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Corrosion Effective of Condensed Synthetic Automotive Solution Containing Selective Organic Component Mixtures on Al-alloys

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Abstract

This work involves studying the effect of adding some selective organic component mixture on corrosion behavior of pure Al and its alloys in condensed synthetic automotive solution (CSAS) at room temperature. This mixture indicates the increasing of octane number in previous study and in this study show the increasing in corrosion resistance through the decreasing in corrosion rate values.

Electrochemical measurements were carried out by potentiostat at 3 mV/sec to estimate the corrosion parameters using Tafel extrapolation method, in addition to cyclic polarization test to know the pitting susceptibility of materials in tested medium.

The cathodic Tafel slope (b_c) were increased after adding the organic component mixture. But the anodic Tafel slopes (b_a) were varied after addition of the mixture. The increase in cathodic 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. This behavior can be achieved by the electronic density on oxygen and nitrogen atoms in the organic component mixture.

Keyword: *corrosion of Al- alloys, potentiostatic measurements, corrosion in fuel.*

1. Introduction

Aluminium and most aluminium alloys have good corrosion resistance in natural atmospheres, fresh water, seawater, many soils, many chemicals and their solutions, and most foods. This resistance to corrosion is the result of the presence of a very thin, compact, and adherent film of aluminium oxide on the metal surface [1].

Whenever a fresh surface is created by cutting or abrasion and is exposed to either air or water, a new film forms rapidly, growing to a stable thickness. The film formed in air at ambient temperature is ≈ 5nm (50 A^o) thick. The thickness increases with increasing temperature and in the presence of water. The oxide film is soluble in alkaline solutions and in strong acids, with some exceptions, but is stable over a pH range of (≈ 4.0 to 9.0).

Aluminium alloys are used in storing, processing, handling, and packaging of a variety of chemical products. They are compatible with most dry inorganic salts. Within the passive pH range, the resist corrosion in solutions of most inorganic chemicals but are subject to pitting in aerated solutions, particularly of halides [1].

There are many studies concerned with gasoline such as the effect of ethanol-gasoline blends on corrosion rate in the presence of different materials of construction used for transportation, storage and fuel tanks [2] and fuel pumps [3]. Hamilta and co-workers [4] studied corrosion performance of Al-Si-Cu alloys in a synthetic condensed automotive solution, while other works [5,6] in alcoholic fuels. Nie et al. [7]

studied corrosion behavior of metallic materials in Ethanol-Gasoline alternative fuels. Eiman and Jehad [8] studied the relative performance of compression ignition engine using various blends of diesel – ethanol fuels. Alessandra Regina Pepe Ambrozin et al.[9] studied metallic corrosion related to mineral fuels and biofuels utilization. The utilization of these fuels implies their closer contact to metallic materials, which comprise vehicle, storage, and transportation systems. Thus, metallic corrosion could be related to fuels and biofuels utilization. They observed that the ethanol is the most corrosive and gasoline the least.

2. Experimental Procedure

Pure aluminium and its alloys were cut into square shape with (1cm*1cm) area, and made into electrode by pressing a copper wire into a hole on one side and then insulating all but one side with an epoxy resin.

The open side was polished mechanically to a mirror finish, rinsed in distilled water and stored in desiccators. The alloys were used Al-Cu-Mg, Al-Mg, and Al-Si-Cu .The composition were measured by using Niton XRF(Portable X-ray Fluorescence Spectroscopy) device –model XLt (UK),in laboratories of Materials Engineering Department -University of Technology .Table (1) shows the chemical composition of Al-alloys.

The electrochemical glass was of the usual type with provision for working electrode (pure metal and its alloys), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an SCE reference electrode.

Two electrolyte was used in this study, first one consist of condensed synthetic automotive solution [4] (CSAS) [ammonium nitrate (0.077 $g.L^{-1}$), ammonium sulphate (1.017 $g.L^{-1}$), potassium chloride (0.1345 $g.L^{-1}$), ammonium hydroxide (0.33 $ml.L^{-1}$) and 1M hydrochloric acid (5.8 $ml.L^{-1}$)], these salts obtained from BDH Chemical Ltd. The pH of this solution was (3.3); the second electrolyte consist of condensed synthetic automotive solution (CSAS) with adding 7.3% of [54% Isopropanol - 20% Aniline - 16%Toluene -10% Oxygenol (50% Methanol + 50% Tertbutanol)] (IATO) mixture [10].

