Influence of the Alloying Elements on Uniform and Pitting Corrosion Events Induced by SCN\(^{-}\) Anions on Al-6061 and Al-Cu Alloys Surfaces

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Abstract

The electrochemical and corrosion behaviour of Al-6061, Al-4.5\%Cu and Al-7.5\%Cu alloys were studied in 0.50 M KSCN solution at 25 \(^{\circ}\)C. Open-circuit potential, Tafel polarization and ICP-AES measurements were used to study the uniform corrosion process on the surfaces of the tested alloys. Cyclic polarization measurements were employed for pitting corrosion studies. Obtained results were compared with pure Al. Alloyed copper was found to enhance uniform corrosion of Al in SCN\(^{-}\) solutions to an extent depending on its content in the Al sample. The pitting potential (\(E_{\text{pit}}\)) and the repassivation potential (\(E_{\text{rp}}\)) increased with an increase in the alloyed copper content. Thus alloyed copper suppressed pit nucleation and propagation. The effect of temperature was also studied and the apparent activation energies were determined as a function of alloy composition. Among the investigated materials, Al-6061 alloy has the highest corrosion resistance towards uniform and pitting corrosion processes in KSCN solutions.

Keywords: Uniform corrosion; Pitting corrosion; Al; Al-6061 alloy; Al-Cu alloys; KSCN solutions.

Introduction

The electrochemical behaviour of aluminium and aluminium alloys is a subject of a large number of studies due to increased industrial application of these materials (construction, metallurgy, mechanical engineering and transport vehicle industry, from automobiles to aircrafts, as well as food processing industry in the production of packaging material, etc.). These applications are often possible because aluminium spontaneously forms stable oxide films in air and in aqueous solutions. Oxide films can be also formed artificially by anodising processes. The behaviour of aluminium during the anodising process has been extensively studied and it has been found that the anodic film properties depend on the electrolyte compositions, current density, passivation potential, time of anodising, as well as on the composition of aluminium substrates\(^{[1-6]}\).

Although pure Al is too soft to be used as a heavy duty material for large structures, high-strength Al alloys can be produced by addition of appropriate alloying elements, such as Cu, Mg and Zn and by suitable heat treatment procedures\(^{[7-9]}\). For these reasons, studies of the corrosion and stability of aluminium and its alloys are still

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of considerable interest. Aggressive anions, such as the halides, induce breakdown of the protective passive film \[^{10–16}\] and can result in catastrophic failure of the material. There have been extensive investigations on the role of chloride ions in the breakdown of the passive film, repassivation and initiation of localized corrosion of Al and high-strength Al-based alloys. Furthermore, the effect of alloy content \[^{11,17–19}\], electrolyte composition \[^{20}\], heat treatment \[^{21}\] and mechanical stress \[^{22}\] on pitting and repassivation of Al-based alloys in halide media have been reported.

A program is in progress in our lab to study the pitting corrosion, corrosion inhibition and electrochemical behaviour of Al and some of its alloys in some aqueous media \[^{23–28}\]. It was shown recently that Al and Al-Zn alloys pit in KSCN solutions \[^{29}\]. The purpose of this work is to study the effect of the alloying elements on the uniform and pitting corrosion processes of the following alloys: Al-6061, Al-4.5%Cu and Al-7.5%Cu in KSCN solutions. Pure Al was also used in this work for comparison. Open-circuit potential, Tafel polarization and cyclic polarization measurements were applied in this study. An independent method of chemical analysis, namely inductively coupled plasma atomic emission spectroscopy (ICP-AES) was also used to clarify the role of the alloying elements in the uniform corrosion process of the tested Al samples.

**Experimental**

The working electrodes employed here were made of pure Al wire (SIGMA-ALDRICH, 1.0 mm diam., 99.999), Al-Mg rod (Al-6061 alloy): 6.35 mm diam., Stock # 42052, Lot # G14K32 (97.93% Al, 1.0% Mg, 0.60% Si, 0.27% Cu, 0.20% Cr), (Al-4.5%Cu) and (Al-7.5%Cu) alloys. The composition of the two (Al-Cu) alloys is presented elsewhere \[^{30}\]. The pure Al wire was mounted into Teflon leaving a constant surface area of 0.00785 cm\(^2\) to contact the solution. The two (Al-Cu) alloys were in the form of cylindrical rods of base diameter 0.50 cm. These rods of Al-6061 and Al-Cu alloys were welded with Cu-wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active flat disc shaped surface for the working electrode, to contact the test solution. The surface pre-treatment of each electrode was carried out by grinding with different grades of emery papers down to 1200 grit. The electrode was then, rinsed with acetone, distilled water and finally dipped in the electrolytic cell.

