An evaluation of the anticorrosion effect of ethylene glycol for AA7075-T6 alloy in 3.5% NaCl solution

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ABSTRACT

The corrosion behaviour of AA7075-T6 aluminum alloy in 3.5% NaCl devoid of and containing various amounts of ethylene glycol (EG) has been examined by DEIS (dynamic electrochemical spectroscopy), PDP (Potentiodynamic polarization), SEM (scanning electron microscope), EDAX (energy dispersive X-ray spectroscopy), and AFM (atomic force microscope). AA7075-T6 alloy specimen corroded significantly in 3.5% NaCl solution. In 3.5% NaCl containing EG, the alloy is protected but the extent of protection is a function of immersion duration and concentration of EG. EG affects both the anodic and cathodic corrosion reactions according to PDP results. The adsorption of EG molecules onto AA7075-T6 surface follow Langmuir adsorption isotherm model. The $\Delta G^{\text{ads}}$ value calculated for the adsorption process reveals that physiosorption is the prevailing mechanism. SEM and AFM pictures support the experimental results and EDAX results confirm the presence of EG molecules on AA7075-T6 surface.

1. Introduction

AA7075 is an alloy of aluminum with Zn, Mg, and Cu as the alloying elements. Notable characteristics of this alloy include high strength, excellent ductility, toughness, and high fatigue. Depending on the heat treatment, AA7075 is differentiated into 7075-0, 7075-T6, 7075-T651, 7075-T7, 7075-T73, and 7075-RRA. Compared with other grades, the AA7075-T6 has higher strength and better machinability and thus gains wider application in aerospace, automobile, and construction industries [1]. Nevertheless, the AA7075 alloy is susceptible to different forms of corrosion. Localized [2], pitting [3,4], and intergranular [5,6] forms of corrosion of AA7075 had been reported.

Glycols are organic compounds which have attracted great attention owing to their low volatility and viscosity, good electrical conductivity and heat transfer capacity, remarkable hydrophobicity and miscibility with polar solvents, as well as low cost [7]. They are used as an anti-freezing, dehydrating, and cooling agent as well as chemical intermediate [8]. They also gain application as heat transfer fluid and as solvent [8]. Ethylene glycol (EG), a colourless, odourless, and sweet tasting syrup is the second member of this family and is deemed most essential [7] because of its moderate toxicity compared to others. One of its uses is as a coolant in engines [9,10]. It is known that engine coolants are often contaminated by chlorides and as acid products of EG-water solution (glycolic, formic, acetic, and oxalic acids) on the corrosion pattern of low carbon steel. The authors noted that the nature and relative proportion of the carboxylic acids detect the level of deterioration of the metal in the studied environment. Khomami et al. [11] examined the effect of rotating speed on the electrochemical properties of steel alloy specimen in EG-water solutions and concluded that the corrosion rate of the specimen was not significantly changed by rotating speed. Most recently, Medhashere and Shetty [9] assessed the corrosion of Mg-Al-Zn-Mn alloy in EG-water solution enriched with chloride ions. They documented that the corrosion rate of the alloy varied directly with the amount of chloride ions and system temperature.

In this work, we deploy dynamic electrochemical spectroscopy (DEIS) to track the changes in the electrochemical properties of AA7075-T6 alloy in 3.5% NaCl solution free from and enriched with different amounts of EG with time. The DEIS which is an optimized method for impedance studies of corrosion processes in galvanostatic-time domain mode is best suited for corrosion and corrosion inhibition measurements because; corrosion process is dynamic in nature [12].
The PDP curves of this alloy in the NaCl-EG solutions have also been obtained. Surface examination of the exposed alloy is achieved using SEM and EDAX respectively.

2. Experimental

2.1. Specimens and medium

The alloy specimens utilized in the investigation were made from AA7075-T6 aluminum alloy sheet which was supplied by Erdemir Steel Co., Turkey. The alloy has the chemical composition given in Table 1. The medium studied was 3.5% NaCl solution prepared from analytical grade NaCl pellets. The concentrations of ethylene glycol added to the corrosive medium were 10%, 20%, 30%, 40%, and 50%. Distilled water was used in all preparations. The EG and other chemicals used in the study were of AR and were used as procured.