Potentiodynamic 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 $mV.sec^{-1}$. Polarization experiments were started when the rate at which open circuit potential (E_{ocp}) changed was less and more 200mV. The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slops by Tafel extrapolation method.

3. Results and Discussion

The variation of potential with time for pure aluminium and its alloys in CSAS can be shown through open circuit potential values, this behavior indicate that behavior of Al-Mg and Al-Cu-Mg alloys more stable than pure Al and Al-Si-Cu alloy with time. The open circuit potential values take the following sequence for Al and its alloys:

$-E_{oc}$ Al-Si-Cu > pure Al > Al-Cu-Mg > Al-Mg

The various equilibria of Al–H_2O system has been collated by Pourbaix et.al. [11] in a potential versus pH diagram. This diagram indicates the theoretical circumstances in which aluminium should show corrosion (forming Al^{3+} at low pH value and AlO_2^- at high pH value), passivity due to hydragillite, i.e. $Al_2O_3.3H_2O$ (at near – neutral pH values) and immunity (at high negative potentials).

The nature of the oxide actually varies according to temperature, boehmite ($Al_2O_3.H_2O$) is the stable form.

The potentiodynamic polarization curves for pure Al and its alloys in CSAC in absence and presence of (IATO) mixture are shown in Fig. (1). These figures show the main two behavior of alloy in active region, the lower section, represent the cathodic reaction of reduction of hydrogen because of acidity the medium as follow:

$$2H^+ + 2e \rightarrow H_2 \qquad \ldots(1)$$

While the upper section represent the anodic reaction, where the oxidation of metals in alloys, mainly aluminium, can occur according to the following reaction:

$$Al \rightarrow Al^{3+} + 3e \qquad \ldots(2)$$

The value of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) and Tafel slops (b_c , b_a) were getting directly from the potentiostat. The value of polarization resistance (R_p) have been calculated from Stern-Geary equation [12], [13]:

$$R_p = (\frac{dE}{di})_{i=0} = \frac{b_a \times b_c}{2.303 \times i_{corr.} \times (b_a + b_c)} \qquad \ldots(3)$$

Where: (b_c) and (b_a) are cathodic and anodic Tafel slop respectively,(i_{corr} .): corrosion current density.

And the value of corrosion rate have been calculated by using the following equation [14]:

$$C_R(\frac{mm}{Y}) = 3.27\frac{e}{\rho}i_{corr.} \qquad \ldots(4)$$

Where: (e) equivalent weight of corroded alloy, (ρ) density of alloy.

The corrosion parameters listed in Table (2) show that the sequence of corrosion potential of pure Al and its alloys take the following sequence:

-E_{corr} : Al-Si-Cu > pure Al > Al-Cu-Mg > Al-Mg

But these results don`t agreement of the result of corrosion current density which take the following sequence:

i_{corr} :pure Al < Al-Cu-Mg < Al-Si-Cu < Al-Mg

The data concerned corrosion current density enhanced corrosion rate. The data of corrosion rate take the same sequence of corrosion current density. This result indicates that pure Al less sensitive to corrosion than its alloys and this result agreement with the data of polarization resistance which take the following sequence:

Rp : pure Al > Al-Cu-Mg >Al-Si-Cu >Al-Mg

The corrosion parameters listed in Table (2) show that addition of (IATO) mixture shift corrosion potentials (E_{corr}) toward active direction, and shift corrosion current density (i_{corr}) value to lower values and take the following sequence:

i_{corr} : Al-Si-Cu = Al-Cu-Mg < pure Al < Al-Mg

This result mean that Al-alloys with Si and Cu content became more resistance to corrosion in fuel after adding the(IATO) mixture and favor to use as fuel tank, also its known that Al-alloys has mechanical properties better than pure Al.

