Al-Khwarizmi Engineering Journal,Vol. 12, No. 4, P.P. 50- 58(2016)

Al-Khwarizmi Engineering Journal

Effect of Magnesium Addition on Corrosion Resistance of Aluminum -17%Silicon Alloy

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(Received 15 September 2015; accepted 9 May 2016)
http://dx.doi.org/10.22153/kej.2016.05.003

Abstract

The electrochemical behavior of Al-17%Si alloy is investigated in 3.5wt% NaCl solution. Many alloys with addition of the different wt% magnesium metal of 1wt%, 2%, 3wt% ,4.5wt% ,and 9wt% were prepared by gravity die casting . The microstructures of prepared alloys were examined by optical and SEM microscopes. Corrosion behavior was investigated by using potentiostat instrument under static potentials test and corrosion current was recorded to determine corrosion resistance of all prepared samples. It was found that the addition of Mg metal improves the corrosion resistance of Al-17%Si alloy in 3.5%NaCl solution. The alloy containing 1%Mg shows less corrosion rate than the others while the alloys containing 4.5%Mg, 9%Mg content have the better pitting corrosion resistance than other alloys.

Keywords: *Al-Si Alloys, magnesiumaddition ,corrosion behavior, microstructure.*

1. Introduction

In industry Aluminum and Silicon alloys are used largely in different life fields and industrial applications and these alloys are modified by various additives, before 50 years ago the scientific known this alloy having increasing in strength hypereutectic when increasing the Si content and having decreasing in strength hypereutectic when decreasing the Si content.[1].

Hypereutectic Al- 18%Si it's widely used to product the light weight pieces such as (connecting rods, pistons, air conditioner, compressors, cylinder liners and engine cover), this alloy having a good mechanical properties like wear and corrosion but it's has a low thermal expansion and reduce density [2]

Although when added the small amount of (Cu, Ni and Mg) these elements lead to increasing the casting properties' improvement of the work hardening characteristics, good corrosion resistance and weldability, but when added the Si, this element reduce the thermal expansion coefficient and lead to poormachinability [3,4].
It is found that the coarser structures having high corrosion resistance than finer structures. Silicon is contained another important parameter which effect on the mechanical and corrosion resistances [5].

Corrosion was the interaction between the metal surface and the wet media where the metal atoms dissolve as ions. To control the corrosion must prevent the contact between the aqueous media and the metal surface and this can be obtained by interactive between the oxygen and the surface metal formed oxide film, this film prevent any interaction . Then the Aluminum can be consider the metal which formed this film rapidly[6].

Many studies were performed on this item Nikanorov*et al.*[7] [2005]studied the microstructure and behavior of Aluminum alloys which content Silicon between (11.5 wt% - 35 wt%)using rapid cooling of melts of various compositions alloys . Theyfound that properties are depend on solidification factors during cooling of the alloys and it limited the yield values by elasto-plastic of microstructure of the Silicon crystals and Silicon grain boundaries.

Hamilta de Oliveira Santosa[8], studied the corrosion resistance performance of (Al- Si – Cu) alloy in a solution condensate from automotive fuel combustion, which selected four alloy three of them were commercial alloys , all this alloys put in this solution . The results shown the differences in corrosion resistance and the fourth alloy have corrosion resistance higher than the commercial alloys.

Wislei R. Osório et al.[9][2009], studied the effect of add some parameter to the Aluminum such as (9% Silicon) on the mechanical and the electro-chemical behavior of as cast and laser remeltedand observed that the fine silicon fibers have low effect on the electrochemical corrosion resistance and also observed the samples have high corrosion resistance as cast samples than laser remelted samples.

Rodríguez-Diaz et al.[10] [2015], investigated the electro-chemical methods which consists of the potentiodynamic polarization curves, linear polarization resistance (LPR), electro-chemical impedance spectroscopy (EIS) and electro-chemical noise measurements (EN).On the Al-Mg – Si alloy immersion in (3.5% NaCl) solution as a function of time. They observed formed the Mg_2Sicomplex compound and the formation of the galvanic couple (Al-Mg) which led to changed of the current density to maximum values.

