



PITTING CORROSION STUDIES OF MG-BEARING HYPEREUTECTIC AL-17% SI ALLOY

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ABSTRACT :-

In this study pitting corrosion is investigated in hypereutectic Al- 17wt% Si alloy bearing magnesium . Many alloys were prepared by die casting with adding different percentages of magnesium : 1 wt%, 4wt% & 9 wt% to the Al-17%Si alloy in order to study the influence of magnesium addition on the corrosion behavior and pitting properties in 3.5% NaCl solution. Results of microstructure examination show that primary silicon (Si) and eutectic silicon in base alloy was more susceptible to pitting corrosion compared to the other alloys containing magnesium . It was found that the corrosion rate of alloy Al-17%Si bearing Mg (in all percentages) was lower than that of base alloy. The corrosion potential shifts to less negative value (to more noble direction) and Epit to more positive value with increasing Mg content to 9%wt. It means that the addition of Mg to Al-17% Si alloy improves resistance to pitting corrosion and that no pitting appears in passive region during the cyclic polarization test.

KEYWORDS: Al-Si alloy, pitting corrosion, microstructure, Mg effect

دراسة التآكل النقري لسبيكة الالمنيوم- 17% سيليكون فوق اليوتكتيكية

المحتوية على المغنيسيوم

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المخلص:

في هذا البحث تم دراسة التآكل النقري في سبائك الالمنيوم-17% سيليكون المحتوية على نسب وزنية مختلفة من معدن المغنيسيوم (1، 4، 9)% والتي تم تحضيرها بطريقة السباكة في القوالب المعدنية وذلك لبيان تأثير اضافة المغنيسيوم على سلوك التآكل النقري في محلول ملحي من 3.5% كلوريد الصوديوم. وقد اظهرت نتائج الفحص المجهرى ان السيليكون الاولي واليوتكتيك في السبيكة الاساس يكون اكثر ميلا للتآكل النقري مقارنة بالسبائك الحاوية على المغنيسيوم. وقد وجد ان معدل التآكل لسبيكة الالمنيوم 17% سيليكون المحتوية على المغنيسيوم (لكل النسب المضافة) اقل مما هو عليه في حالة السبيكة الاساس . وقد لوحظ ان

جهد التآكل ينتقل الى الی قيمة اقل سالبية (الی الاتجاه الاكثر نبلا) وجهد التتقر الی قيمة اكثر موجبة مع زيادة نسبة المغنيسيوم الی 9% وهذا يعني ان اضافة المغنيسيوم عملت علی تحسين مقاومة التآكل النقری. كذلك لوحظ اختفاء النقر وحلقة الهسترة من منطقة السلبية في منحنی التفاعل الانودي خلال اجراء فحص الاستقطاب الدوري .

INTRODUCTION :-

We know that Aluminum–silicon (Al–Si) alloys are significant of aluminum casting alloys since having great fluidity, little shrinkage in cast, great corrosion confrontation, perfect weld ability, facility brazing and little coefficient of thermal distention and the alloys are largely applied in the manufacturing of automotive in zones like vehicle weight decrease and fuel economy betterment [Vončina,2012] . Hypereutectic alloys comprise Al-Si alloys which have silicon greater than 12%. Al–Si alloys likes A390 (Al–17% Si–4.5% Cu–0.5% Mg) are used in many implementation like pistons, connecting rods , cylinder liners ,air conditioner compressors, and engine blocks [Naglaa, 2014 , Nikanorova ,2005].

