

## Corrosion Behavior for Al-Cu-Mg Alloy by Addition of SiO<sub>2</sub> Particles in Seawater

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Received on: 30/1/2013

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Accepted on 5/9/2013

### ABSTRACT

This work involves studying the effect of adding SiO<sub>2</sub> particles on corrosion behavior of Al-Cu-Mg alloy in 3.5% NaCl solution at room temperature using polarization method at scan rate 3 mV.sec<sup>-1</sup>.

According to potentiodynamic polarization test, the results of corrosion rate indicate that Al-Cu-Mg composites (1, 2, 3 wt% SiO<sub>2</sub>) gave decreasing in corrosion rate compared with Al-Cu-Mg alloy due to the covering the anodic sites for alloy by SiO<sub>2</sub> particles and enhancing the passivity of surface and reducing the dissolution of aluminum. The cathodic Tafel slope (b<sub>c</sub>) were decreased after adding SiO<sub>2</sub>, while the anodic Tafel slopes (b<sub>a</sub>) were increased. It is inferred that the rate of change of current with change of potential was smaller during anodic polarization than that during cathodic polarization. Cyclic polarization measurements were carried out to estimate the pitting resistance of Al-Cu-Mg composites. The results show that a stable oxide film is formed during the forward scan on the surface of composites; also the hysteresis loop disappears, especially for composite with 3 wt%SiO<sub>2</sub>.

**Keyword:** Corrosion of Al-Cu-Mg Composite, SiO<sub>2</sub> Particles Additives, Potentiostatic Measurements.

السلوك التآكلي لسبيكة المنيوم-نحاس-مغنيسيوم باضافة دقائق السليكا في ماء البحر

### الخلاصة

تتضمن هذه الدراسة تأثير دقائق السليكا على السلوك التآكلي لسبيكة المنيوم – نحاس – مغنيسيوم في محلول كلوريد الصوديوم بنسبة 3.5% عند درجة حرارة الغرفة باستخدام طريقة المجهاد الساكن عند معدل سرعة مسح مساوية لـ 3 ملي فولت لكل ثانية، ووفقاً لنتائج اختبار الاستقطاب الخطي فان معدل

التآكل للمواد المترابطة ذات اساس معدني من سبيكة الالمنيوم مع دقائق السليكا بنسب وزنية ثلاثة 1 و 2 و 3 % قد اصبح اقل مقارنة بمعدل التآكل للسبيكة الاساس وذلك بسبب تغطية المواقع الانودية للسبيكة بدقائق السليكا وتعزيز سلبية السطح وتقليل ذوبان الالمنيوم من السبيكة. لوحظ نقصان في قيم ميل تافل الكاثودي بعد اضافة دقائق السليكا، بينما لوحظ زيادة في قيم ميل تافل الانودي مبيناً ان التغير الحاصل في التيار مع تغير الجهد كان اقل خلال الاستقطاب الانودي مما في الاستقطاب الكاثودي. وقد بينت نتائج قياس الاستقطاب الحلقي استقرارية غشاء السلبية المتكون في حالة المواد المترابطة اضافة الى اختفاء الحلقة الهستيرية وخصوصاً في حالة اضافة (3 wt%) من السليكا.

## INTRODUCTION

The stress corrosion cracking in a 3.5% NaCl solution of a pure aluminum matrix composite reinforced by alumina borate whiskers (Al<sub>18</sub>B<sub>4</sub>O<sub>3</sub>) was studied by Hu et al. [1]. Crack propagation was predominantly along the whisker/matrix interface. This was attributed by Hu et al. [1] to dissolution of the matrix surrounding the whiskers as evidenced by pits that formed at the crack tips. A SiC-coated graphite fiber/Al alloy matrix composite was developed to overcome the reaction of graphite with aluminum above 500°C forming Al<sub>4</sub>C<sub>3</sub> [2]. This phase formed as hexagonal plates with subsequent degradation of fiber strength. In addition, Al<sub>4</sub>C<sub>3</sub> is hygroscopic causing further deterioration.

