Effect of Oxygenated Additives on the Corrosion Behavior of Al-Si-Cu Alloy in Synthetic Condensed Automotive Solution

**Rana A. Majed, Abdulmajeed, Slafa I. Ibrahim* and
Hawraa Deaa Al-Deen**

University of Technology, Materials Engineering Department and

** University of Technology, Energy and Fuel Research Center, Iraq*

Abstract. This work involves studying the effect of adding alcohols on corrosion behavior of Al-Si-Cu alloy in synthetic condensed automotive solution (CSAS) at room temperature. Alcohols used were methanol (MeOH), ethanol (EtOH), propanol (PropOH), Butanol (ButOH), and mixture of (MeOH-EtOH), (MeOH-PropOH) and (MeOH-ButOH).

According to potentiodynamic polarization test, the results of corrosion resistance indicate that additive alcohols increase the resistance of Al-Si-Cu alloy, except addition of ethanol to the CSAS and the resistance follows the sequence: *MeOH. > ButOH > MeOH-ButOH > MeOH-PropOH > PropOH > MeOH-EtOH*. Cyclic polarization measurements were carried out to estimate the pitting resistance of Al-Si-Cu alloy in CSAS in the absence and presence of alcohols, this test shows that the hysteresis loop appears only in cases of presence of ethanol and (MeOH-EtOH) mixture in CSAS indicating the disadvantage of adding ethanol and (MeOH-EtOH) mixture to automotive fuel.

Keywords: Corrosion of Al-Si-Cu alloy, Oxygenated additives, Potentiostatic measurements.

1. Introduction

Gasoline is not a single substance. It is a complex mixture of components which vary widely in their physical and chemical properties. Gasoline should cover a wide range of operating conditions, such as variations in fuel systems, engine temperatures, fuel pumps and fuel pressure.

Although not specifically included in ASTM standards, a variety of specially formulated additives are added to gasoline to enhance fuel quality and performance, and to maintain fuel standards during distribution^[1].

Gasoline additives include anti-icers to provide protection against fuel line freeze up; fluidizer oils used in conjunction with deposit control additives to control intake valve deposits; corrosion inhibitors to minimize fuel system corrosion; anti-oxidants to minimize gum formation while gasoline is in storage.

In some cases metal deactivators are utilized to minimize the effect of metal based components sometimes present in gasoline. Alcohols add to enhance the octane number such as methanol, ethanol, iso-propanol, tertiary butanol.....*etc*, but if the alcohol inducted into an automobile's cylinder is not sufficiently vaporized, the liquid fraction of the alcohol (ethanol or methanol) can act as a solvent for its combustion products. These products are corrosive (including formic acid; for example), degrading the lubricants and greatly increasing wear on cylinder walls^[2].

A few of literatures were available regarding corrosion of nonautomotive engine fuel systems using ethanol-blended fuels. Limited confidence is gained by the fact that the majority of engine manufacturers currently allow the use of 10% ethanol gasoline fuel blends. Some manufacturers report corrosion of metallic fuel system components when gasoline oxygenated with alcohol was used in older engines. Apart from prolonged storage, this does not appear to be a concern with late model engines. These corrosion problems may be aggravated by phase separation, where the alcohol-water phase tends to be more corrosive than the alcohol gasoline blend^[3]. Johnson^[4] also suggests corrosion is aggravated by the occurrence of phase separation of ethanol gasoline blend fuels. Metals at risk of corrosion by ethanol-blended fuels are: steel; zinc diecastings and aluminium fuels system components. The addition of ethanol to gasoline accelerates the corrosion of steel due to the increased water content and presence of organic acids^[5].

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^[6] and fuel pumps^[7]. Hamilta and co-workers^[8] studied corrosion performance of Al-Si-Cu alloys in a synthetic condensed automotive solution, while other works^[9,10] in alcoholic fuels. Nie *et al.*^[11] studied

corrosion behavior of metallic materials in Ethanol-Gasoline alternative fuels. Eiman and Jehad^[12] studied the relative performance of compression ignition engine using various blends of diesel – ethanol fuels. Alessandra Regina Pepe Ambrozin *et al.*^[13] 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.