2.2. DEIS measurements

This set of experiments were performed utilizing a National Instrument Ltd PCI-4461 digital-analog card. This card was equally used in recording the current and voltage perturbation of the investigated environment. Fig. 1 shows a generalized form of the DEIS set-up. All experiments were undertaken under galvanostatic condition achieved using an Autolab HGMEM-01 equipment. This equipment also serve as a current-voltage converter. A package of about 20 elementary current sinusoids was the source of perturbation signal. The frequency range of perturbation was 4.5 kHz to 300 mHz and the perturbation amplitude of 10 mV was utilized through out the measurements. A more detailed information on the use of DEIS under galvanostatic condition can be found in Slepski et al. [12]. The obtained DEIS spectra were analyzed using a ZsimpWin 3.21 software.

2.3. PDP measurements

An application software DC105 embedded in a Gamry instrument potentiostat/galvanostat/ZRA (Reference 600) was used for PDP experiments. The electrochemical assembly is a tri-electrode type with a silver/silver chloride glass as the reference electrode, a platinum mesh as the counter electrode and the AA7075-T6 specimen as the working electrode. Before the AA7075-T6 sample was used as the working electrode, it was subjected to mechanical abrasion. Emery papers of various grades (600, 800, 1500 and 2000) were used in the abrasion process. The abraded sample was washed in running water and ethanol and then dried in acetone in order to remove the dust generated from the abrasion. The working electrode was scanned starting from the cathodic direction to anodic direction at a rate of 1 mV/s in the potential range of $-250$ to $+250$ mV relative to corrosion potential ($E_{corr}$). To obtain the electrochemical polarization parameters, the PDP curves were extrapolated as described by Hefni et al. [13].

2.4. SEM and EDAX characterization

After DEIS experiments, the AA7075-T6 samples were submitted for SEM and EDAX analysis. Before the submission, the retrieved specimens were allowed to dry at ordinary temperature. The surface analysis was done on a Quanta FEG 250 scanning electron microscope (FEI, The

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn</th>
<th>Mg</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA7075-T6</td>
<td>5.81</td>
<td>2.55</td>
<td>0.21</td>
<td>0.008</td>
<td>1.67</td>
<td>89.752</td>
</tr>
</tbody>
</table>

The general view of DEIS setup.
Fig. 2. DEIS spectra of AA7075-T6 aluminum alloy recorded in 3.5% NaCl solution (a) without and with (b) 10%, (c) 20%, (d) 30%, (e) 40%, and (f) 50% ethylene glycol for 6 h at 25°C.
Netherlands) coupled with a probe for elemental composition measurement.

3. Results and discussion

3.1. DEIS studies

Instantaneous corrosion progress on a metal surface in a changing environment can be accurately track using DEIS. Fig. 2 shows the DEIS spectra recorded for AA7075-T6 alloy specimen immersed in 3.5% NaCl solution free of and enriched with various amounts of EG for 6 h at ordinary temperature. Notable features of the spectra are: (i) in all cases, the spectra are semi-circular in shape indicating that the corrosion of the metal substrate in the studied environment is controlled by charge transfer [14]; (ii) the semi-circular is continuous spanning the time of measurement. This means that the metal sample will corrode as long as it remains in the investigated environment. (iii) The semicircles are not perfect. The imperfectness usually referred to as ‘frequency dispersion phenomenon’ [15,16] could arise due to the heterogenous nature of the working electrode surface. (iv) At point of introduction of EG into the corrosive solution (2 h), there is a disconnection and the size of the semicircle becomes bigger (Fig. 2b-f). This may mean stiff resistance to the flow of electron on the specimen surface which can be caused by the adsorption of EG molecules onto the surface. (v) The increase in the size of the semicircular graph is concentration dependent suggesting larger surface coverage by hydrophobic film formed by EG. (vi) It appears from close inspection that size of the spectra in Fig. 2b-f is directly proportional to immersion time. This could be possible if more of EG molecules are adsorbed on the AA7075-T6 surface as time elapses and also if the adsorbed film is more stable at longer time.