Silicon enrichment on the outer surface of the fibers inhibited the formation of Al<sub>4</sub>C<sub>3</sub>; however, it allowed improvements of only short duration. Galvanic corrosion between the matrix metal and the reinforcement fibers can occur, especially when in contact with aqueous solutions. The seawater corrosion of SiC/Al was found to be more resistant than graphite/Al by Aylor and Kain [3]. This was attributed to a lack of a galvanic driving force between the SiC and the aluminum matrix, although both composites exhibited similar mechanisms of corrosion—essentially pitting of the metal matrix around the reinforcement material.

Ahmad et al. [4] studied effect of copper and silicon carbide content on the corrosion resistance of Al-Mg alloys in acidic 1M HCl and alkaline 1M NaOH solution using weight loss method to evaluate corrosion resistance, the results show that copper and silicon carbide have a negative effect on the corrosion resistance of monolithic aluminium.

Budruk et al. [5] studied the corrosion behavior of pure magnesium, Mg-Cu (0.3, 0.6, and 1 vol.%) and Mg-Mo (0.1, 0.3, and 0.6 vol.%) composites in 3.5% NaCl solution by weight loss and polarization methods. The corrosion rate increased with increasing volume fraction of reinforcement in Mg-Cu and Mg-Mo composites.

Nickel et al. [6] studied the effect of plastic deformation on the corrosion and wear behavior of composites based on an Al-Cu alloy. Al<sub>2</sub>O<sub>3</sub> or SiC particles in two different fraction (5 or 15 vol. %) as well as size (fine or nano) as reinforcements by potentiodynamic polarization in NaCl solution.

Jamaludin et al. [7] studied the influence of heat treatment on the corrosion behavior of two Al-Cu matrix composites (15 vol% Al<sub>2</sub>O<sub>3</sub>p and 20 vol% SiCw) in 3.5% sodium chloride solution by gravimetric measurements.

## EXPERIMENTAL PROCEDURE

### Preparation of Specimens

Al-Cu-Mg alloy was used in this work. The chemical composition of this alloy is shown in Table (1) obtained by atomic absorption spectroscopy in the ministry of science and technology. The reinforcement by SiO<sub>2</sub> particles with grain size (<50)μm, with three percentages (1, 2 and 3 wt%) was achieved to obtain new modified alloy as composite materials. A measured amount of the matrix alloy was melted at 700°C in an electrical furnace (carbolite type), after that, the melt was stirred inside the furnace at 300 rpm speed and 3 min times to make a vortex in order to disperse the modifier in the melt. The melt temperature was controlled and checked with thermocouple (K type) before pouring into a carbon steel die.

The specimens were polished, degreased with acetone and rinsed with distilled water and then mounted by hot mounting using formaldehyde (Bakelite) at 138°C for 8 minute to insulate all but one side and made a hole on one side (with surface area 1 cm<sup>2</sup>) to electrical connection.

The microstructure evolution was investigated by means of optical microscope using (BEL photonics) microscope was connected to computer.

### Electrochemical Measurement

Potentiostatic and cyclic polarization measurements were carried out with WINKING MLab 200 Potentiostat from Bank-Elektronik with electrochemical standard cell. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate 3 mV.sec<sup>-1</sup>. Polarization experiments were started when the rate at which open circuit potential (E<sub>ocp</sub>) changed was less and more 200mV.

## RESULTS AND DISCUSSION

### Open circuit potential – time measurements

Figure (1) shows the potential – time measurement. This figure indicates that the potential began at (-717 mV) for Al-Cu-Mg alloy and then gradually decreases to stable at (-737 mV). Presence of 1 wt%SiO<sub>2</sub> in matrix alloy make the potential began at (-544 mV) and then increases to (≈ -400 mV), but gradually decreases to stable at (- 604 mV), while presence of 2 wt% of SiO<sub>2</sub> gave reverse behavior compared with 1 wt%, since began at (-802 mV) and gradually increases to (-720 mV). Addition of 3 wt% SiO<sub>2</sub> gave E<sub>oc</sub> more negative than base alloy and rather stable at (-961 mV).