Rodríguez-Diaz et al. studied theeffect of the Mg metal addition to Al-17%Si alloy with different percentages as follows:1.0%, 2.0%, 3.0% 4.5% and 9.0% and studied its effect on the corrosion resistance in 3.5%NaCl solution

2. Experimental Work

2.1 Materials Used

A liquid metallurgy route has been adopted to fabricate the cast Al-17%Siwith various addition of percentage of Mg metal. The basealloy was melted in graphite crucible in furnace work by electric at 750ºCand then the preheated Mg metal powder with size of 50µm was introduced into the alloy (Al- 17%Si) molten alloy with using vortex technique of the effectively degassed molten alloy,and then pouring the molten alloy in preheat cylindrical shape steel mold. The addition of the magnesium powder in the matrix alloy was by different percentages:1%,2%, 3% ,4.5% ,and 9.0%. Table 1 shows the base alloy’s chemical composition .

Table 1,
Chemical composition of Al-17%Si alloy.

Element wt%	Si	Fe	Cu	Mg	Cr	Ni	Zn	Al
	17	1.0	1.3	1.0	0.1	1.3	0.25	Rem

2.2. Fabrication of Specimens

The specimens was manufacturing with dimensions (1.5 X 1.5 X 0.2) cm for corrosion test according to ASTM (G70-30)The samples fabrication with increased the Magnesium element in the alloy as shown in the Table (2).

Table 2,
Classification of Al-Si alloy.

Specimen symbol	State of specimen
A	Base alloy without Addition
B	Base alloy with addition 1wt%Mg
C	Base alloy with addition 2wt%Mg
D	Base alloy with addition 3wt%Mg
E	Base alloy with addition 4.5wt%Mg
F	Alloy with addition 9.0wt%Mg

2.3 Microstructure Examination

In order to examine the microstructuresof all prepared specimens groups, the specimens were prepared in sequence processes :The specimens were ground with using Si Cemery paper of grades :350,500,800 and 1000, and then they were polished with using special cloth and alumina Al_2O_3 solution of grain size 0.3 µm. Etching process was carried out by immersion the specimen in etchant solution, Keller's reagent thatcontains of 95 ml distilled water, 2.5ml HNO_3, 1.5 ml HCl and 1 ml HF then washed the specimen with water and alcohol then dried by air. Optical testes of specimens was done by optical microscope (Ep-typ2) provided with computer and digital camera .

2.4 Electrochemical Corrosion Test

A specimen of an exposed area (1 x 1 cm^2)ismounted with holder. Theelectrode's reference ismounted with (1 mm) away from the surface of the specimen. The electrode's reference used in this workis saturated calomel electrode (SCE). The electrode's auxiliary used in the electro-chemical cell is platinum type. The holder of specimen , together with the reference and auxiliary electrode areputted in the respective positions in the electro-chemical cell used for this aim, as shown in Figure 1.

A current reading of cell is taken for a short, slow drag of the potential. The drag was taken from (–200 to +200) mV relative to (OCP) . In this range the relation between the current density and voltage is almost nearly linear. A data for linear fitting of the standard model is givenas an estimation of the polarization resistance, that calculated the corrosion current density (I_{corr}) and corrosion rate (mpy). The investigation are achievedusing a WENKING MLab multi channels and SCI-Mlab corrosion measuring system from Bank Electronics- Intelligent controls GmbH, Germany 2007.

When used all the samples in 3.5% NaCl solution with pH of 6.8 to calculate the corrosion parameters, (corrosion potential (Ecorr) and corrosion current (Icorr)), by Tafel extrapolation method. Then after calculate the (Ecorr) and (Icorr) these lead to calculate the corrosion rate as shown in equation (1).[11]

$$C.R\,(mpy) = 0.13 * I_{corr} * eq.wt / \rho \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where:

mpy= mils -inches per year

I_{corr}=corrosion current density (µA/cm^2)

E.W=equivalent weight of the corroding species,

ρ= density of the corroding specimens, (g/cm^3).