The experiments were performed in a 100 ml volume Pyrex glass cell using Pt wire and a saturated calomel electrode (SCE) as auxiliary and reference electrodes, respectively. The SCE was connected via a Luggin capillary, the tip of which was very close to the surface of the working electrode to minimize the IR drop. All potentials given in this paper are referred to this reference electrode. The experiments were carried out in 0.50 M KSCN solution freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. For each run, a freshly prepared solution as well as a cleaned set of electrodes was used.
Each run was carried out in aerated stagnant solutions at the required temperature (±1°C), using water thermostat.

Tafel extrapolation method was used to monitor the rate of the uniform corrosion of the tested Al samples in 0.50 M KSCN solutions as a function of solution temperature (278-338 K). Cathodic and anodic polarization curves were determined by the potentiostatic method using 10 mV increments of potential, and steady state currents were observed within 30 min at each applied potential. ICP-AES (inductively coupled plasma-atomic emission spectroscopy) method of chemical analysis has been used alongside the Tafel extrapolation method to evaluate the effect of the alloying elements on the rate of the uniform corrosion process. In the ICP method, the Al\(^{3+}\) ions concentration was determined as a function of sample composition and immersion time (from 1.0 day up to 30 days) using Perkin-Elmer Optima 2100 Dual View inductively coupled plasma atomic emission spectrometry (ICP-AES) instrument connected with AS 93 Plus auto sampler.

Cyclic polarization measurements were carried out by sweeping linearly the potential from the starting potential into the positive direction at a scan rate of 0.50 mV s\(^{-1}\) to required potential value and then reversing the scan direction at the same scan rate until forming a well-defined hysteresis loop. In all cases, the potential scan was reversed at the same current density to evaluate the influence of the alloyed elements on the pit growth of the tested Al samples. The stabilization period prior to collecting data was 12h. The open circuit potential of the working electrode was measured as a function of time during this stabilization period. This period of 12 h was quite sufficient to reach a quasistationary value for the open circuit potential.

A Potentiostat/Galvanostat (EG&G model 273) and a personal computer were used. M352 corrosion software from EG&G Princeton Applied Research was used for the potentiodynamic polarization, galvanostatic and the potentiostatic measurements.

**Results and discussion**

*Open-circuit potential vs. time measurements*

The time evolution of the open-circuit potential (OCP) for pure Al, Al-6061, Al-4.5%Cu and Al-7.5%Cu alloys in 0.50 KSCN solution is presented in figure 1. It can be seen, in all cases, that in the first moments of immersion the open circuit potential moves rapidly towards less negative values due to the initial formation and growth of the passive oxide film. Then the electrode potential shifts towards the more negative values to an extent depending on sample composition. This trend may be attributed to dissolution of the protective alumina layer as the result of SCN\(^{-}\) adsorption and subsequent formation of Al-SCN soluble complex species (see later). Increased alkalinity of the solution layer close to the electrode surface, due to cathodic processes, may also cooperate with SCN\(^{-}\) anions to damage the protective alumina layer; more clarifications are presented in polarization measurements (section 3.2.1).
Figure 1 - Open-circuit potential (OCP) vs. time plots recorded for the tested Al samples in 0.50 KSCN solution at 25 °C.

As a result of increasing immersion times, the open circuit potential goes towards a more positive value and keeps a constant value (steady potential) after certain time of immersion (depending on sample composition; see later) due to the formation of a porous layer of alumina $^{[31]}$. This steady potential corresponds to the free corrosion potential, $E_{\text{corr}}$, confirmed from polarization studies, see also section 3.2.1, of the metal. Similar results were previously obtained during the corrosion inhibition of pure Al in neutral and acidic chloride solutions $^{[32]}$. 
Comparison of the pure Al (Figure 1a) and the two Al-Cu alloys (Figure 1b) shows that the obtained OCP values of the two tested Al-Cu alloys were always more negative, which is indicative of a more active corrosion surface when compared with Al. This difference could be related to the acceleration influence of the alloyed copper (see later). The more negative potentials of the Al-Cu alloys suggest that the presence of the alloyed copper influences the kinetics of the cathodic reaction. This negative shift in the OCP enhances with increase in the content of the alloyed copper (see again figure 1b).