The goals of this work is to study the effect of adding alcohols on corrosion behavior of Al-Si-Cu alloy in synthetic condensed automotive solution at room temperature to reduce corrosion problems in addition to improve the octane number.

2. Material and Chemicals

Specimens of Al-Si-Cu alloy were polished to mirror finish, degreased with acetone and rinsed with distilled water. The specimens were then insulated with hot mounting leaving (2.27 cm²) area exposed to electrolyte. The chemical analysis of experimental alloy is shown in Table 1 which achieved in the chemistry Laboratory.

An electrolyte of condensed synthetic automotive solution^[8](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)] was used in this study, these salts obtained from BDH Chemical Ltd. The pH of this solution was 3.3. Alcohols were added to studying effect of oxygenated additives with 10.7 vol.%^[14].

Table 1. Chemical composition of Al-Si-Cu alloy.

Element	Si	Cu	Mg	Fe	Zn	Ni	Mn	Ti	Cr	Al
Wt%	12.587	3.563	1.168	0.857	0.683	0.513	0.335	0.070	0.049	Bal.

2.1 Electrochemical Cell

The electrochemical standard cell used in this work was locally fabricated according to the ASTM standard G5-94^[15] with provision for working electrode (Al-Si-Cu alloy), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with an SCE reference electrode.

2.2 Instruments

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 $3 \text{ mV} \cdot \text{sec}^{-1}$. Polarization experiments were started when the rate at which open circuit potential (E_{ocp}) changed was less and more 200 mV , *i.e.* from -800 mV to -300 mV . 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 slopes by Tafel extrapolation method. From the values of Tafel slopes and corrosion current density, the polarization resistances values can be calculate according to Stern-Geary equation, while experimental parameters for cyclic polarizations were obtained directly from SCI electrochemical software of potentiostat.

3. Results and Discussion

As a result, the electrochemical reactions at this interface vary with time. Figure 1 shows the open circuit potential – time measurements for Al-Si-Cu alloy in CSAS in absence and presence of alcohols. The data of open circuit potential (E_{oc}) that listed in the Table 2 indicate that addition of alcohols shift E_{oc} toward active direction, except in the presence of methanol, this means that there are some reactions can occur between the solution and alcohols until equilibrium can take place.

Fig. 1. Variation of potentials with time for Al-Si-Cu alloy in CSAS in the absence and presence of alcohols.

Table 2. Corrosion parameters of Al-Si-Cu alloy in synthetic condensed automotive solution in presence of different alcohols at room temperature.

Medium	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)
				-b _c	+b _a	
CSAS	585	487.6	35.48	351.1	42.4	0.4636
CSAS(MeOH)	582	481.2	11.50	220.9	53.8	1.6357
CSAS(EthOH)	597	467.3	24.13	42.5	45.8	0.3972
CSAS(PropOH)	608	600.5	26.65	99.4	97.5	0.8030
CSAS(ButOH)	604	550.6	11.74	122.3	64.0	1.5560
CSAS(MeOH+EthOH)	632	621.7	33.78	109.9	93.0	0.6484
CSAS(MeOH+PropOH)	604	607.0	32.46	118.5	124.1	0.8119
CSAS(MeOH+ButOH)	607	519.1	10.81	112.9	29.8	0.9483

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, 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^[16].

The potentiodynamic polarization curves for Al-Si-Cu alloy in the absence and presence of alcohols are shown in Fig. 2 to 9. 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:

While the upper section represents the anodic reaction where the oxidation of alloy can occur according to the following reaction:

Moreover, the active dissolution of aluminium (matrix) can be also partly balanced by the following reaction^[17]:

Due to the low pH (3.3) of the test solution, the oxygen reduction reaction is not expected to contribute to the overall cathodic reaction rate^[8]:

This reaction is controlled by oxygen diffusion to the metallic interface.

Fig. 2. Potentiodynamic polarization of Al-Si-Cu alloy in condensed synthetic automotive fuel (CSAS) at room temperature.

Fig. 3. Potentiodynamic polarization of Al-Si-Cu alloy in CSAS in presence of methanol at room temperature.

