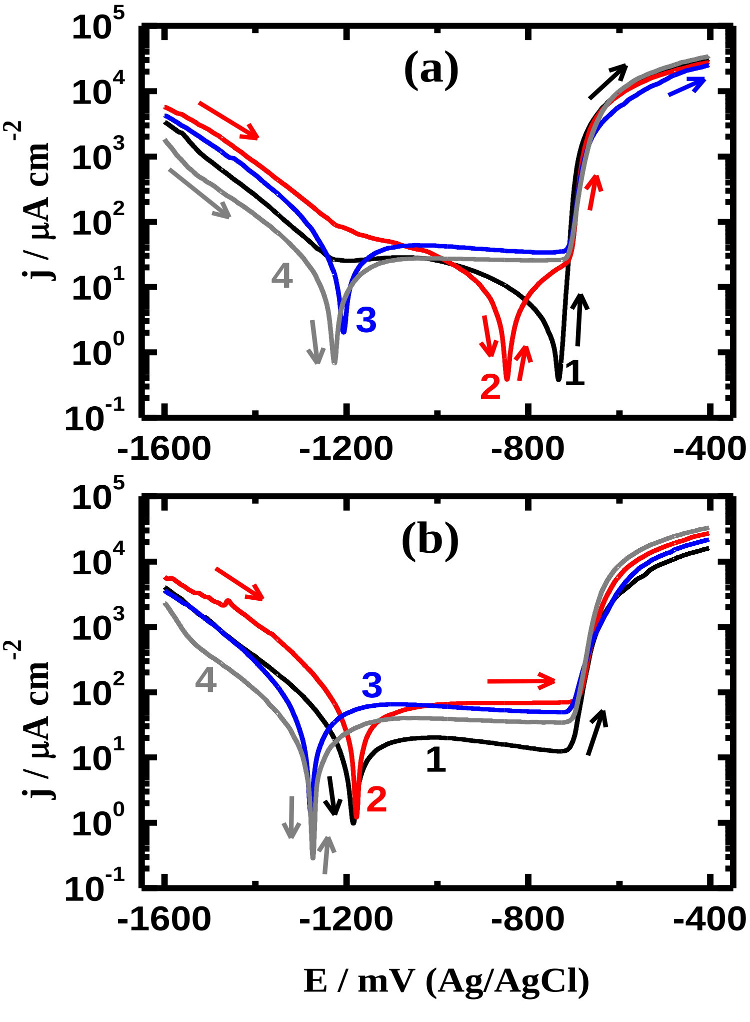

Figure 3. Potentiodynamic polarization curves obtained for aluminum electrode that was processed after (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4) 5.0 h milling time respectively, after (a) 1.0 h and (b) 24 h of their immersions in 4.0% NaCl solutions.

The polarization data obtained after 24 h immersion in 4.0% NaCl solutions before measurements (Figure 3b) showed that the increase of milling time from 0.0 to 5.0 h shifts the values of E_{Corr} to the more negative values. The best performance for the fabricated aluminum against corrosion was provided by the sample milled for 5.0 h before sintering. This was confirmed by the values of the corrosion parameters listed in Table 2, where the highest value of Rp and the lowest values of j_{Corr} and R_{Corr} were for the aluminum sample that was ball milled for 5.0 h. It is also noted from Figure 3 and Table 2 that the increase of exposure period of time from 1 h to 24 h in 4.0% NaCl solutions before measurements slightly increases the corrosion of aluminum in the chloride test solution. This is due to the increase of chloride ions attack on the aluminum surface with increasing the immersion time.

Table 2. Polarization parameters obtained for the different Al composites in the 4.0% NaCl solutions.