During anodic or cathodic polarization, or at open circuit, ion transfer reaction of metal ions and oxygen ions will take place. A clear process is the anodic corrosion of a passive metal in the steady state. In such a case, Schultze et al. [8] observed that metal ions travel through the oxide film with a constant rate and are transferred in an ion transfer reaction at the interface oxide/electrolyte. The rate of that passive film dissolution depends on the local potential drop at the interface, the pH and the activity of the metal ions at the oxide surface.

### Potentiodynamic polarization

Figure (2) shows the potentiodynamic polarization for Al-Cu-Mg alloy before and after addition of three percent of SiO<sub>2</sub>. This figure shows the anodic reaction which represents dissolution of metals in alloy, mainly aluminum and magnesium due to

more negative potential in galvanic series ( $E_{Al}^{\circ} = -1.66V$  and  $E_{Mg}^{\circ} = -2.36V$ ) according to the following reactions [9]:



While copper forms phase of Al<sub>2</sub>Cu [10] which dissolves with the formation of aluminium and copper ions as follow:



The presence of chloride ions enhanced the dissolution of metals because of chloride ion is bonded chemically in the interface as an initial step of the formation of different mixed oxohydroxo – and chloro complexes according to the following formula [11]:



Finally the  $[AlCl_6]^{3-}$  complex is produced.

At cathodic sites, reduction of oxygen can occur according to the following reaction:



The presence of Cu in the matrix has favored to the degradation. Intermetallic of Al-Cu compound is strongly cathodic against the metallic matrix and act as cathodic site, facilitating dissolution of the protective Al<sub>2</sub>O<sub>3</sub> and enhancing pitting corrosion.

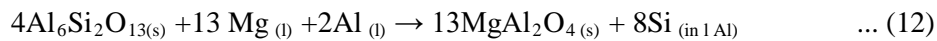
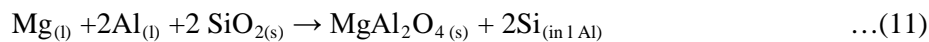
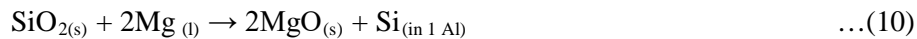
Also, the formation of Al-Cu-Mg intermetallic particles promotes the cathodic reduction of oxygen and then accelerates corrosion process [12]. Consequently the passive films formed on the Al-Cu-Mg intermetallic particles were chemically different and less protective than those formed on the aluminum matrix [12, 13]. Copper and magnesium-rich intermetallics strongly influenced the corrosion behavior of aluminum.

According to Blanc et al. [12] the reactivity of Cu and Mg intermetallics can be described by a three-step process consisting of homogeneous dissolution, copper re-deposition followed by local dissolution of the surrounding matrix. Many other

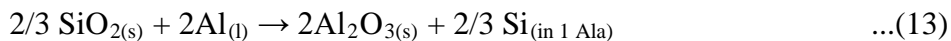
researchers have discussed the importance of intermetallic particles as initiation sites for corrosion [14, 15-21].

Tafel extrapolation method was used to estimate corrosion parameters which are tabulated in Table (2). These data show that presence of 1, 2 and 3% SiO<sub>2</sub> shift the corrosion potential E<sub>corr</sub> to active direction. The corrosion current densities i<sub>corr</sub> values show that presence of SiO<sub>2</sub> decreases the current density of Al-Cu-Mg alloy and increasing of weight percent decreases the current density. This phenomenon indicates the role of SiO<sub>2</sub> particles to increasing corrosion resistance through covering the anodic sites for alloy and enhancing the passivity of surface and reduces the dissolution of aluminum. This can be observed through the values of corrosion rate in (mpy)