The corrosion parameters listed in Table 2 show that addition of methanol and ethanol alcohol shift corrosion potentials (E_{corr}) toward noble direction, while other alcohols (propanol, butanol, methanol-ethanol, methanol-propanol and methanol-butanol) shift E_{corr} toward active direction. All additive alcohols shift corrosion current density (i_{corr}) value to lower values.

The Tafel slopes were very much influenced in the presence of alcohols. The cathodic Tafel slope (b_c) was decreased after adding alcohols. But the anodic Tafel slopes (b_a) were increased in the presence of alcohols except in case addition of methanol-butanol mixture and have values lowers than those of cathodic Tafel slopes except in the case of addition of ethanol and (methanol-propanol) mixture. It is inferred that the rate of change of current with change of potential was smaller during anodic polarization than that during cathodic polarization.

Fig. 4. Potentiodynamic polarization of Al-Si-Cu alloy in CSAS in presence of ethanol at room temperature.

Fig. 5. Potentiodynamic polarization of Al-Si-Cu alloy in CSAS in presence of propanol at room temperature.

Fig. 6. Potentiodynamic polarization of Al-Si-Cu alloy in CSAS in presence of butanol at room temperature.

Fig. 7. Potentiodynamic polarization of Al-Si-Cu alloy in CSAS in presence of methanol-ethanol mixture at room temperature.

Fig. 8. Potentiodynamic polarization of Al-Si-Cu alloy in CSAS in presence of methanol-propanol mixture at room temperature.

Fig. 9. Potentiodynamic polarization of Al-Si-Cu alloy in CSAS in presence of methanol-butanol mixture at room temperature.

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^[10,18]. It is known that the surface oxide on Al alloys permits the movement of ionic species and an electron or vacancy flux across it^[10,18].

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^[11] 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.

The values of R_p are presented in Table 2. These data indicate that the polarization resistance value increases in presence of alcohols except in the case of addition ethanol to CSAS. The increasing of polarization resistance in the presence of alcohols follows the following sequence:

R_p in the presence of $\text{MeOH} > \text{ButOH} > \text{MeOH-ButOH} > \text{MeOH-PropOH} > \text{PropOH} > \text{MeOH-EthOH}$

Cyclic polarization data were recorded by M Lab electrochemical laboratory system with electrochemistry software. 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.

The breakdown potential (E_{br}) is the one at which the anodic current increases considerably with applied potential. The potential, at which the hysteresis loop is completed upon reverse polarization scan, is known as the protective potential or repassivation potential.

Breakdown potential is a sign of local corrosion but the measure of pitting susceptibility is the difference between the breakdown potential and the repassivation one. The protection potential represents the potential at the intersection of hysteresis curve with passive domain. Below this potential the propagation of existing localized corrosion will not occur.

If the difference between breakdown and the repassivation potential is increasing, the chance in the appearance of pitting is greater and its propagation in depth is more intense.

In other words, the hysteresis loop increases as the susceptibility of material to corrosion increases. Figures 10 to 17 show the cyclic polarization of Al-Si-Cu alloy in CSAS in the absence and presence of alcohols. These figures indicate that the potentials for the reverse scan curves are more positive than those for the forward scan as shown in Table 3. These results show that a stable oxide film is formed during the forward scan. Also the hysteresis loop appears only in cases of presence ethanol and (MeOH-EtOH) mixture in CSAS indicating the disadvantage of adding ethanol and (MeOH-EtOH) mixture to automotive fuel.

Fig. 10. Cyclic polarization of Al-Si-Cu alloy in (CSAS) at room temperature.

Fig. 11. Cyclic polarization of Al-Si-Cu alloy in CSAS in presence of methanol at room temperature.

Fig. 12. Cyclic polarization of Al-Si-Cu alloy in CSAS in presence of ethanol at room temperature.

Fig. 13. Cyclic polarization of Al-Si-Cu alloy in CSAS in presence of propanol at room temperature.

Fig. 14. Cyclic polarization of Al-Si-Cu alloy in CSAS in presence of butanol at room temperature.