To better understand the changes in the charge transfer resistance ($R_{ct}$) on the metal surface as time of immersion progresses, a plot of $R_{ct}$ against immersion time (t) is made (Fig. 3). It is interesting to see from the figure that $R_{ct}$ graph for the metal in NaCl solution without EG first increases and reaches a peak at about 2500 s. At about 7200 s the $R_{ct}$ graph assumes a steady plateau. This seems to reflect the protective tendency of the oxide layer on the Al alloy surface. Al is known to exhibit some form of resistance to corrosion [17–19]. However, this oxide layer may have been broken down as time prolonged resulting in the observed decline and steady plateau observed in the graph. Compared with the graphs representing the NaCl-EG systems, one could visibly see significant improvement on the charge transfer resistance of the metal surface occasioned by the presence of EG. The effect, as could be seen in Fig. 3 is a direct function of EG concentration and immersion time. It is obvious from this figure that EG in NaCl solution, particularly the higher concentration offered stiff opposition to the transfer of charge from the alloy surface.

To provide quantitative information on the corrosion of AA7075-T6 in the investigated environment and the extent of inhibition by EG, the DEIS spectra were analyzed utilizing $R_{ct}(Q_R_{dl})$ equivalent circuit (Fig. 4). $R_s$ denotes the solution resistance, $R_{ct}$ charge transfer resistance while Q represents the constant phase element. $Q$ is defined in impedance representation as:

$$Z_{CPE} = Y_0^{-1}((j\omega)^{-n}) \tag{1}$$

where $Y_0$ is the Q constant, $\omega$ is the angular frequency (in rad s$^{-1}$), $P = -1$ is the imaginary number and $n$ is a Q exponent. The choice of this equivalent circuit was necessitated by the low chi square values and percentage error which did not exceed 5% throughout the analysis. The quantitative information obtained from the analysis are presented in Table 2. The double-layer capacitance ($C_{dl}$) also given in Table 2 was calculated using Eq. (2) [20].

$$C_{dl} = (Y_0^{-1}R_{ct}^{-1-n})/n \tag{2}$$

As clearly seen in the table, the solution resistance ($R_s$) and the $R_{ct}$ values for the blank are smaller than those of the EG containing systems while the reverse is noted for the $C_{dl}$ value. Increase in the amount of EG is seen to further increase in increase in the $R_s$ and $R_{ct}$ values and a decline in the $C_{dl}$ value. For instance, the $R_s$ and $R_{ct}$ values for the NaCl solution devoid of EG are 8.782 $\Omega$ cm$^2$ and 5655 $\Omega$ cm$^2$ respectively while the $C_{dl}$ value is 1.781 $\mu$F cm$^2$. When 10% EG was added to the considered aggressive solution, the $R_s$ and $R_{ct}$ values increased to 9.78 $\Omega$ cm$^2$ and 8664 $\Omega$ cm$^2$ respectively while the $C_{dl}$ value decreased to 1.095 $\mu$F cm$^2$. By increasing the concentration of EG to 50%, the $R_s$ and $R_{ct}$ values further increase to 14.86 $\Omega$ cm$^2$ and 18,540 $\Omega$ cm$^2$ respectively and the $C_{dl}$ value declined to 0.319 $\mu$F cm$^2$. This clearly shows that EG can act as inhibitor in chloride containing environment.

The decline in $C_{dl}$ value with increasing EG amount is in perfect conformity with the Helmholtz equation written as [21,22]:

$$\delta_{dl} = \frac{\varepsilon_0 \varepsilon A}{C_{dl}} \tag{3}$$

where $\delta_{dl}$ = thickness of adsorbed layer, $\varepsilon_0$ = permittivity of air, $\varepsilon$ = local dielectric constant, and A = surface area of electrode.