The presence of many additives alloying elements with limited solubility's in aluminum has been shown to promote localized corrosion and we see aluminum passives in H_2SO_4 due to formation of a porous oxide film but HCl gives rise to rapid aluminum corrosion. Mazhar *et al.* [2001] studied the chloride ions role of the pitting corrosion of some Al–Si alloys in HCl solutions using electrochemical impedance spectroscopy and chemical polarization (EIS) measurements, as well as SEM studies. Pitting by chloride ions initiates more readily in acidic media. The presence of chloride ions in aqueous media in contact with aluminum metal or aluminum alloys causes pitting attack. The presence of chloride ions was found to accelerate corrosion of aluminum in aqueous media; the corrosion depended strongly on the pH of the solution. Also, in acidic and alkaline media, where the solubility of aluminum oxide is enhanced, aluminum corrodes more rapidly. Thus, the passivation of aluminum can be suppressed by lowering or increasing the pH, as well as by addition of chloride ions [Mazhar *et al.* ,2001] . Modern researches on Al-Si alloys have told that larger dendritic structures produce better corrosion resistance than finer dendritic structures due to the morphology of the interface dendritic eutectic mixture[Wislei, 2005]. We can got this microstructure by additive alloying elements such as magnesium, the work of magnesium was prepared the elemental strengthening and reform the work-hardening features of aluminum. It can give good corrosion resistance and weldability or maximum elevated strength. The addition of magnesium to aluminum in 4–8 wt %, improves the properties. But when its amount is increased to more than 8 wt. %, lower thermo-mechanical properties are produced elevated porosity in the composite resulting from the lower pressure of the magnesium [Hemantk ,2014, Srdjan,2009].

Rodríguez-Díaz *et al.* [2015] studied the corrosion comportment of Al-Mg-Si alloy in 3.5 % NaCl solution as a job of time of dipping and evaluated by means of electrochemical techniques. These contained inside curves of potentiodynamic polarization, linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) measurements and electrochemical noise measurements (EN). They existing greater corrosion rate of Al-Mg-Si alloy comparering with pure Aluminum. The formation of the galvanic couple Al-Mg and the sedimentation of Mg_2Si phase persuaded a shift of the current density towards upper values. The hydroxide or oxide layers shaped over the surface of Al-Mg-Si alloy were not completely defensive. Thus, the aim of this work is to investigate the influence of Mg addition on the pitting corrosion resistance when is exposed to 3.5%NaCl solution.

EXPERIMENT WORK :-

1-The Materials

We used (Al-17% Si) alloy because it has many applications in industry for instance pistons ,connecting rods, air conditioner compressors, cylinder liners and engine blocks and exploration of the chemical composition was perform by ARL spectrometer device and the result was listed in Table (1)

2-Alloys Preparation

The alloy Al-17%Si was melted using graphite crucible which was put in electric furnace at evaluated temperature of 750° C then the liquefy was poured and discard in the heated cylindrical steel template with measurements of 12mm diameter and 100mm height. Different amount of weight percentages of Mg (1.0%, 4.0% & 9.0%)were added to the melt of aluminum alloy (Al -17% Si) applying gravity die casting technique. The preparing alloys included melting the base alloy, stirring the melt, adding 1.0% Mg in the melt at moving speed of 600 rpm for 6 min and spilling the liquefy in the steel template. The alike actions were perform for preparations for the rest alloys comprising 4.0% and 9.0%wt Mg. Cast ingots which prepared by casting technique were grouped into specimens as presented in **Table(2)** .

3-Microstructure Examination

We equipped the Specimens for microstructure examination which involves grinding by SiC emery paper having grit of (220,320,500 &1000) and then were polished by applying diamond past of size (1 μ m) by unusual polishing cloth with using lubricant as coolant, and etching method was carried out by using solution of (99% H₂O+1%HF). Then specimens were washed with water and alcohol and dried. Optical examination of specimens was implemented by optical microscope prepared with camera and linked to a computer.

4- Examination of Corrosion

Many specimens for corrosion examinations were produce with dimensions (1.5x1.5x0.2 cm) agreeing to ASTM (G 70-30)specifications from the alloys used.