The Tafel slopes were very much influenced in the presence of (IATO) mixture. The cathodic Tafel slope (b_c) were increased after adding (IATO) mixture comparable to the value of (b_c) with absence of (IATO)to the same electrode material. But the anodic Tafel slopes (b_a) were varied after addition of the mixture as it shown in table (2).

The small cathodic 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[5,6]. It is known that the surface oxide on Al alloys permits the movement of ionic species and an electron or vacancy flux across it [5, 6].

Determination of the nature of the cathodic process in organic solutions is extremely difficult. The proposed cathodic reaction in the ethanol-gasoline fuel is oxygen reduction when no efforts were made to remove dissolved oxygen from the solutions. Previous works [7] reported that the main factor affecting the corrosion rate of mild steel in the ethanol/water/sulphuric acid system is the conductivity of the medium, and the conductivity increased when the water percentage in the ethanol-water mixture increased.

In present study, the film which can be presence on the surface of material forming because of the electron density on oxygen and nitrogen atoms in (IATO) mixture.

Cyclic polarization data were recorded by M Lab electrochemical laboratory system with electrochemistry software M Lab Sci-Multi Channel Potentiostat. Potentiodynamic measurements were carried out in order to determine the initiation and propagation of local corrosion, which is associated with the breakdown of passive protective film. Figures (2) and (3) show the cyclic polarization for pure Al and its alloys, Figure(2) indicate that the potentials for the reverse scan curves are more negative than those for the forward scan, this results means a stable oxide film is formed during the forward scan but after adding the (IATO) mixture, Figure (3), gave the forward scan the same of reverse scan and show there is no chance to pitting corrosion due to the protective film which formed because of electronic density of oxygen and nitrogen atoms in components of mixture on the aluminium and its alloys surface.

4. Conclusion

Adding of some selective organic component (7.3% of [54% Isopropanol - 20% Aniline - 16%Toluene -10% Oxygenol (50% Methanol + 50% Tertbutanol)] (IATO) mixture to (CSAS) solution which increase the octane number as shown in previous studied, we found that this mixture also increased the corrosion resistance of pure Al **,**
Al-Si-Cu , Al-Mg and Al-Cu-Mg alloys. The rate of corrosion takes the following sequence:

CR in mpy (in CSAS only): Al < Al-Cu-Mg<
Al-Si-Cu < Al-Mg

CR in mpy (in CSAS+ LATO mixture): Al-Cu-Mg= Al-Si-Cu < Al< Al-Mg

Enhancement of corrosion resistance due to electronic density on oxygen and nitrogen atoms in the organic component mixture.

Table 1,
Chemical composion of Al-alloys.

Element	Wt% Cu	Wt% Mg	Wt% Mg	Wt% Fe	Wt% Si	Wt% Mn	Wt% Zn	Wt% Ti	Wt% Cr	Wt% Ni	Wt% Al
Al-Cu-Mg	3.8-4.9	1.2 – 1.8	1.168	0.5	0.5	0.0.3-0.9	0.25	0.15	0.1	-	Bal.
Al-Mg	0.1	4 -4.9	-	0.4	0.4	0.4-1	0.25	0.15	0.05-0.25	-	Bal.
Al-Si-Cu	3.563	1.168	-	0.857	12.587	0.335	0.683	0.070	0.049	0.513	Bal.

Table 2,
Corrosion parameters of Al- alloys in synthetic condensed automotive solution (CSAS) and in synthetic condensed automotive solution in presence of IATO mixture (CSAS+IATO) at room temperature.