Also, silicon dioxide (SiO<sub>2</sub>) as it formed from reaction between aluminum and oxidized silicon carbide particles in Al/SiC composites would have various beneficial effects [23] through preventing the formation of Al<sub>4</sub>C<sub>3</sub> and iii) promoting in situ growth of thermodynamically stable phases (MgO, MgAl<sub>2</sub>O<sub>4</sub>) that may act as reinforcements, according to [22] the following reactions may take place:



In addition to these reactions, the following chemical reaction between molten aluminum and SiO<sub>2</sub> is also thermodynamically possible [20]:



The Tafel slopes were very much influenced in the presence of SiO<sub>2</sub>. The cathodic Tafel slope (b<sub>c</sub>) were decreased after adding SiO<sub>2</sub>. But the anodic Tafel slopes (b<sub>a</sub>) were increased in the presence of SiO<sub>2</sub>. It is inferred that the rate of change of current with change of potential was smaller during anodic polarization than that during cathodic polarization.

The small slope indicates the presence of a film on the surface of the tested material, which is less permeable and can even obstruct the metal dissolution reaction but still permits an electrochemical reaction to occur. It is known that the surface oxide on Al alloys permits the movement of ionic species and an electron or vacancy flux across it [23,24].

### Cyclic polarization

Figure (3) shows the cyclic polarization for Al-Cu-Mg composites to measure of pitting susceptibility for material. These figures indicate that the potentials for the reverse scan curves are more positive than that for the forward scan. These results show that a stable oxide film is formed during the forward scan on the surface of composites, also the hysteresis loop disappears. The composite with 3 wt%SiO<sub>2</sub> show the good pitting resistance and no chance to breakdown the passivity on Al-Cu-Mg alloy surface.

### Microstructure Test

Figure (4) shows the microstructure of based alloy and composite of Al-Cu-Mg alloy reinforced by SiO<sub>2</sub> particles before and after corrosion test in seawater. The microstructure consist of solid solution as a homogeneous grains, since most of the copper is present in the solid solution which increase the corrosion resistance of aluminium, and this behavior can be attributed to the nature of passive film covering this alloy. Also this effect attributed to the preferential dissolution of aluminium from the pit region leading to the formation of Cu – rich surface inside pits. Also the surface of this alloy displays black marks after the first few hours of corrosion, according to the reaction:



While the microstructure of composites show the distribution of reinforced particles in based material and precipitate it at grain boundaries and within grains. Silica particles behave as cathodic sites where reduction reactions can occur and reducing the dissolution of metals in material in corrosive medium.

### CONCLUSIONS

Improvement of corrosion resistance of Al-Cu-Mg alloy to pitting in seawater can be achieved by adding SiO<sub>2</sub> particles to fabricate Al-Cu-Mg composites due to covering the surface of alloy by protective layer decreases corrosion rate as shown from potentiodynamic tests in seawater. Cyclic polarization test can be show the stability of passive layer for composite and no chance to pitting occur.

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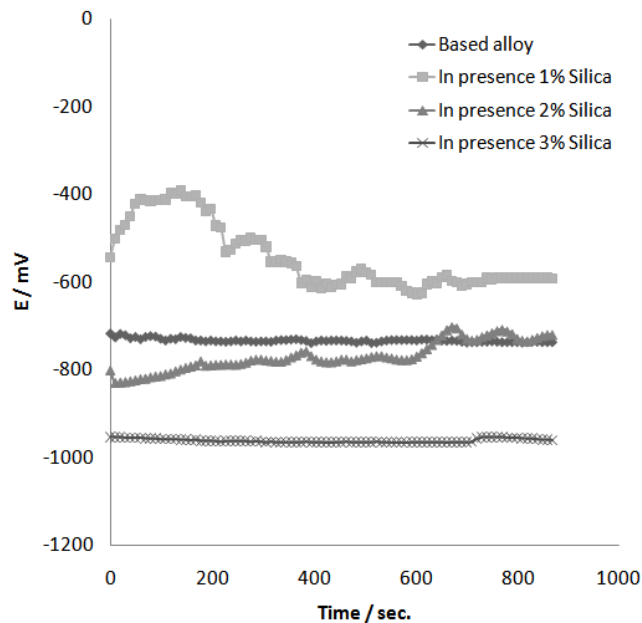
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**Table (1) Chemical composition of based alloy.**