The prepared specimen of an exposed area (1 x 1 cm²) was settled in the holder. We settled the reference electrode for distance a bout (1 mm) from the surface of the specimen which to be examined. Potentiodynamic polarization and electrochemical cyclic method was implemented for and corrosion test by a Wenking Mlab multi channels potent dynamic and SCI-Mlab corrosion measuring system from Bank Electronics-Intelligent control GmbH, Germany 2007 and **Figure(1)**show its. The potential cell current readings were taken during a short, slow sweep from (-1000 to + 1000 mV relative to (OCP). Scan rate explains the speed of the potential sweep in mV/sec and it's taken (10 mV/ sec). The extent of current density opposite the voltage curve is nearly linear. In this test, the aluminum – silicon alloy with magnesium additions samples were used as working electrode (WE), The reference electrode used in this work was calomel electrode(SCE) and auxiliary electrode was platinum type.

All samples which were prepared for corrosion test were immersed in solution of sodium chloride at 3.5wt% NaCl with PH of 6.66 to conclude corrosion factors, like corrosion potential (E_{corr}) and corrosion current (I_{corr}) at each time . These factors were applied to compute the corrosion rate agreeing to Tafel equation as shown in equation (1)[Annual Book of ASTM ,2004],the obtained result was listed in **Table(3)** . Optical microscope was used to take photomicrographs for all specimens after corrosion test.

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

Where

(mpy)= corrosion rate (mils-inch per year) or (0.0254mm/year)

(I_{corr}) = corrosion current density (μA/cm²)

(Eq.wt) = equivalent weight in grams / equivalent of the corroding species

ρ = density of the corroding specimens (g/cm³)

RESULTS AND DISCUSSION :-

1- Microstruture Results

The microstructure of the as-cast Al-Si alloy is shown in **Figure 2a**, this micrograph exhibits an interdendritic structure of α-Al phase. It is well known, that microstructure is strongly dependent of solidification process, especially by the solidification rate.

The observations by optical microscopy revealed that Si needles distributed in different orientation in Al-Si matrix and also Si particles enter between dendritic regions.

Figure 2B shows the microstructure of hypereutectic Al–17% Si alloys containing 1%Mg . It was revealed the presence of primary silicon (Si) in small blocky shape and eutectic silicon in needle shape and larger size phases . Optical micrograph shows this distributed of solid solution (α) phase in the matrix of aluminum. **Figure 2(C & D)** shows that the silicon combine with magnesium to form the hardening phase Mg₂Si that provides the strengthening ,also the hardness and strength values increase as a result of refining the dendritic structure and of precipitation of a new precipitate due to period and heat from supersaturated solid solution.

It was noticed the structure is refined that means the α-Al dendrite grains become more finer and Si needles disappear and change into nearly spherical shape particles distributed in Al-alloy matrix which reduce the stresses induced in alloy. This is attributed to Mg addition to Al-Si alloy which form Mg₂Si precipitates and intermetallic compound such as Al₃FeSi as indicated in x-ray diffraction analysis. As Mg increases from 1wt% to 9wt% the microstructure improves and modify more and the grains become finer than that of alloy without Mg addition. These results are in agreement with the researcher [Muna ,2010] who added Cd metal to Al-12%Si that leads to modification the microstructure and improved the mechanical properties of alloy.

2- Electrochemical Corrosion Results

Corrosion of aluminum is thought to occur by ionic migration followed by dissolution at the oxide/electrolyte interface . Due to its relative mechanical weakness it is usually strengthened by alloying, which may cause reduced corrosion resistance [Vončina ,2012]. Potentiodynamic polarization test by using potentostat is performed and cathodic and anodic curves are drawn which agreed to oxidation and reduction reactions severally. The corrosion rate is calculated by finding the point at which the oxidation reactions, would be equal to the reduction reactions. Tafel extrapolation method was used to find E_{corr.}, and I_{corr.} which represents the rate of dissolution. It should be noted that I_{corr.} also corresponds to the rate at which hydrogen gas is evolved [Uhlig & Revie,2008].