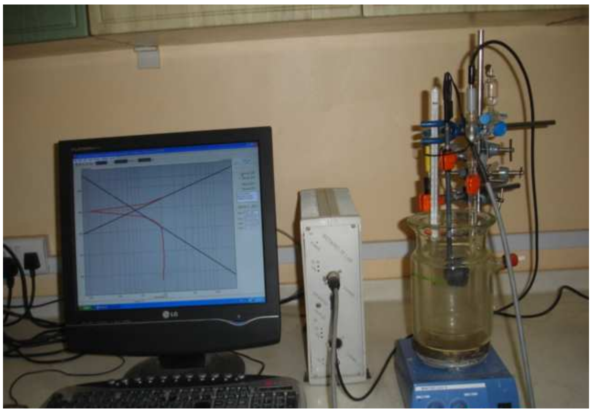

Fig. 1. The electrochemical cell unit used in this work.

3. Results & Discussions

3.1 Microstructure Results

In the Figure (2A) shows the microstructure of hypereutectic Al–17 Si alloys. It was revealed the presence of primary silicon in cuboids shape and eutectic silicon in needle shape and larger size phases . Figure (2B) shows that the silicon interact with magnesium which lead to complex compound (Mg2Si). It gives the alloy higherhardness and strength values .This is because of precipitation of a new precipitate or 2^{nd} phase particles due to period and heat from supersaturated solid solution.

The results lead to when the Aluminum is pure, it don't generated dendrite. But when Magnesium, Silicon and other materials are added to pure Aluminum the dendrite will growth through the microstructure as shown in Figures(2C&2D). The feature of the dendrites are fine, have shape edge like needle (the dendrite are symmetry to the Sandarac tree paper), growth freely into the structure of the metal liquid and the dendrite are largely at the neighboring Aluminum grains. After some time the alloy becomes more solidification and more growth in dendrite the growing aluminum grain by a snow plow is represented inFigures(2E&2F).

Figure 3shows SEM micrographs of Al-17%Si alloy and with addition of Mg. It was seen that silicon needle with various size and orientation and this phase is distributed of solid solution (α and eutectic phase (Figure 3a) while theaddition of Mg lead to change of microstructure, it was observed grain refinement of α- dendrites and silicon flakes in addition to distributed of Mg_2Si particles in aluminum matrix as shown in Figure (3 b &3c).