Material	Composition wt%
Al-Cu-Mg alloy	Cu:4.37, Mg:1.41, Si:0.56, Fe:0.15, Sb:0.0218, Zn:0.018, Ni:0.01, Mn:0.008, Sn:0.0056, Ti:0.004, Cr:0.002, Pb:0.00144, Al:Rem.

**Table (2) Corrosion parameters of Al-Cu-Mg composites reinforced by SiO<sub>2</sub> in seawater.**

Percent of SiO <sub>2</sub>	-E <sub>oc</sub> mV	-E <sub>corr</sub> mV	i <sub>corr</sub> μA/cm <sup>2</sup>	Tafel slope mV/dec.		CR mpy
				-b <sub>c</sub>	+b <sub>a</sub>	
0%	737	711.4	1.87	120.3	66.5	0.810
1%	604	742.7	1.74	44.2	91.1	0.754
2%	820	855.3	1.31	71.7	90.4	0.567
3%	961	965.5	0.248	101.5	89.3	0.107



**Figure (1) Variation of potential - time of Al-Cu-Mg alloy reinforced by SiO<sub>2</sub> particles with three weight percent in seawater**



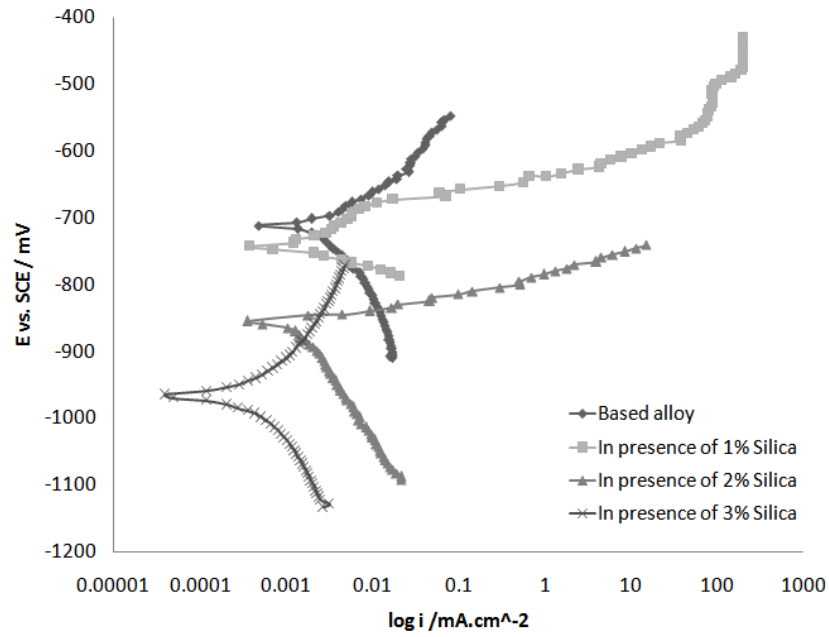
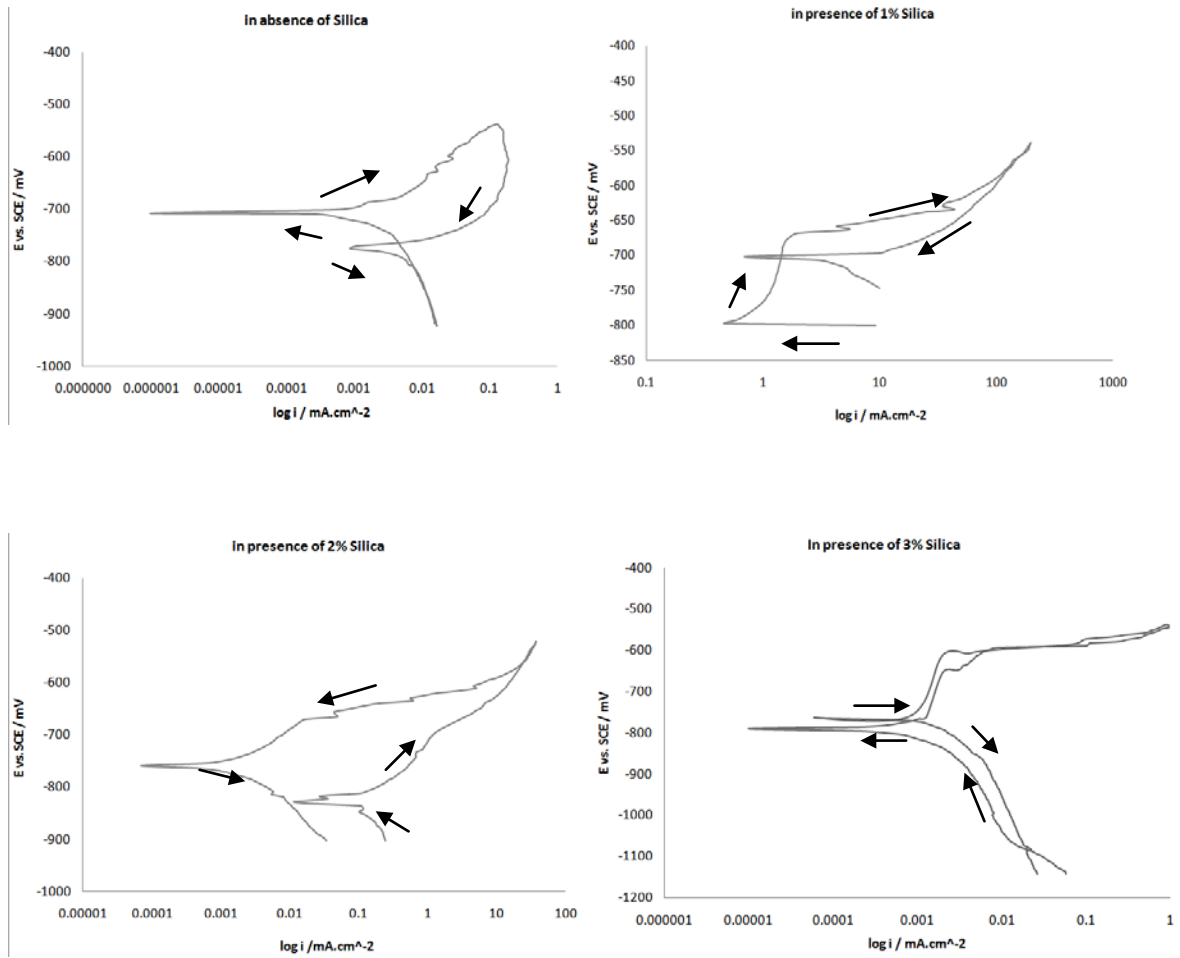
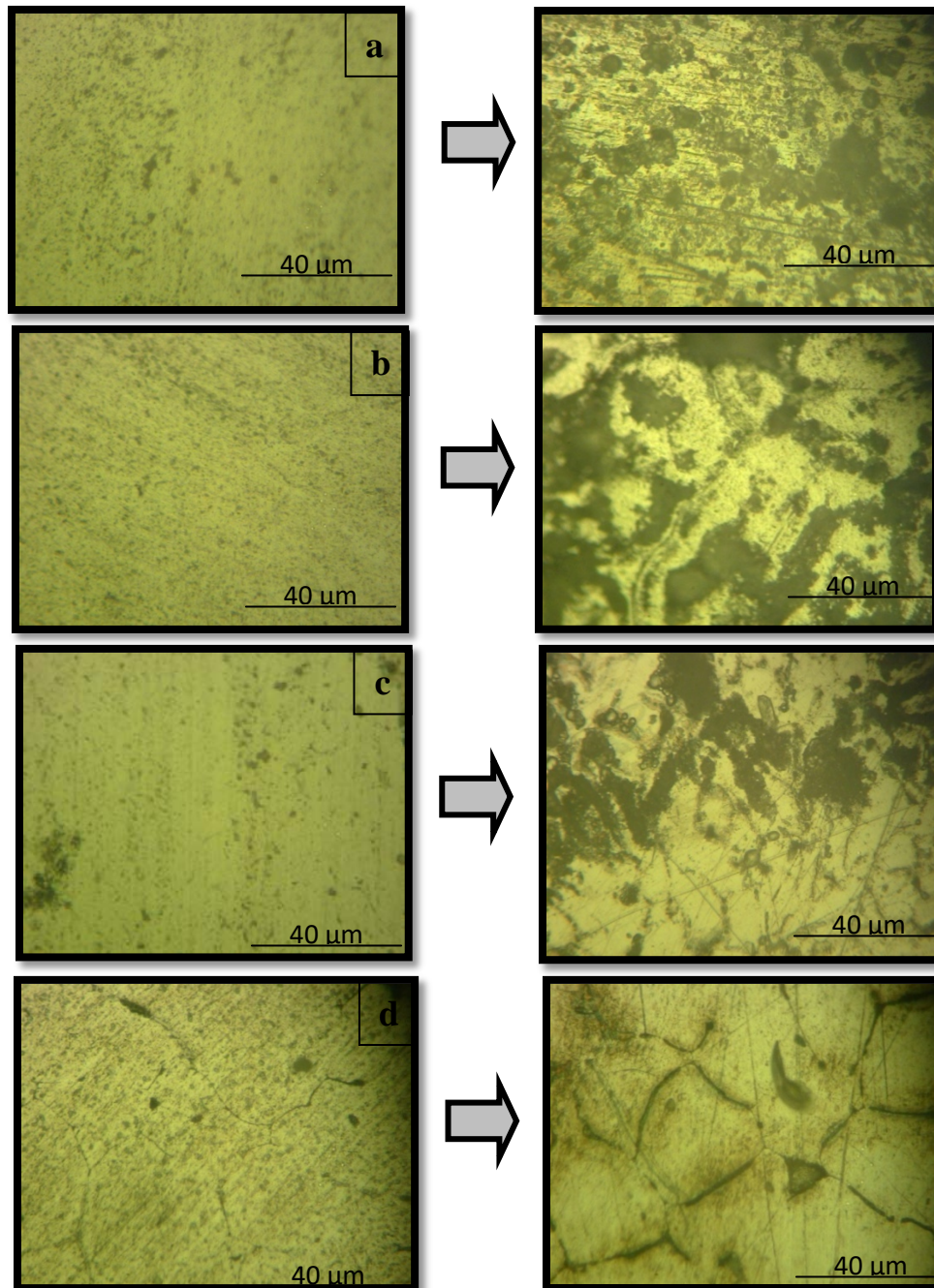


Figure (2) Potentiodynamic polarization of Al-Cu-Mg alloy reinforced by SiO<sub>2</sub> particles with three weight percent in seawater.



**Figure (3) cyclic polarization of Al-Cu-Mg alloy reinforced by SiO<sub>2</sub> particles with three weight percent in seawater**



Figure(4): Microstructure of Al-Cu-Mg alloy reinforced by SiO<sub>2</sub> particles with three weight percent before and after corrosion. (a): Al-Cu-Mg alloy, (b): Al-Cu-Mg alloy reinforced by 1%SiO<sub>2</sub>, (c): Al-Cu-Mg alloy reinforced by 2%SiO<sub>2</sub>, (d): Al-Cu-Mg alloy reinforced by 3%SiO<sub>2</sub>.