Milling and immersion periods of time	Corrosion parameter					
	β_c / V/dec^{-1}	E_{Corr} / V	β_a / Vdec^{-1}	j_{Corr} / µA cm^{-2}	R_p / Ω cm^2	R_{Corr} / mpy
0.0 h (1 h)	0.215	–0.750	0.04	5.0	2932	0.0545
1.0 h (1 h)	0.198	–0.828	0.050	6.0	2893	0.0654
3.0 h (1 h)	0.095	–1.200	0.105	10.2	2126	0.1112
5.0 h (1 h)	0.110	–1.230	0.115	4.0	6111	0.0436
0.0 h (24 h)	0.080	–1.175	0.090	6.0	3069	0.0654
1.0 h (24 h)	0.070	–1.170	0.085	10.5	1590	0.1145
3.0 h (24 h)	0.078	–1.270	0.105	10.3	1889	0.1123
5.0 h (24 h)	0.085	–1.270	0.115	5.5	3864	0.0599

3.3. Electrochemical impedance spectroscopy (EIS)

EIS test is a strong method that has been employed in understanding the corrosion and corrosion protection of metals and alloys in corrosive media [23,28-34]. We have been using EIS to report the kinetic parameters for electron transfer reactions at the metal/environment interface [16,17,23,32-34]. Here and in addition to reporting the kinetics for the electron transfer at the Al/NaCl solution interface, the EIS data will be compared to the obtained polarization measurements. Typical Nyquist plots obtained for aluminum electrode that was processed after (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4) 5.0 h milling time respectively, after (a) 1.0 h and (b) 24 h immersion in 4.0% NaCl solutions are shown in Figure 4. The EIS experimental data were best fitted to the equivalent circuit model shown in Figure 5. This circuit was also used to fit EIS data obtained for aluminum-titanium carbide alloy in NaCl solutions [23]. The symbols shown on the circuit of Figure 5 can be defined as following; R_S is the solution resistance, Q is the constant phase elements, CPEs, Rp1 is the polarization resistance between aluminum surface and NaCl solution interface, C_{dl} is the double layer capacitance at the electrode/solution interface, and Rp2 is the polarization resistance between the corrosion product and/or oxide layer formed on aluminum and solution interface and can also be defined as the charge transfer resistance. The values of all these parameters were determined for the aluminum after the different ball milling after its immersion in the chloride solutions for both 1.0 h and 24 h as listed in Table 3.