The percentage protection ability (%IP) of EG in the studied environment was computed using Eq. (4):

$$\%IP = \left(1 - \frac{R_{ct}^0}{R_{ct}}\right) \times 100 \tag{4}$$

where $R_{ct}^0$ is the charge transfer resistance in the absence of EG and $R_{ct}$ is the charge transfer resistance in the presence of EG. The values as presented in Table 2 are in perfect agreement with the qualitative results (Figs. 2 and 3) revealing that the inhibiting efficacy of EG is determined by the concentration used. The highest studied concentration (50%) of EG can protect AA7075-T6 surface in 3.5% NaCl solution by
was rougher in NaCl-EG solutions than in NaCl solution[23]. Adsorption of EG molecules onto the alloy surface could give rise to the observation.

3.2. PDP studies

Table 2
Dynamic electrochemical impedance parameters for AA7075-T6 alloy in 3.5% NaCl solution in the absence and presence of EG at 25 °C.

<table>
<thead>
<tr>
<th>System/concentration</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$Q$</th>
<th>$n$</th>
<th>$R_h$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (µF cm$^2$)</th>
<th>%IP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8.78</td>
<td>0.309</td>
<td>0.81</td>
<td>5655</td>
<td>1.781</td>
<td>70%</td>
</tr>
<tr>
<td>3.5% NaCl + 10% EG</td>
<td>9.78</td>
<td>0.253</td>
<td>0.84</td>
<td>8664</td>
<td>1.095</td>
<td>35</td>
</tr>
<tr>
<td>3.5% NaCl + 20% EG</td>
<td>10.17</td>
<td>0.185</td>
<td>0.85</td>
<td>12420</td>
<td>0.725</td>
<td>54</td>
</tr>
<tr>
<td>3.5% NaCl + 30% EG</td>
<td>10.98</td>
<td>0.161</td>
<td>0.86</td>
<td>14600</td>
<td>0.570</td>
<td>61</td>
</tr>
<tr>
<td>3.5% NaCl + 40% EG</td>
<td>11.97</td>
<td>0.131</td>
<td>0.88</td>
<td>16030</td>
<td>0.372</td>
<td>65</td>
</tr>
<tr>
<td>3.5% NaCl + 50% EG</td>
<td>14.86</td>
<td>0.103</td>
<td>0.87</td>
<td>18540</td>
<td>0.319</td>
<td>70</td>
</tr>
</tbody>
</table>

Also given in Table 2 is the derived values for the parameter $n$. The parameter is often used as a gauge on the degree of roughness of the working electrode [15] and also the nature of the interface [21]. In our case, $n$ value is in the range of 0.81–0.87. This value reflects a capacitive interface [15,21].

All the obtained electrochemical polarization parameters are listed in Table 3. An inspection of the PDP graph obtained for AA7075-T6 in the free 3.5% NaCl solution reveals that the anodic branch exhibit long passive region. It is accepted that oxide film on Al surface formed following Eqs. (6) & (7) offer some degree of protection against corrosion [24–26].

$$
\text{Al}^3+ + 3\text{OH}^- \rightarrow \text{Al(OH)}_3_{\text{ads}} + 3\text{e}^- \\
2\text{Al(OH)}_3_{\text{ads}} \rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}
$$

However, in aggressive environment such as the one considered in this investigation, the oxide layer will be broken down and the bare metal surface attack by corrosive ions. In NaCl environment, the bare Al surface will undergo the following deterioration reactions [24,25]:

$$
\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^- \\
\text{Al}^{3+} + 3\text{Cl}^- \rightarrow \text{AlCl}_4^-
$$

Correspondingly, the reactions in Eqs. (10) and (11) will proceed at the cathodic side [25,27]:

$$
1/2\text{O}_2 + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^-_{\text{ads}} + \text{OH}^+ \\
\text{OH}^-_{\text{ads}} + \text{e}^- \rightarrow \text{OH}^-
$$

Interaction of adsorbed Cl$^-$ ions with Al$^{3+}$ in the oxide lattice forming oxychloride complex (Eq. (12)) had also been reported [24,27].

$$
\text{Al}^{3+} + 2\text{Cl}^- + 2\text{OH}^- \rightarrow \text{Al(OH)}_2\text{Cl}_3
$$