Cyclic polarization was carried out to estimate the initiation and propagation of pitting corrosion in “3.5%NaCl solution”. **Figures (3, 4, 5 & 6)** show the cyclic polarization curves of all Al-Si alloys specimens (A,B ,C &D) respectively after corrosion test in “3.5% NaCl solution” .These curves show the cathodic and anodic regions which indicate that the specimen (A) has an increase in corrosion current density (I_{corr}) then corrosion rate

increases. When magnesium is added to Al-17%Si at different percentages, it was 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 Mg₂Si particles in specimens (B) which act as cathodic and Al matrix as anode. Also the specimens (C & D) give more corrosion resistance due to finer dendritic structures that this is associated with the morphology of the inter dendritic eutectic mixture. These results are in agreement with those of researcher Wislei *et al.* [2009], they studied the effect of silicon content on microstructure and electrochemical behavior of hypoeutectic Al-Si alloys. They concluded that the increase on silicon content has provided a dendritic refinement and a more extensive redistribution of the eutectic mixture which has resulted a decrease on the corrosion resistance. Cyclic polarization curves confirm the more pitting resistance for Al-17%Si containing Mg with 1.0%, 4.0% & 9.0 wt% for alloys B, C & D respectively as compared to base alloy without Mg. From **Table (2)** it can be seen there is a significant improvement in corrosion resistance of Al-Si bearing different percentages of Mg and I_{corr} of these alloys is lower than base alloy and shows a passive region in anodic polarization curve in current value $I_{passive}$. This is due to forming of thin protective oxide layer of Al₂O₃ on surface which is passive until reach to repassivation in same path without intersection the anodic curve with passive region during cycling polarization. This confirms that these alloys are susceptible to form a protective layer against corrosion in "3.5%NaCl solution". While it was noticed from the anodic curve in (**Figure 6**) in case of alloy D the presence of two passive regions, this confirmed the formation of thin protective layers on alloy surface which represents the best alloy in pitting corrosion resistance among other bearing Mg alloys. It was seen that $I_{passive}$ changes from 92.3 $\mu\text{A}/\text{cm}^2$ (alloy A) to 1.7 $\mu\text{A}/\text{cm}^2$ (alloy D) which bearing (9 wt%Mg), also the corrosion rate decreases as Mg % increases to 9wt%, while the $E_{passive}$ shifts to positive value (+2149.4 mV) in passive region. Similar behavior observed in Al6061 which reaches to the passivity rapidly when exposed to oxygen containing environment forming protective oxide film (Al₂O₃) which is good adherence to metal surface and increased the pitting resistance in chloride solution [Muna et al., 2015].

3 - Electrochemical Reactions

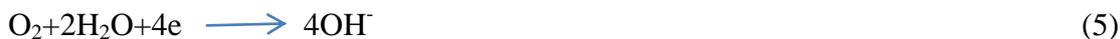
Based on the electrochemical reactions of aluminum and its alloys in natural chloride containing environment, the following anodic reactions for anodic polarization of Aluminum is proposed:



Because the pitting potential of the alloy is coincident to the resulting potential, 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 reactions:



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



The dissolution process mechanism depends on the rise of the film-free surface areas with increasing anodic potential on which the anodic and cathodic partial reactions shown in equation 3 and 4, can take place more freely than on the surface coated by Al_2O_3 film

4 - Micrographs After Corrosion

Figure (7) shows the micrographs after corrosion in “3.5%NaCl solution”. It was shown that the specimen with Mg gives the lowest number of pits as compared to the base alloy that means exhibit good resistance to pitting corrosion. It means that no pitting exist in specimens bearing Mg. This is due the effect of Mg in forming finer dendritic structures and small precipitates of Si particles which uniform distributed in α -Al matrix as mention above (in paragraph of microstructure) of alloys. It was shown that the base alloy (**Figure 7A**) contains small number of pits while the alloys bearing Mg as shown in **Figure 7(B, C &D)** are free –pits and only small corrosion products are deposited on surface in some regions. It was noticed that surfaces were unaffected by corrosion test.

CONCLUSIONS :-

1-As the Mg weight percentage of binary Al-17%Si alloy surpassed the limit of solid solubility in Al then the Mg_2Si particle was sedimentation in the inter dendritic regions of α -Al phase in alloy that leads to the formation of the galvanic couple between Al-Si matrix and Mg_2Si which shifts of the corrosion rate near greater importance.