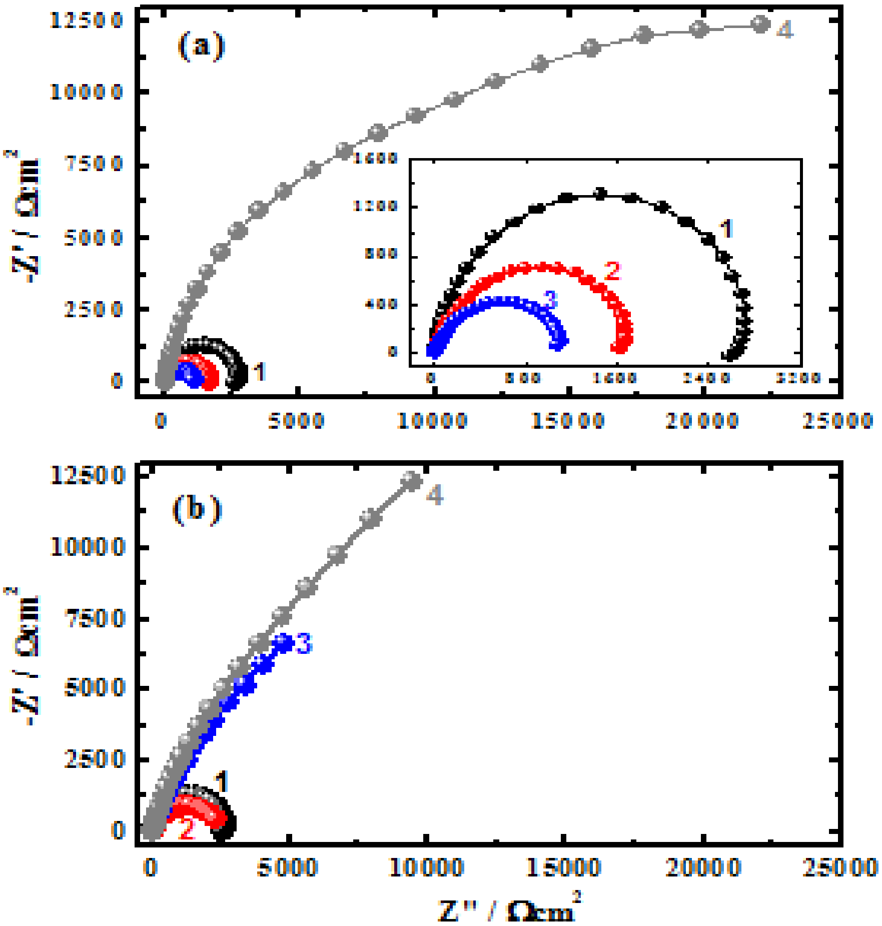

Figure 4. Typical Nyquist plots obtained for aluminum electrode that was processed after (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4) 5.0 h milling time respectively, after (a) 1.0 h and (b) 24 h immersion in 4.0% NaCl solutions.

Figure 4a depicts that the increase of milling time from 0.0 h to 1.0 h and further to 3.0 decreases the diameter of the semicircle as seen from the inset of the figure indicating that the corrosion resistance of aluminum decreases with increasing the milling time to 3.0 h. Increasing the milling time to 5.0 h highly increased the diameter of the semicircle (Figure 4a, curve 4). Table 3 also shows that the increase of milling time of Al to 3.0 h decreases the values of R_S, R_{P1} and R_{P2} confirming that the corrosion of aluminum increases with the time of milling. These values were the highest for the aluminum that was processed after 5.0 h milling time, which proves that the corrosion of aluminum at this condition is the lowest. It is also noted that the values of CPEs, Y_{Q1} with its n value, which is close to unity represents a double layer capacitor with some pores that permits the dissolution of aluminum in the chloride solution. The value of Y_{Q1} increased from 0.0 h to 3.0 h milling time then significantly increased for the aluminum produced after 5.0 h. Similar trend was also recorded for the values of C_{dl} and confirms that the corrosion of aluminum increased with increasing its milling time from 0.0 h to 3.0 h and incredibly decreased again via increasing the corrosion resistance when the milling time was increased to 5.0 h.

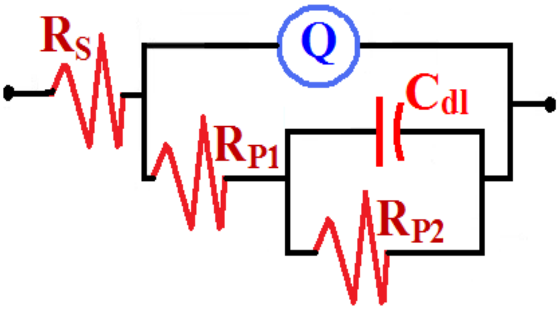

Figure 5. The equivalent circuit model used to fit EIS data shown in Figure 4.

Table 3. Electrochemical impedance spectroscopy parameters obtained for aluminum after different milling and exposure periods of time in the 4.0% NaCl test solution.

Milling and immersion periods of time	EIS Parameter					
	R_S / Ω cm^2	Q		R_{P1} / Ω cm^2	C_{dl}	R_{P2} / Ω cm^2
		Y_{Q1}/ µF cm^{-2}	n_1			
0.0 h (1 h)	11.25	0.00537	1.0	816	0.1831	3662
1.0 h (1 h)	10.99	0.02719	0.94	772	0.2346	2199
3.0 h (1 h)	10.12	0.10710	0.8	613	0.6621	2097
5.0 h (1 h)	13.45	0.00211	0.62	1271	0.0657	5693
0.0 h (24 h)	11.27	0.03592	0.94	573	0.1450	3463
1.0 h (24 h)	11.02	0.11904	0.85	359	0.7369	3027
3.0 h (24 h)	12.90	0.01253	0.79	854	0.0541	5675
5.0 h (24 h)	13.73	0.00638	0.74	1137	0.0942	8685

As seen from Figure 4b, prolonging the immersion time for the aluminum composites to 24 h before measurements shows that the diameter of the semicircle slightly decreased except for the semicircle corresponding to the sample that was milled for 3.0 h (curve 3), which was increased. This means that the increase of immersion time decreases the corrosion resistance of the milled aluminum samples through increasing its corrosion. The impedance parameters listed in Table 3 confirmed also that the values of polarization resistances, R_{P1} and R_{P2}, recorded lower values for the aluminum samples immersed for 24 h in the chloride solutions compared to those electrodes immersed for only 1.0 h before measurements.