Material		Open circuit potential (E_{oc}/mV)	Corrosion potential (E_{corr}/mV)	Corrosion current density (i_{corr}/μA.cm^{-2})	Tafel slope (mV.dec^{-1})		Corrosion resistance x10^3 (R_p/Ω.cm^2)	Corrosion Rate mpy
					$-b_c$	$+b_a$		
Pure Al	In CSAS	-459	-430.3	3.44	135.9	156.2	9.1851	1.4895
	In CSAS+ IATO	-492	-433.1	2.94	110.7	114.4	1.5241	1.2730
Al-Cu-Mg	In CSAS	-249	-282.1	14.07	132.3	93.2	1.6896	6.0707
	In CSAS+ IATO	-484	-487.3	0.067	90.0	84.2	0.2818	0.0290
Al-Mg	In CSAS	-179	-203.1	78.76	170.1	98.7	0.3448	34.103
	In CSAS+ IATO	-501	-500.9	22.78	119.5	125.5	0.001166	9.8637
Al-Si-Cu	In CSAS	-585	-487.6	35.48	351.1	42.4	0.4636	15.3628
	In CSAS+ IATO	-490	-487.8	0.067	88.0	82.2	0.2754	0.0290

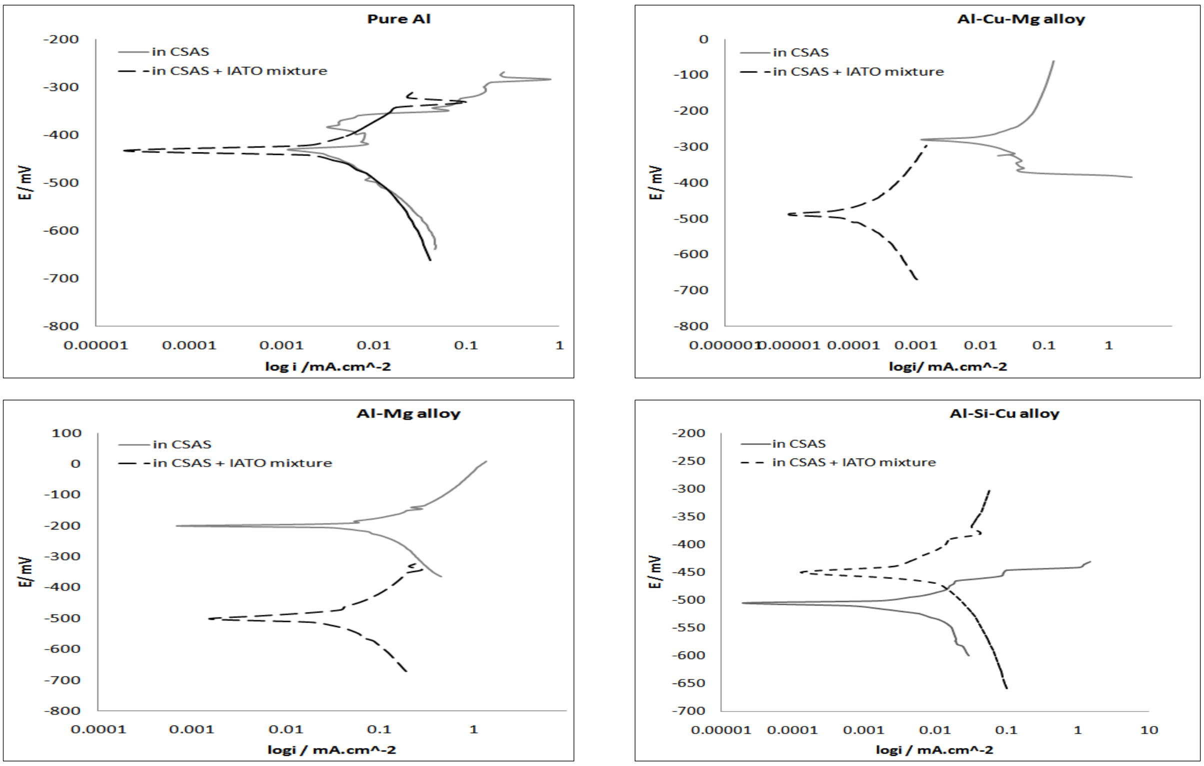

Fig. 1. Potentiodynamic polarization for Al and its alloys in condensed synthetic automotive solution in absence and presence IATO mixture .