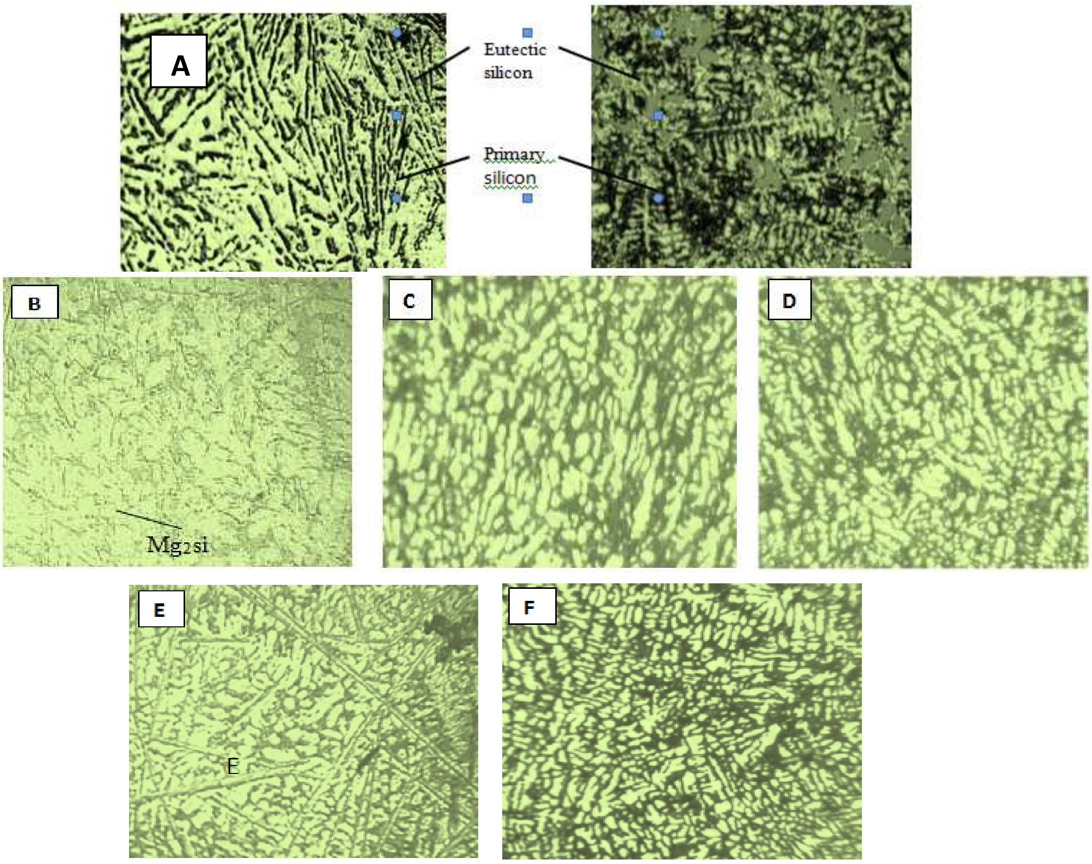

Fig. 2. Shows the microstructures of hypereutectic Aluminum and 17% Silicon Al–17 Si alloys of specimens (A,B,C,D, E&F) at magnification 400x.

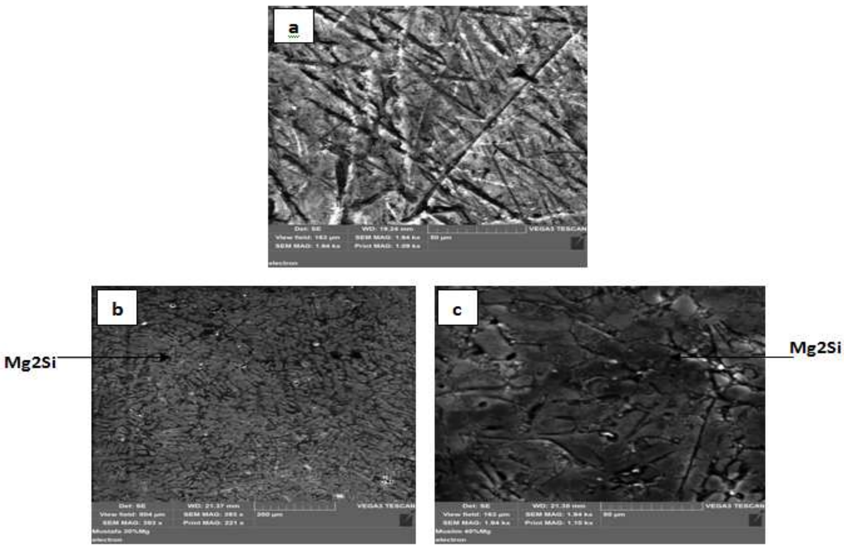

Fig. 3. SEM micrographs of base alloy Al-17%Si specimen and with addition of Mg (a) Base alloy Al-17%Si , (b) Base alloy +1%Mg , (c) Base alloy +4.5%Mg.

3.2. Electrochemical Corrosion Results

Figure (4) Al-Si alloys samples(A,B,C,D,E&F) after corrosion test in the solution have 3.5% NaCl or sea water .These figures shows the regions of cathodic and anodic, where the reduction of oxygen and dissolution of aluminum can take place respectively. Corrosion parameters measured by Tafel extrapolation of potentiodynamic curves.