This behavior was further confirmed by plotting the change of (a) the Bode impedance of the interface (|Z|) and (b) the Bode phase angle (Φ) with frequency for the aluminum that was immersed in 4.0 NaCl solutions for 1.0 h and 24 h as shown in Figure 6 and Figure 7, respectively. Where, the high values of |Z| at low frequency regions represent indicates the higher the resistance of aluminum against corrosion. Also, the increased the value of Φ at its maximum, particularly at low frequency values, reveals the increased corrosion resistance. Here, the highest values for |Z| and Φ at the low frequency regions seen in Figure 6 and Figure 7 are recorded for the aluminum that was ball milled for 5.0 h. The impedance data thus confirm the measurements obtained by polarization that the increase of milling time to 5.0 h increases the corrosion resistance for aluminum, whether it was immersed for 1.0 h or 24 h, to its highest and in turn decreases its corrosion rate.

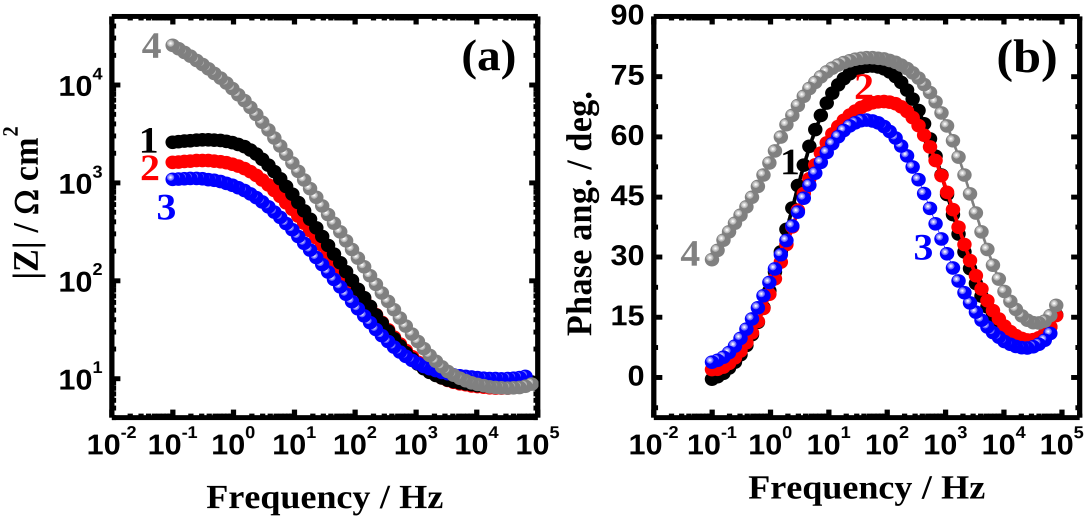

Figure 6. Typical Bode (a) impedance of the interface, |Z|, and (b) phase angle plots obtained for aluminum electrode that was processed for (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4) 5.0 h milling time respectively, after 1.0 h immersion in 4.0% NaCl solutions.