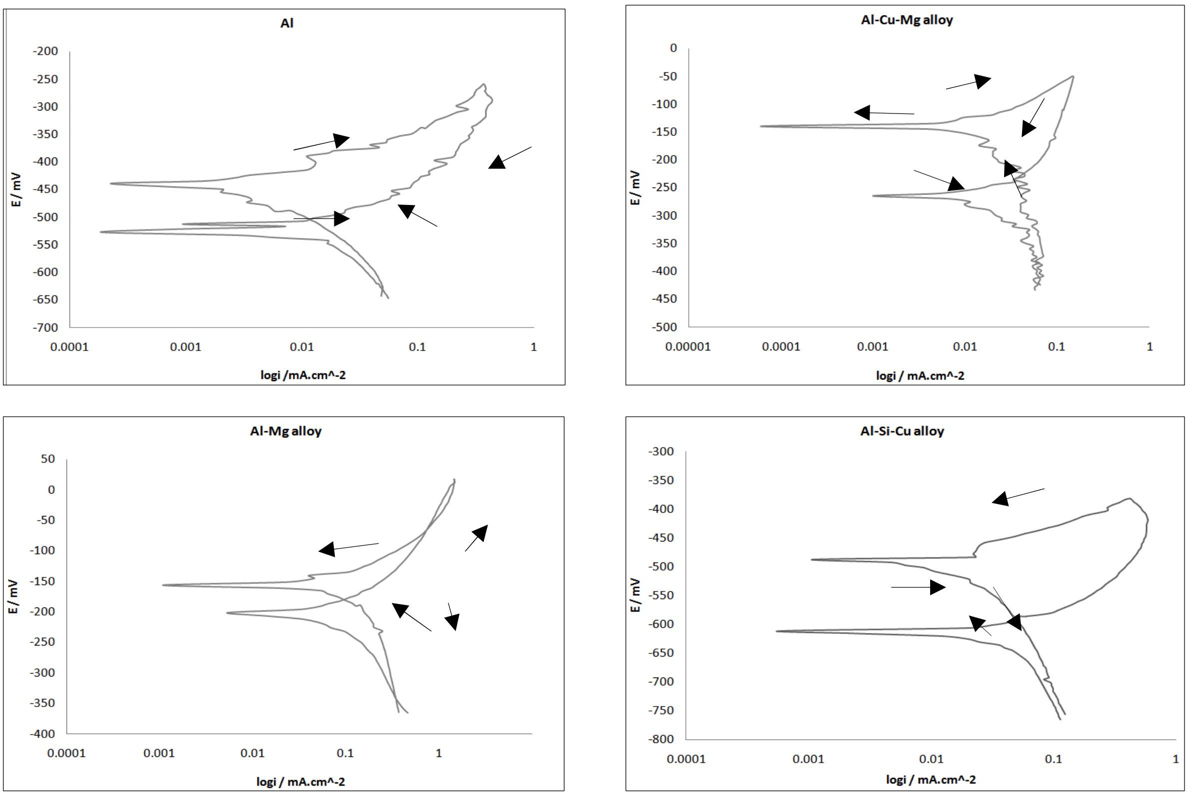

Fig. 2. Cyclic polarization for Al and its alloys in condensed synthetic automotive solution.