2-The corrosion rate of base alloy Al-17%Si alloy resulted higher than that of alloys bearing Mg in different percentages .

3- The resistance to pitting corrosion improves as Mg content increases from 1% to 9%Mg in “Al-17wt%Si alloy”.

4- The addition of Mg to Al-17wt%Si alloy shifts the corrosion potential to less negative value (i.e more noble direction) and E_{passive} shifts to more positive value at 9wt%.

Table (1): Chemical composition of Al-Si alloy

Element wt%	Si%	Fe%	Cu%	Mn%	Mg%	Cr%	Ni%	Zn%	Sn%	Pb%	Al%
Measured value	17	1.6	1.81	0.252	0.184	0.026	0.36	2.28	0.059	0.214	Rem

Table(2): Classification of Specimens

Specimen Symbol	State of specimen
A	Base alloy (Al-17%Si)
B	Base alloy with addition of 1wt%Mg
C	Base alloy with addition of 4wt% Mg
D	Base alloy with addition of 9% wt Mg

Table (3) Pitting corrosion parameters for all specimens

Symbol	I corr. $\mu\text{A}/\text{cm}^2$	E corr. mV	I passive $\mu\text{A}/\text{cm}^2$	E _{passive} mV	Corrosion Rate Mpy
Base Alloy A	24.3	-614.4	92.3	1228.1	39.6
AlloyB (1.0%Mg)	8.7	-656.5	21.1	923	9.073
Alloy C (4.0% Mg)	7.7	-587.8	2.9	821	1.247
AlloyD (9.0%Mg)	7.3	-597.4	1.7	2149.4	0.731