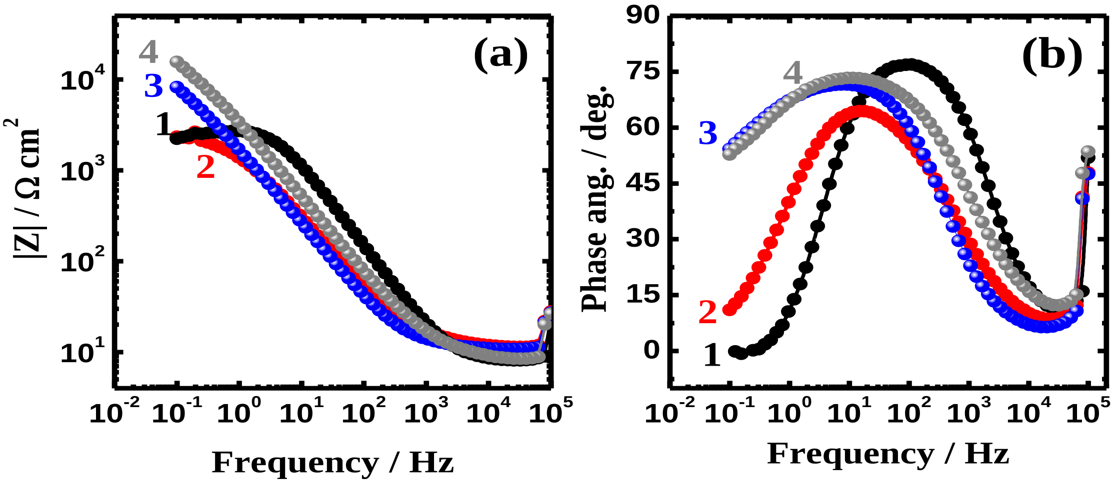

Figure 7. Typical Bode (a) impedance of the interface, |Z|, and (b) phase angle plots obtained for aluminum electrode that was produced after (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4) 5.0 h milling time respectively, after 24 h immersion in 4.0% NaCl solutions.

3.4. Chronoamperometric current-time measurements

The chronoamperometric current-time experiments were carried out in order to report whether increasing the milling hours will affect the severity of pitting corrosion of the produced nanocrystalline aluminum after different immersion periods of time in 4.0 NaCl solutions. The chronoamperometric curves obtained for aluminum electrode that was produced after (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4)

5.0 h milling time respectively, after (a) 1.0 h and (b) 24 h immersion in 4.0% NaCl solutions before stepping the potential to -0.6 V vs. Ag/AgCl are shown in Figure 8. The aluminum that was processed for 0.0 h and immersed only for 1.0 h in the chloride solution (Figure 8a, curve 1) recorded high values of current, which were slightly decreasing with increasing the time of the experiment. These current values increased up on increasing the milling time to 1.0 h and further to 3.0 h and this current increment was accompanied with the appearance of some oscillations. This indicates that the increase of milling time to 3.0 h increases the uniform corrosion as well as causes pitting attack for aluminum in 4.0 NaCl solutions. Further increasing the ball milling time to 5.0 (Figure 8, curve 4) highly decreased the current values over the whole time of the experiment. Moreover, the current was decreasing with time, which reveals that the aluminum at this condition does suffer little uniform corrosion and does not experience any pitting attack.

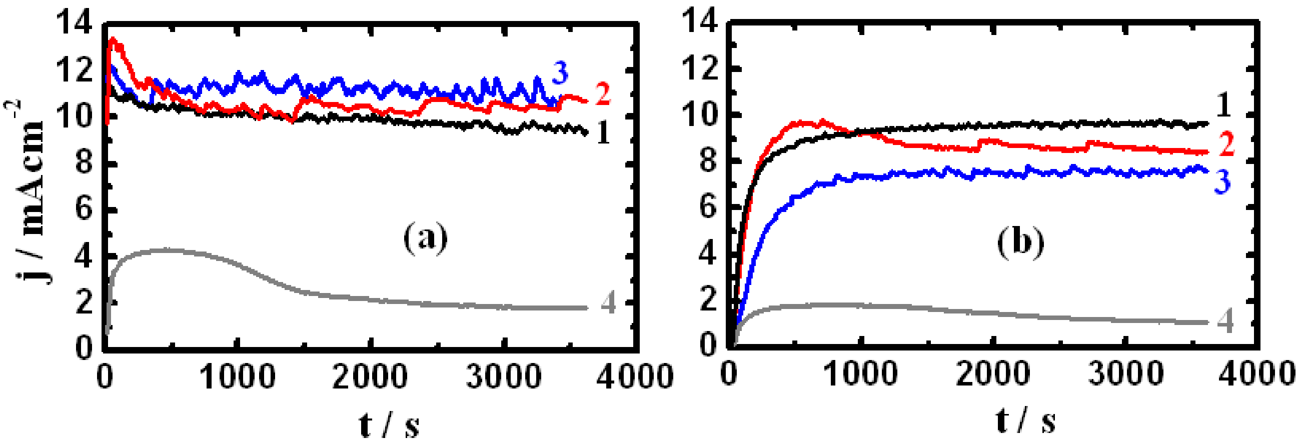

Figure 8. Chronoamperometric curves obtained for aluminum electrode that was produced after (1) 0.0 h, (2) 1.0 h, (3) 3.0 h, and (4) 5.0 h milling time respectively, after (a) 1.0 h and (b) 24 h immersion in 4.0% NaCl solutions before stepping the potential to -0.6 V vs. Ag/AgCl.