The curves above show the regions of anodic and cathodicwhich indicate that, the specimen (A) has an increase in corrosion current density (Icorr) then corrosion rate increases. When magnesium is add to Al-17%Si at different percentages, it was we seen improvement in corrosion rate for all specimens . This is due to the change in microstructure after casting due to refinement in eutectic (Al+Si) and silicon phase and also forming Mg_2Si particles in specimens (B)which act as cathodic and Al matrix as anode . while the specimens C,E&F give convergent in result due to coarser dendritic structuresinter dendritic mixture's eutectic.These results are in agreement with those of researcher Wislei R. Osório*et al.[*12], they studied theeffect of silicon content on microstructure and electrochemical behavior of hypoeutectic Al–Si alloys ,They concluded that the increased on silicon content had provided a dendritic refinement and a more extensive redistribution of the eutectic mixture which has result the decreased on the resistance's corrosion.

Based on the electrochemical reactions of aluminum and its alloys in a natural chloride containing environment, the following anodic reaction for anodic polarization of aluminum is proposed:

$Al + 3H_2O \rightarrow Al(OH)_3 + 3H^+ + 3e^-$ …(2)

The formation of the pit leads to the dissolution of aluminum, which causes the migration of chloride ions into the pit and the formation of aluminum chloride inside the pit, according to the following reaction:

$Al \rightarrow Al^{+3} + 3e^-$ …(3)

$Al^{+3} + 3Cl^- \rightarrow AlCl_3$ …(4)

Conversely, the following electrochemical reaction is proposed for the cathodic polarization of aluminum:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ … (5)

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$ …(6)

In the present work the addition of Mg metal to Al-17%Si alloy lead to formationthe complex phase (Magnesium Hydroxide) which product the alloy from corrosion. These results are getting by researcher Song et al. 1997[13]who show the complex compound Mg(OH)2 are product the Aluminum alloy from corrosion behavior according following reactions:

$2H^+ + 2e^- H_2 \longrightarrow$ (cathodic partial reaction) …(7)

$2Mg \longrightarrow 2Mg^+ + 2e^-$ (anodic partial reaction) …(8)

$2Mg^+ + 2H_2O \longrightarrow 2Mg^{2+} + 2OH^- + H_2$ …(9)

$2Mg^+ + 2H+ + 2H_2O \longrightarrow 2Mg^2 + + 2OH- + 2H_2$ (overall reaction) … (10)

$Mg^{2+} + 2OH^- \longrightarrow Mg(OH)_2$ (corrosion product formation) …(11)

Equations 7 and 8, represent cathodic and anodic reactions whichtaken place more than on a surface coated using the film that the chemical reaction in Eq.9 represents the chemical oxidation of Mg+ to Mg2+. The displayed of the overall reaction in Eq.10andfinally, Eq.11was the responsible for the forming of Mg(OH)2 corrosion product.