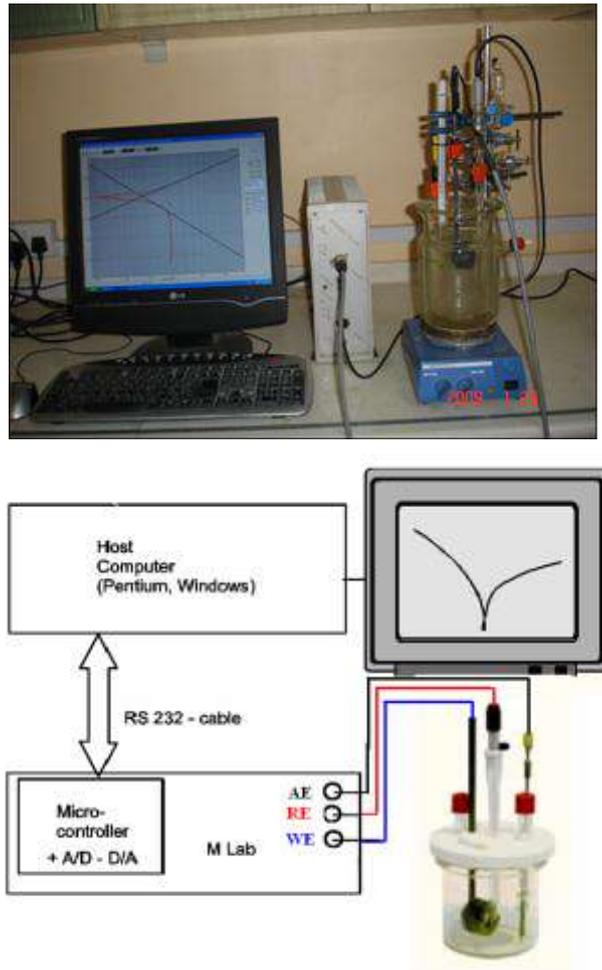


Fig. (1) : The unit used for electrochemical corrosion

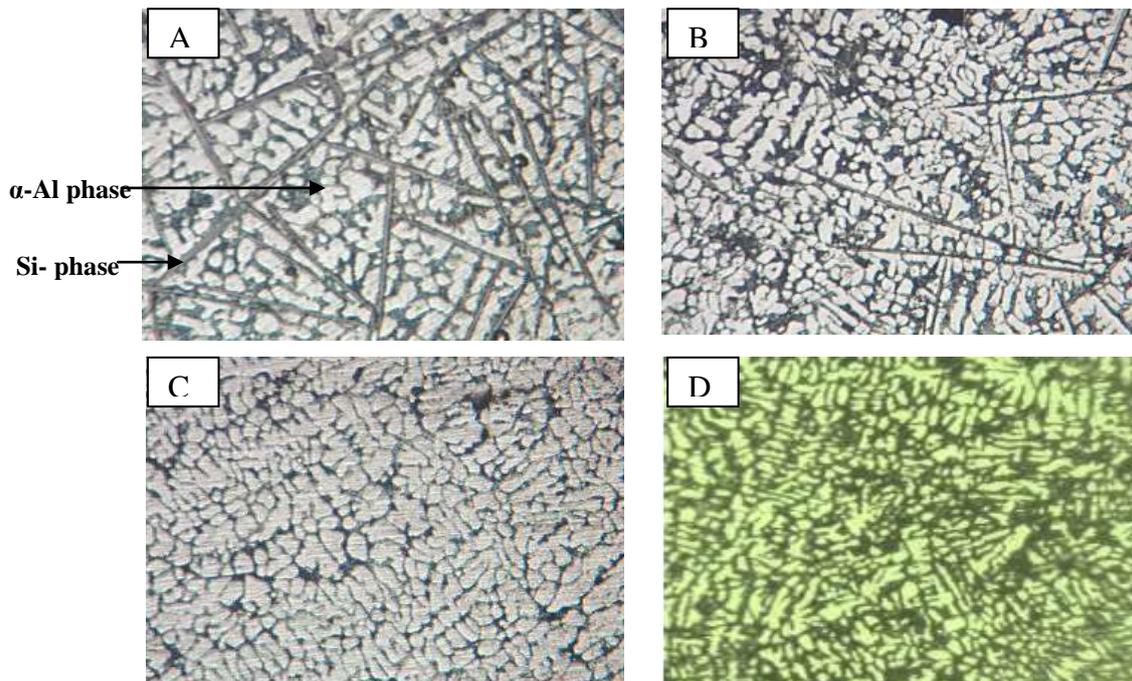


Fig. (2): Microstructures of all specimens (A,B ,C &D) at magnification 400x

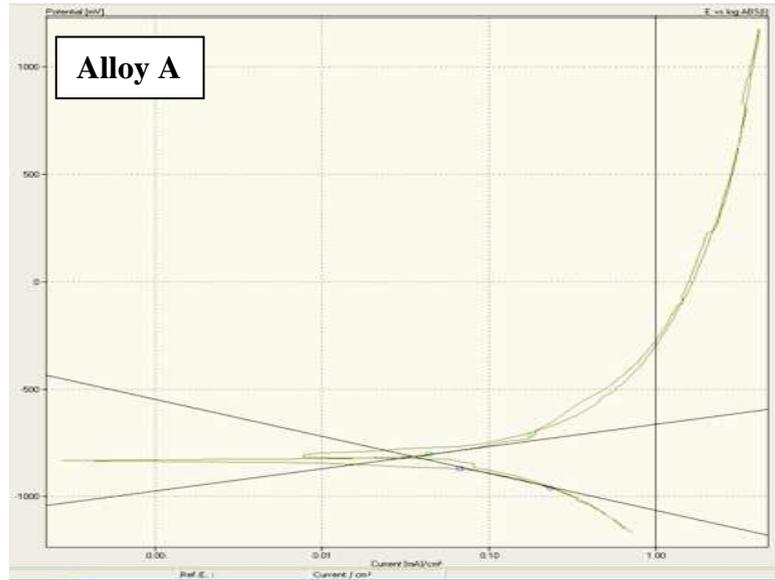


Fig. (3) Cyclicpolarization curve for base alloy (Alloy A)