Increasing the immersion time to 24 h in the chloride solutions (Figure 8b) showed that the current values obtained for aluminum that was milled for 0.0 h (curve 1) increased from almost zero to 8.0 mA/cm^2 in the first 300s. This is because immersing the aluminum in 4.0 NaCl solution for long period of time leads to the formation of aluminum oxide film (see Eq. 7 and Eq. 8), which rapidly dissolved under the effect of the less negative anodic potential, -0.6 V vs. Ag/AgCl, and thus increased the measured current. Applying the constant potential for longer time was found to slightly increased the current values indicating that the aluminum at this condition is suffering both uniform and pitting corrosions [23,27]. The aluminum electrodes that were ball milled for 1.0 h and 3.0 h (Figure 8, curve 2 and curve 3) showed almost the same current-time behavior but with lower absolute current values compared to those obtained from the milled aluminum for 0.0 h. This decrease in the current with time indicates that the uniform corrosion of aluminum decreased with increasing the milling period of time. This was further confirmed by the obtained current values for the aluminum that was milled for 5.0 h, Figure 8b (curve 4). Where, the current showed very low values compared to the aluminum samples that were milled for shorter periods of time. The chronoamperometric current-time measurements thus confirm the data obtained from polarization and EIS that the ball milling aluminum for 5.0 h decreases its uniform corrosion and prevents the occurrence of pitting attack even after applying less negative values of constant anodic potential.

3.5. Scanning electron microscope (SEM) investigations

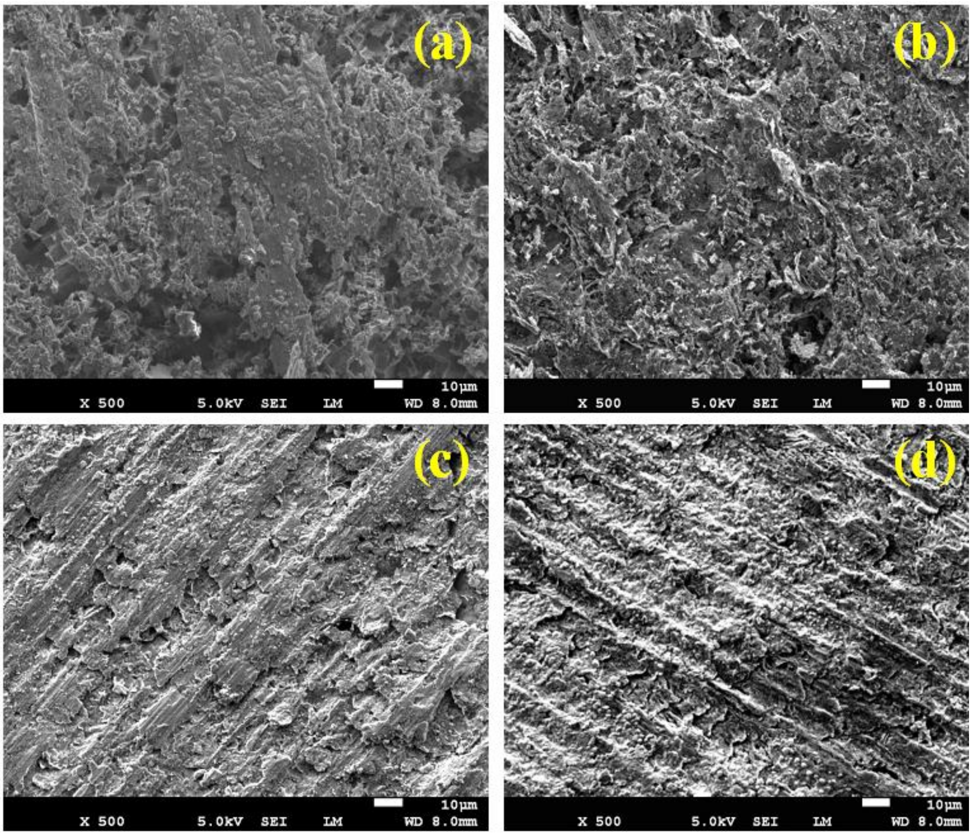

Figure 9. SEM micrographs taken from the aluminum surface that was processed for (a) 0.0 h, (b) 1.0 h, (c) 3.0 h, and (d) 5.0 h milling time after 24 h immersion in 4.0% NaCl solutions before stepping the potential to -0.6 V vs. Ag/AgCl.