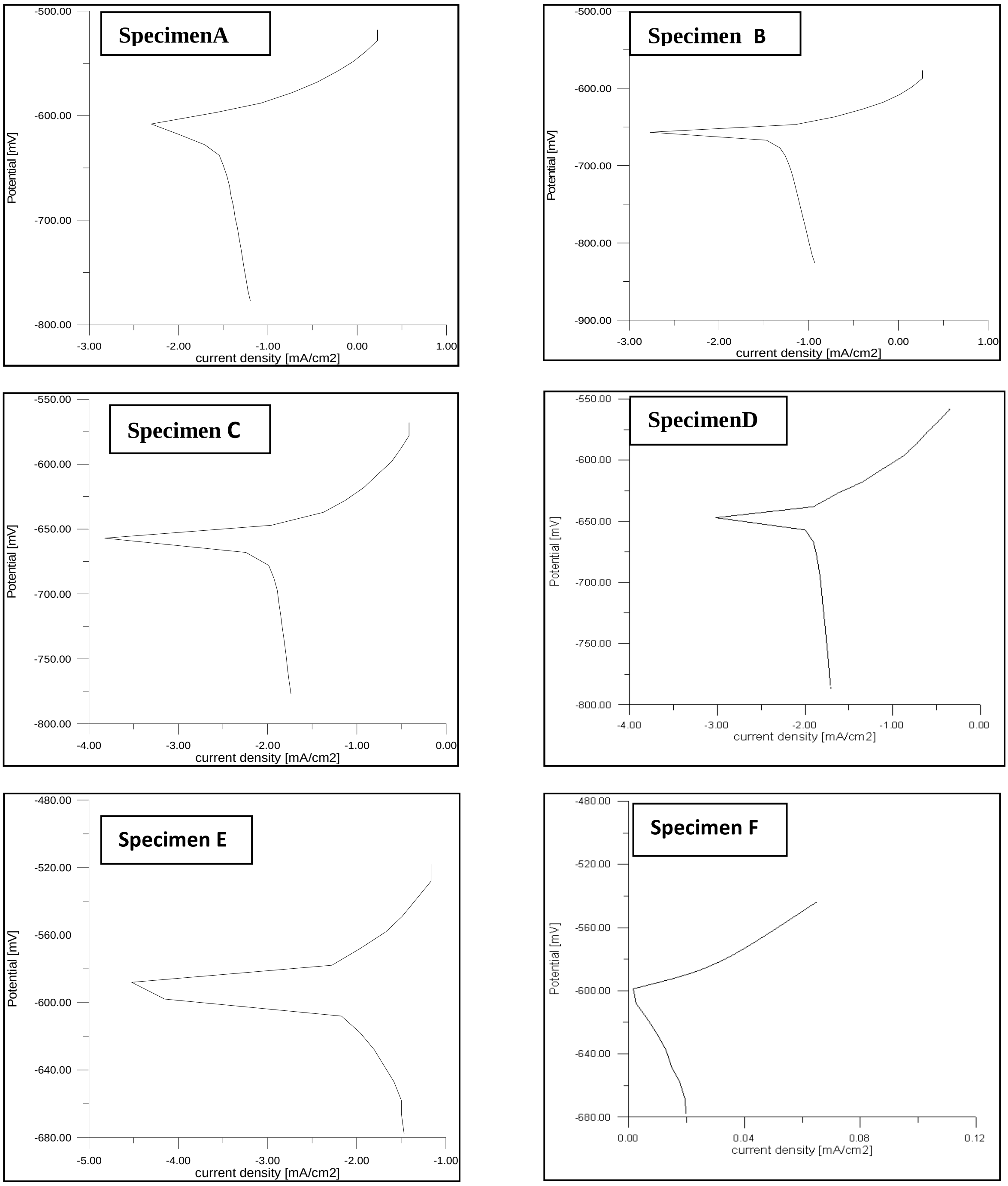

Fig. 4. Polarization curves of the Al-Si alloy for specimens (A,B, C,D,E&F)

Table 2,
The results of corrosion tests of studied samples of Al-Si alloy in 3.5 % NaCl solution.

Symbol	Mg %content	I [$\mu A/cm^2$]	E (mV)	I_{corr} [$\mu A/cm^2$]
A	Base alloy	24.3	-614.4	10.449
B	1wt%Mg	2.8	-561.7	1.204
C	2wt%Mg	8.7	-656.5	3.741
D	3wt%Mg	9.4	-646.5	4.042
E	4.5wt%Mg	7.7	-587.8	3.311
F	9.0 wt%Mg	7.3	-597.4	3.139

3.3. Micrographs after Corrosion

Figure 5 shows the micrographs of all specimensafter putting all samples in solution have 3.5% NaCl and the electrochemical corrosion is done. It was shown (specimen A) contains number of large pits while the specimens containing different amount of Mg have less number of small (specimens B, C&D) and the pits become shallow pits as Mg % increases or pits may be disappear as shown in specimens E&F. Figure 5B gives the lowest value of corrosion rate due the effect of Mg in forming finer dendritic structures.It was observed that the pit morphology on the Al-17%Si alloys showed hemispherical isolated deeper pits on the specimen A , while specimen C revealed a higher number of shallow pits. These results are in agreement with those results of Hosni Ezuber*et al.[*14].