It is noted in Fig. 5 that the presence of EG in NaCl solution interrupted both the anodic and cathodic reactions but the principal effect seems to be on the cathodic reactions. For instance, the presence of 50% EG in the studied solution caused a marked decline in $\beta_c$ value of the blank from 315 mV/Dec to 198 mV/Dec but only shifted the anodic slope value by 4 points (22 mV/Dec to 18 mV/Dec). In the system, EG is reduced thus [28]:

$$
\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}} + \text{e}^- \rightarrow \text{OHCH}_2\text{CH}_2\text{OH}^- + \text{H}^+
$$

Our results suggest that Eq. (13) is preferred over Eqs. (10) and (11). The OHCH$_2$CH$_2$O$^-$ anions can also interrupt the formation of Al (OH)$_3_{\text{ads}}$ (Eq. (6)) as shown in Eq. (14) and by so doing protect the alloy surface against corrosive attack.

$$
\text{Al}^{3+} + 3\text{OHCH}_2\text{CH}_2\text{O}^- \rightarrow \text{Al(OHCH}_2\text{CH}_2\text{O)}_3
$$

This inhibition which is found to depend on the concentration of EG used is reflected in the reduction of corrosion current and displacement.
of $E_{corr}$ toward more nobler position relative to the blank (Table 3). The highest protection efficiency achieved by 50% EG from this technique is 76%.

3.3. Surface assessments

3.3.1. SEM and EDAX investigations

Fig. 6 displays the SEM pictures and EDAX spectra obtained for AA7075-T6 aluminum alloy in (a, b) abraded state, (c, d) exposed to 3.5% NaCl solution, and (e, f) exposed to 3.5% NaCl solution containing 50% EG after 6 h of immersion at 25 °C.

EDAX studies are inserted in the EDAX diagrams. The surface in Fig. 6(a) is well abraded giving rise to a very intensified Al peak in Fig. 6(b). The weight percentage of the Al peak is 88.94% (inserted table in Fig. 6(b)). When this specimen was immersed in 3.5% NaCl solution, it was destroyed due to attack by corrosive ions present in the solution. As could be seen in Fig. 6(c), the surface is covered with corrosion products. The corresponding EDAX spectrum (Fig. 6(d)) reveals that the corrosion products are mainly chlorides and oxides thereby agreeing with Eqs. (9) & (10). From the inserted table in Fig. 6(d), the percentage content of oxygen increased from 1.91% in the abraded surface to 26.04% while the chloride ions content on the surface stands at 24.49%. The information in the table inserted in Fig. 6(f) discloses that, in NaCl + EG solution, adsorbed EG molecules displaces...
chloride ions from the surface and by so doing protect the surface from corrosion. The chloride content on the surface decreased to 4.73% while percentage O increased from 26.04% to 33.93%. The protection occasioned by the adsorption of EG onto the alloy surface is also obvious in the smoother surface in Fig. 6(e) compare to Fig. 6(c). The appearance of C peak in Fig. 6(f) with weight percentage of 0.83% provide experimental evidence to the claim of adsorption of EG onto AA7075-T6 alloy sample.

Fig. 7. 3D and 2D AFM images respectively of AA7075-T6 steel (a, b) unexposed, (c, d) exposed to 3.5% NaCl solution, and (e, f) exposed to 3.5% NaCl solution containing 50% EG for 6 h at 25°C.
3.3.2. AFM investigations