In order to confirm the electrochemical corrosion behavior of the obtained aluminum samples after different ball milling periods of time, scanning electron microscopy (SEM) investigations were carried out. Figure 9 shows the SEM micrographs taken from the aluminum surface that was processed for (a) 0.0 h, (b) 1.0 h, (c) 3.0 h, and (d) 5.0 h milling time after 24 h immersion in 4.0% NaCl solutions before stepping the potential to -0.6 V vs. Ag/AgCl. It is seen from Figure 9a and Figure 9b that the aluminum surface processed for 0.0 h and 1.0 shows severe uniform corrosion as well as pitting attack. The image depicted in Figure 9c indicates that for the surface of the aluminum that was ball milled for 3.0 h also suffers uniform corrosion with fewer pits. On the other hand, the surface shown in Figure 9d for the milled aluminum after 5.0 h exhabits little uniform corrosion and the presence of its pitting is not clear. This is in good agreement with the chronoamperometric current-time curves shown in Figure 8b from which the increase of the absolute current values was corrosponding to the increase of uniform corroison. In addition, the severity of both uniform corrosion and the occurrence of pitting attack decreased with the increase of milling time of the aluminum, where both forms of corrosion were minimum for the aluminum that was processed for 5.0 h as milling time.

4. CONCLUSIONS

The effect of increasing the time of ball milling on the corrosion of aluminum that was fabricated using high energy ball mill in 4.0 wt.% sodium chloride solutions was reported. It has been found that the increase of ball milling periods of time from 0.0 h to 5.0 h highly decreases the crystallite size of aluminum as indicated by the XRD investigations. The increase of ball milling time was also found to strongly increasing the Vickers hardness of the manufactured aluminum samples. Several techniques such as CPP, EIS, CCT, and SEM were employed to report the corrosion behavior of aluminum in the chloride test solution. CPP measurements indicated that the increase of milling time to 5.0 h pronouncedly decreased corrosion parameters like j_{Corr} and R_{Corr} and increased the corrosion resistance of the aluminum surface. The EIS data also confirmed that the highest surface and polarization resistances were the highest for the aluminum that was processed for 5.0 h as milling time. Further confirmation was also obtained from the CCT curves and SEM micrographs. Where, the aluminum samples processed for short milling time suffered both uniform corrosion and pitting attack, while those corrosion forms were the lowest for the aluminum that was fabricated after being ball milled for 5.0 h. Moreover, the increase of immersion time of the different ball milled aluminum samples before measurement increased their corrosion in the 4.0% NaCl solutions. All results were consistent with each other and prove clearly that the increase of milling time to longer time, 5.0 h, highly improves the corrosion resistance and minimize the corrosion rate of aluminum in the chloride test solution.

ACKNOWLEDGEMENTS
This project was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia, Award Number (ADV-1853-2).

References

1. E.M. Sherif, S.-M. Park, *Electrochim. Acta*, 51 (2006) 1313.
2. K. Shimizu, K. Kobayashi, P. Skeldon, G.E. Thompson, G.C. Wood, *Corros. Sci.,* 39 (1997) 701.
3. Song-mei Li, Hong-rui Zhang, Jian-hua Liu, *Trans. Nonferrous Metals Soc. China*, 17 (2007) 318.
4. C.M. Abreu, M.J. Cristóbal, R. Figueroa, G. Pena, *Corros. Sci.,* 54 (2012) 143.
5. P. Bala Srinivasan, V. Heitmann, W. Dietzel, *Corros. Sci. Eng. Technol.,* 39 (2004) 174.
6. T. Choh, T. Oki, *Mater. Sci. Technol.,* 3 (1987) 378.
7. L. Garrigues, N. Pebere, F. Dabosi, *Electrochim. Acta,* 41 (1996) 1209.
8. S. Gudić, I. Smoljko, M. Kliškić, *J. Alloys Compd.*, 505, (2010) 54-63.
9. E.M. Sherif, S.-M. Park, *J. Electrochem. Soc.,* 152 (2005) B205.