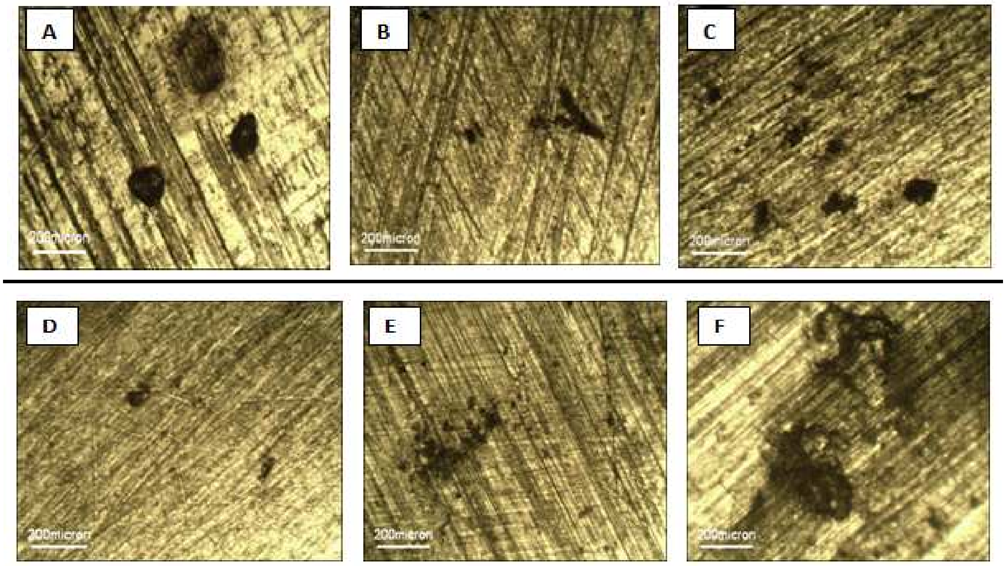

Fig. 5. Micrographs after corrosion test in 3.5%NaCl solution.

4. Conclusions

1. It was found that Mg addition has been effect of an effective modification of eutectic morphology on surface corrosion behavior of Al–17%Si alloy.
2. The increase in Mg content in Al-17%Si has provided a dendritic refinement of α- solid solution and silicon needle phase
3. The addition of Mg lead to more extensive distribution of the Mg_2Si in aluminum matrix which has improved the corrosion resistance.
4. The Al-17%Si alloy containing 1%Mg shows the better corrosion resistance or less corrosion rate than other alloys.
5. When added the Mg toAluminum and 17% Silicon improved the pitting corrosion resistance in 3.5% NaCl solution but the alloys containing 4.5%Mg, 9%Mg content show the better pitting corrosion resistance than other alloys.

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تأثير أضافة المغنيسيوم على مقاومة االتآكل لسبيكة المينيوم – سيليكون ١٧%

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الخلاصة

في هذا البحث تم دراسة السلوك الكهروكيمياوي لسبيكة (Al- 17%Si) في محلول (3.5 wt% NaCl)، وذلك باضافة معدن المغنيسيوم للسبائك وبنسب مختلفة (1wt%, 2wt%, 3wt%, 4.5wt%, 9wt%) حيث تم تحضير السبائك بواسطة قوالب الصب بالجاذبية.وقد تم استعمال المجهر الضوئي والمجهر الالكتروني الماسح لفحص التركيب المجهري للسبائك. وتم بحث اسلوب التآكل بواسطة استعمال جهاز المجهاد الساكن (Potentiostat) وتحت اختبار الجهد الساكن وتم تسجيل تيار التأكل وحساب مقاومة التأكل لكل النماذج المحضرة. وقد لوحظ انه عند اضافة معدن المغنيسيوم يزيد من مقاومة التأكل في سبائك (Al-17%Si) في محلول (3.5% NaCl). ولوحظ ايضاً ان السبائك الحاوية على (1% Mg) اظهرت اقل معدل تآكل من السبائك الاخرى بينما كانت السبائك الحاوية على (9% Mg, 4.5% Mg) تمتلك افضل مقاومة للتاكل النقري من باقي السبائك.