Fig. 7 presents the 3D and 2D AFM photographs respectively for AA7075-T6 steel (a, b) unexposed, (c, d) exposed to 3.5% NaCl solution, and (e, f) exposed to 3.5% NaCl solution containing 50% EG for 6 h at 25 °C. The portions analyzed are shown in the 2D images with red and green lines. Before experiments (Fig. 7a and b), the \( R_a \) (mean of a set of independent measurement of surface peaks and valleys) is between 16.909–20.607 µm while \( R_h \) (the root mean square average of profile height deviations from mean line) stands at 55.760–78.926 µm. These values infer a relatively smooth surface. Upon exposure to 3.5% NaCl solution (Fig. 7c and d), the \( R_a \) and \( R_h \) values increased significantly to 46.241–70.371 µm and 236.950–241.106 µm respectively. As could be seen in Fig. 7c and d, the metal surface is eroded. This agrees with the SEM and experimental results that AA7075-T6 sample was severely damaged in 3.5% NaCl solution. Judging from the \( R_a \) (33.073–46.366 µm) and \( R_h \) (142.460–173.552 µm) values for the surfaces in Fig. 7(e) and (f), the alloy surface was protected against corrosion in 3.5% NaCl + 50% EG environment.

4. Adsorption investigations

The results from the applied techniques suggest the adsorption of EG molecules on AA7075-T6 surface. There are, however two ways in which organic inhibitor molecules can be adsorbed on a metal surface. The physisorption and chemisorption modes. In physical adsorption, the inhibitor molecules and the metal go into covalent or coordinate bonding [29]. Interestingly, this two modes are fitted into adsorption isotherms in order to select the isotherm that best describe the adsorption of inhibitor on a substrate surface. The linear regression coefficient \( R^2 \) is used as a gauge and in literature [21,23,29,30], isotherm plot with \( R^2 \) value in the range of 0.900–1.00 is regarded as giving a good fit to experimental data. In our case, the best fit was obtained with Langmuir adsorption isotherm (Fig. 8). The general form of Langmuir isotherm model is given in Eq. (15) [26].

\[
\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}
\]  

(15)

where \( C_{inh} \) is the amount of EG, \( \theta \) is the surface coverage, and \( K_{ads} \) is the equilibrium constant of adsorption-desorption process. The Langmuir adsorption model assumes monolayer adsorption of inhibitor molecules and non interaction of adsorbed inhibitor molecules with each other [31]. By the assumption of non interplay between adsorbed species, the slope of \( C_{inh}/\theta \) versus \( C_{inh} \) should be unity. In Fig. 8, the slope is slightly bigger than one and thus undermine the requirement of Langmuir model. Authors [31–33] have established that bulky molecules adsorbed on metal surface interact with each other. Adsorbed EG molecules may have interacted with each other resulting in the observed slight deviation of the slope from unity.

From the intercept of the DEIS and PDP linear graphs in Fig. 8, the \( K_{ads} \) value of 3.04 mol\(^{-1}\) and 3.30 mol\(^{-1}\) respectively is derived. The obtained \( K_{ads} \) value is low and signify weak adsorption of EG molecules on AA7075-T6 surface. The \( K_{ads} \) parameter is connected to the standard free energy of adsorption thus [29]:

\[
\Delta G_{ads}^0 = -RT\ln(55.5K_{ads})
\]  

(16)

where \( R \) is the universal gas constant and \( T \) is the absolute temperature. For the investigated system, \( \Delta G_{ads}^0 \) value is \(-7.53 \text{ kJ/mol} \) and \(-8.16 \text{ kJ/mol} \) for DEIS and PDP respectively. The negative sign reflects the possibility of EG molecules adsorption on AA7075-T6 surface. The \( \Delta G_{ads}^0 \) value fall into the category that defines physical adsorption mode. \( \Delta G_{ads}^0 \) value equal to \(-20 \text{ kJ/mol} \) or less indicates physical adsorption mode while value around \(-40 \text{ kJ/mol} \) or more is associated with chemical adsorption [29–31].

5. Conclusion

On the basis of the results of this investigation, the following conclusions are drawn:

1. The corrosion of AA7075-T6 aluminum alloy in 3.5% NaCl solution is controlled by charge transfer;
2. In NaCl + EG system, protective layer formed by adsorbed EG molecules allow corrosion;
3. Adsorbed EG molecules interfere on both the anodic and cathodic corrosion reactions;
4. The adsorption of EG molecules onto AA7075-T6 surface is according to Langmuir adsorption model and the mode of adsorption is physisorption;
5. SEM, EDAX, and AFM results support the claim of EG molecules being adsorbed on AA7075-T6 surface.

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