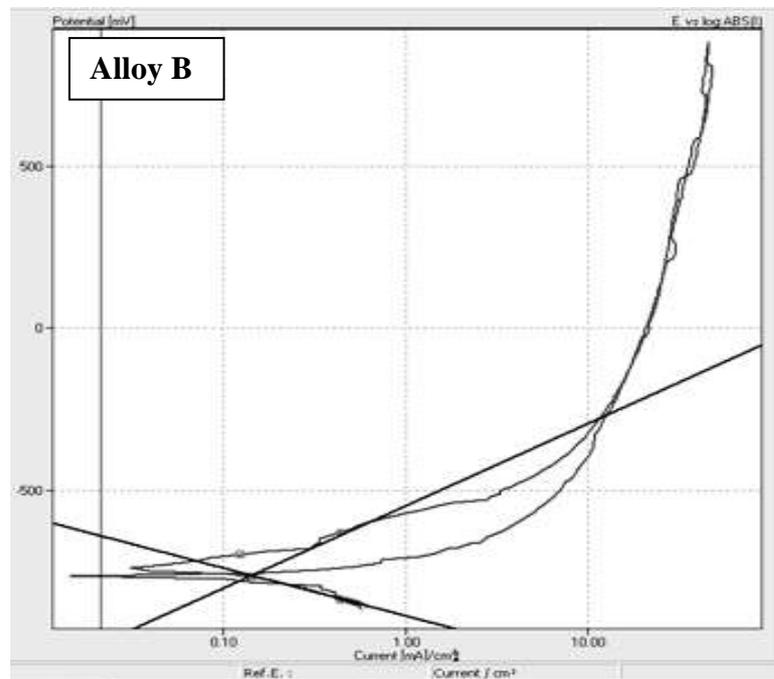


Fig. (4) Cyclicpolarization curve for alloy B(1.0%Mg)

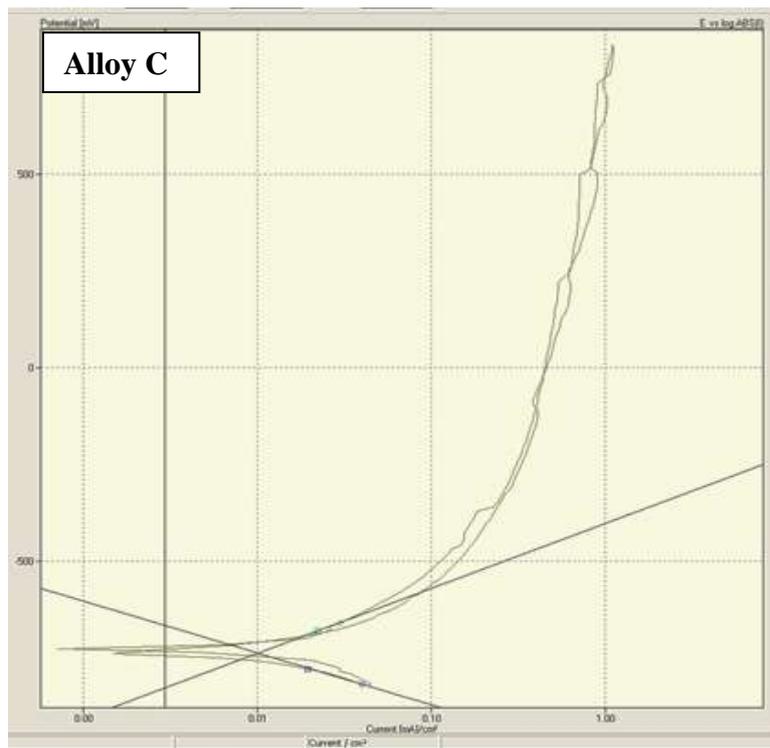


Fig. (5) Cyclic polarization curve for alloy C (4.0%Mg)