Fig. 15. Cyclic polarization of Al-Si-Cu alloy in CSAS in presence of methanol-ethanol mixture at room temperature.

Fig. 16. Cyclic polarization of Al-Si-Cu alloy in CSAS in presence of methanol-propanol mixture at room temperature.

Fig. 17. Cyclic polarization of Al-Si-Cu alloy in CSAS in presence of methanol-butanol mixture at room temperature.

Table 3. Data of cyclic polarization of of Al-Si-Cu alloy in condensed synthetic automotive solution in presence of different alcohols at room temperature.

Medium	Forward potential (-E _{for} /mV)	Reverse potential (-E _{rev} /mV)	Pitting potential (-E _{pit} /mV)
CSAS	638.0	490.3	-
CSAS(MeOH)	611.0	488.2	-
CSAS(EthOH)	480.9	453.0	436
CSAS(PropOH)	616.9	603.9	-
CSAS(ButOH)	669.0	564.7	-
CSAS(MeOH+EthOH)	639.5	636.1	569.0
CSAS(MeOH+PropOH)	632.9	620.0	-
CSAS(MeOH+ButOH)	679.3	507.6	-

3. Conclusions

1- From corrosion parameters of Al-Si-Cu alloy in CSAS in the absence and presence of many alcohols, it can be seen that adding alcohols decrease corrosion current density (i_{corr}) values.

2- Improvement of the polarization resistance of Al-Si-Cu alloy by addition of alcohols to automotive fuel. They have the following sequence of polarization resistance:

Meth. > *But.* > *Meth.-But.* > *Meth.-Prop.* > *Prop.* > *Meth.-Eth.*

4- Cyclic polarization test shows that a stable oxide film is formed during the forward scan; also the hysteresis loop appears only in cases of presence of ethanol alone and (MeOH-EtOH) mixture in CSAS.

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تأثير المضافات الأوكسجينية على السلوك التآكلي لسبيكة ألومنيوم - سليكون - نحاس في محلول وقود المركبات المكثف الصناعي

رنا عفيف مجيد، و ماجد حميد عبد المجيد، و سلافة إسماعيل إبراهيم*،

و حوراء ضياء الدين

الجامعة التكنولوجية - قسم هندسة المواد،

و* الجامعة التكنولوجية - مركز بحوث الطاقة والوقود، بغداد - العراق

المستخلص. يتضمن هذا البحث دراسة تأثير إضافة الكحولات على السلوك التآكلي لسبيكة ألومنيوم - سليكون - نحاس في محلول مكثف وقود المركبات الصناعي عند درجة حرارة الغرفة. تضمنت الكحولات كلا من الميثانول والإيثانول والبروبانول والبيوتانول ومزيج الميثانول - إيثانول والميثانول - بروبانول والميثانول - بيوتانول. أجري فحص التآكل بجهاز المجهاد الساكن عند معدل سرعة ٣ ملي فولت لكل ثانية في المحاليل المذكورة لتقدير متغيرات التآكل كجهد التآكل وكثافة تيار التآكل وميول تافل الكاثودية والأنودية. بالإضافة الى حساب مقاومة الاستقطاب للسبيكة المدروسة. وقد أظهرت نتائج مقاومة الاستقطاب بأن إضافة الكحولات المدروسة تزيد من مقاومة التآكل باستثناء إضافة الإيثانول وأن زيادة المقاومة تتبع التسلسل التالي: ميثانول < بيوتانول < (ميثانول - بيوتانول) < (ميثانول - بروبانول) < بروبانول < (ميثانول - إيثانول). أجريت قياسات الاستقطاب الحلقي لتقييم مقاومة سبيكة ألومنيوم - سليكون - نحاس للتآكل في محلول مكثف الوقود بغياب ووجود الكحولات المدروسة، وقد أظهرت النتائج بأن المنحنى الأنشوطي يظهر فقط في حالتي وجود

الإيثانول ومزيج (ميثانول - إيثانول) في محلول الوقود، مما يبين الضرر
الناجم عن إضافة الإيثانول ومزيجه مع الميثانول إلى وقود المركبات.