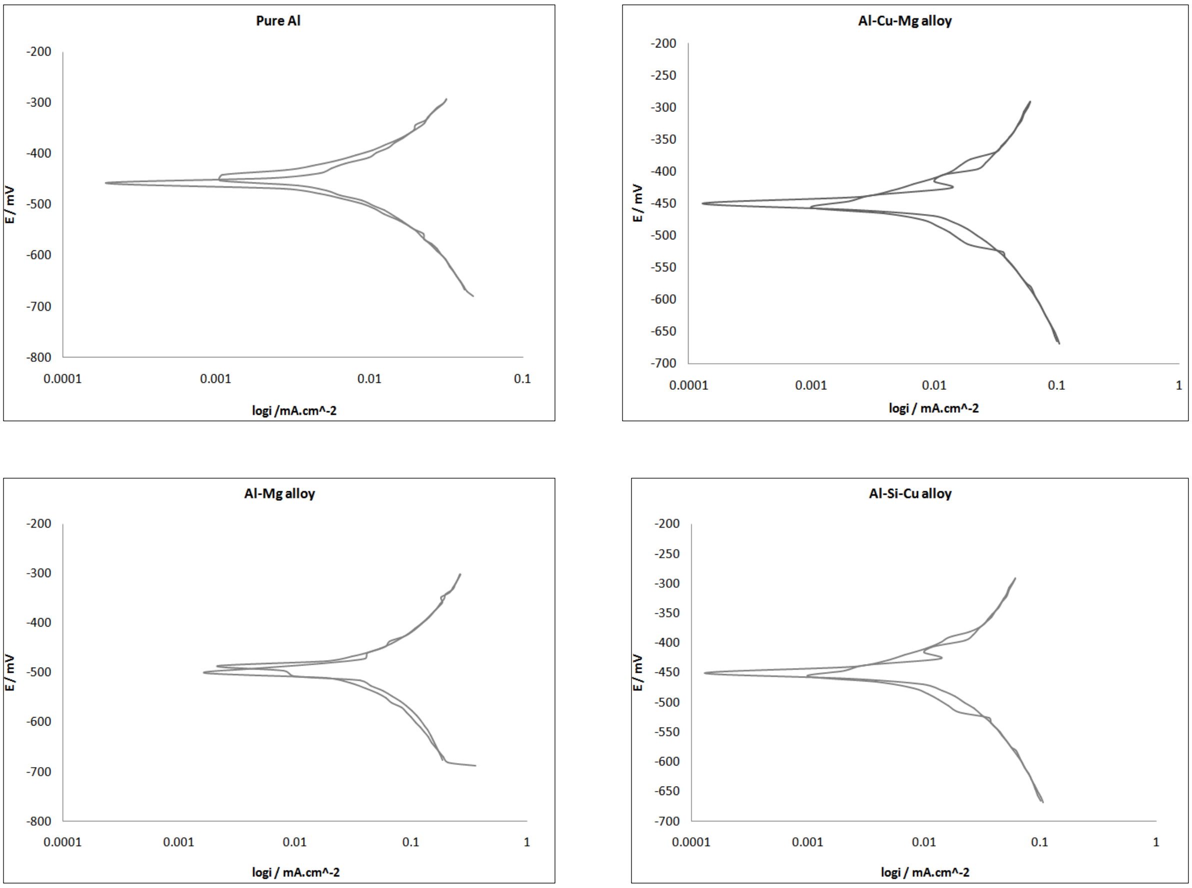

Fig. 3. Cyclic polarization for Al and its alloys in condensed synthetic automotive solution in the presence of IATO.

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التأثير ألتآكلي للمحلول المكثف الصناعي المحتوي على خليط مكونات عضوية مختارة على سبائك الألمنيوم

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الخلاصة

يتضمن العمل دراسة تأثير إضافة مزيج بعض المركبات العضوية على السلوك ألتآكلي للألمنيوم النقي وسبائكه في المحلول المكثف الصناعي (CSAS) في درجة حرارة الغرفة. يُظهر الخليط في دراسة سابقة زيادة في عدد الاوكتان وفي هذه الدراسة يُظهر زيادة في مقاومة التآكل من خلال النقص في قيم سرعة التآكل .

القياسات الكهروكيميائية تم أجراؤها باستعمال المجهاد الساكن عند ٣ ملي فولت لكل ثانية لتخمين معطيات التآكل بطريقة تافل الاستقرائية، بالإضافة إلى اختبار المنحنى الحلقي لمعرفة تأثر المادة بالتنقر في وسط الاختبار.

الزيادة في ميل تافل الكاثودي (b_c) بعد إضافة مزيج المكونات العضوية. ولكن ميول تافل الانودية (b_a) تفاوتت بعد إضافة الخليط. إن الزيادة في ميل تافل الكاثودي يدل على وجود غشاء على سطح مادة الاختبار، والتي هي أقل نفاذا ويمكن أن تعرقل تفاعل انحلال المعدن ولكنها ماتزال تسمح بحدوث التفاعل الكهروكيميائي . هذا السلوك يمكن أن ينجز بوساطة الكثافة الالكترونية على ذرات الأوكسجين والنتروجين في خليط المكون العضوي.