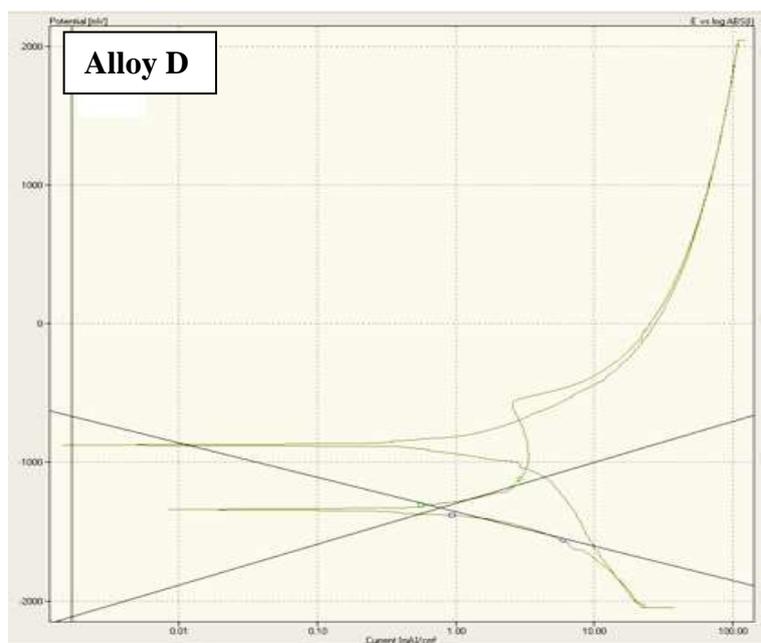


Fig. (6) Cyclic polarization curve for alloy D(9.0%Mg)

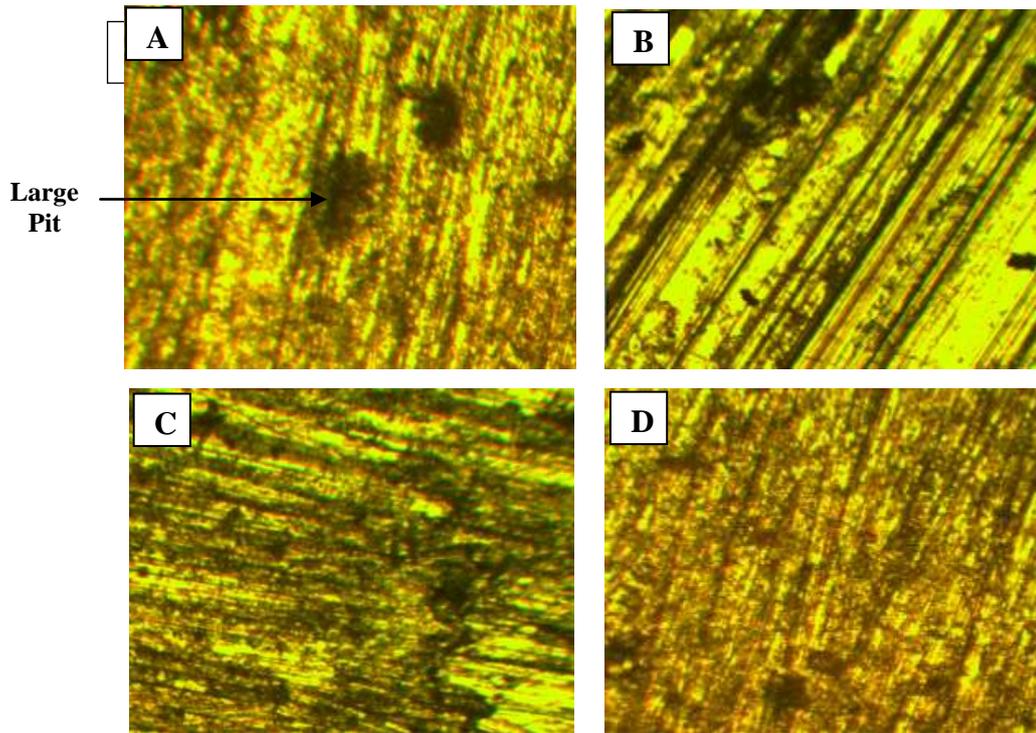


Fig.(7) Micrographs of specimens (A, B, C & D)after corrosion test in 3.5%NaCl solution at 100x

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