10. Su-Il Pyun, Sung-Mo Moon, *J. Solid State Electrochem.*, 3 (1999) 331.
11. K. Jafarzadeh, T. Shahrabi, M.G. Hosseini, *Corros. Sci. Eng. Technol.*, 44 (2009) 144.
12. W. Ensinger, O. Lensch, T. Matsutani, M. Kiuchi, *Surf. Coat. Technol.*, 196 (2005) 231.
13. Chao Cai, Zhao Zhang, Fahe Cao, Zuoning Gao, Jianqing Zhang, Chunan Cao, *J. Electroanal. Chem.*, 578 (2005) 143.
14. El-Sayed M. Sherif, *Int. J. Electrochem. Sci.*, 6 (2011) 2284.
15. El-Sayed M. Sherif, Mohammad Asif Alam, Saeed M. Al-Zahrani, *Int. J. Electrochem. Sci.*, 10 (2015) 373.
16. El-Sayed M. Sherif, H.R. Ammar, K.A. Khalil, *Appl. Surf. Sci.*, 301 (2014) 142.
17. El-Sayed M. Sherif, H.R. Ammar, K.A. Khalil, *Int. J. Electrochem. Sci.*, 10 (2015) 775.
18. X.Y. Wang, D. Y. Li, *Electrochim. Acta,* 47 (2002) 3939.
19. Z. Liu, T. Wu, K. Dahm, F. Wang, *Scrip. Mater.,* 37 (2002) 1151.
20. D. Cui, *Proceedings of the 2010 International Conference on Electrical and Control Engineering.* IEEE Computer Society Washington, DC, USA, pp. 5413-5416 (2010).
21. J.B. Fogagnolo, F. Velasco, J.H. Robert, J.M. Torralba, *Mater. Sci. Eng. A*, 342 (2003) 131.
22. H.R. Ammar, K.A. Khalil, El-Sayed M. Sherif, *Int. J. Chem. Nucl. Mater. Metal. Eng.*, 9 (2015) 154.
23. El-Sayed M. Sherif, H.S. Abdo, K.A. Khalil, A.M. Nabawy, *Metals*, 5 (2015) 1799.
24. El-Sayed M. Sherif, *Int. J. Electrochem. Sci.*, 6 (2011) 1479.
25. El-Sayed M. Sherif, *J. Ind. Eng. Chem.*, 19 (2013) 1884.
26. El-Sayed M. Sherif, A.A Almajid, F.H.; Latif, H. Junaedi, *Int. J. Electrochem. Sci*., 6 (2011) 1085.
27. F.H.; Latif, El-Sayed M. Sherif, A.A Almajid, H. Junaedi, *J. Anal. Appl. Pyrolysis*, 92 (2011) 485.
28. V. Shinde P.P. Patil, *Mater. Sci. Eng. B*, 168 (2010) 142.
29. F.L. Floyd, S. Avudaiappan, J. Gibson, B. Mehta, P. Smith, T. Provder, J. Escarsega, *Prog. Org. Coatings,* 66 (2009) 8.
30. W. Gao, S. Cao, Y. Yang, H. Wang, J. Li, Y. Jiang, *Thin Solid Films*, 520 (2012) 6916.
31. K. Darowicki, S. Krakowiak, P. Ślepski, *Electrochimica Acta*, 49 (2004) 2909.
32. K.A. Khalil, El-Sayed M. Sherif, A.A. Almajid, *Int. J. Electrochem. Sci*., 6 (2011) 6184.
33. El-Sayed M. Sherif, Abdulhakim A. Almajid, *J. Chem.*, 2014 (2014) 7.
34. El-Sayed M. Sherif, H.S. Abdo and A.A. Almajid, *Materials*, 8 (2015) 2127.