The reverse behavior is seen for the Al-6061 alloy (Figure 1a), such that the alloying elements of this alloy shift the OCP towards less negative values, suggesting a predominant influence of the alloying elements on the anodic reaction.

It is obvious in all cases that Al and its tested alloys tend to passivate in these solutions, particularly at longer immersion times despite the aggressiveness of the SCN− anion towards the passive layer [29]. The OCP values get less negative with time. It seems that the ability of the electrode to passivate depends on its composition. Similar results were obtained by Badawy et al. [33,34] during corrosion of Mg and some of its alloys in some aqueous solutions.

Further inspection of figure 1b reveals that the two Al-Cu alloys need longer times from electrode immersion to reach steady-state. This means that the surfaces of the two Al-Cu alloys are subjected to corrosion more than Al and Al-6061 alloy which stabilize readily in these solutions; shorter times are required for Al and Al-6061 alloy to reach steady-state.

Polarization measurements

Uniform corrosion process (Tafel extrapolation method)

Figure 2a shows anodic and cathodic polarization curves recorded for Al in 0.50 M KSCN solution at 25 °C. It is obvious that the cathodic branch displays a typical Tafel behaviour. This makes it possible, as will be seen, to make an accurate evaluation of the cathodic Tafel slope (βc) as well as corrosion currents (jcorr) by the Tafel extrapolation method. On the other hand, the anodic polarization curve does not display the expected log/linear Tafel behaviour over the complete applied potential range due to passivation.
Therefore, due to the absence of linearity in anodic branch, accurate evaluation of the anodic Tafel slope by Tafel extrapolation of the anodic branch is impossible [35-39]. There is, therefore an uncertainty and source error in the numerical values of the anodic Tafel slope ($\beta_a$), and may be in values of $j_{corr}$ too, calculated by the software; the reason why we did not introduce here $j_{corr}$ as well as $\beta_a$ values recorded by the software. It has been shown that in the Tafel extrapolation method, the use of both the
anodic and cathodic Tafel regions is undoubtedly preferred over the use of only one Tafel region \([40]\).

However, the corrosion rate can also be determined by Tafel extrapolation of either the cathodic or anodic polarization curve alone. If only one polarization curve alone is used, it is generally the cathodic curve which usually produces a longer and better defined Tafel region (as in our case here). Anodic polarization may sometimes produce concentration effects, due to passivation, as noted above, as well as roughening of the surface which can lead to deviations from Tafel behaviour. Thus, extrapolation of the cathodic Tafel region back to zero overvoltage gives the net rate of the cathodic reaction at the corrosion potential; this is also the net rate of the anodic reaction at the corrosion potential \([40]\). Consequently, it is possible to calculate the anodic Tafel line from the experimental data, as shown in figure 2a. The Tafel line of the cathodic polarization curve is first extended, since it exhibits a linear Tafel region, to electrode potentials below the corrosion potential, and then the anodic current density \(j_a\) is calculated from \([40]\):

\[
(j_{net})_a = [(j_{Al})_a + (j_{O})_a] - [(|j_{Al}|)_c + (|j_{O}|)_c] \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (1)
\]

or, simply:

\[
(j_{a \ (net\ experimental)}) = j_a - |j_c| \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (2)
\]

where the subscripts a and c refer to the anodic and cathodic direction, respectively. Thus, \((j_{Al})_a\) and \((|j_{O}|)_c\) refer, respectively, to the rates of the anodic dissolution of Al and the cathodic reduction reaction of dissolved oxygen. \(|j_c|\) is the cathodic current density. Thus, the calculated anodic current density \(j_a\) is the sum of the experimentally observed anodic current density and the extrapolated cathodic current density. Based on these calculations, a corrosion current density \(j_{corr}\) of \(10^{-3}\) A cm\(^{-2}\) was obtained for Al in 0.50 M KSCN solution (see again figure 2a).

Figure 2b shows the cathodic and anodic polarization curves recorded for the four tested Al samples at 25 °C. It seems that alloyed copper affected the potentiodynamic polarization characteristics of Al-Cu alloys compared with Al and Al-6061. The cathodic and anodic currents as well as \(j_{corr}\) increased due to the presence of alloyed copper. These events enhance with the copper content in the sample. The increase of the alloyed copper content leads therefore to an obvious decrease in the resistance of the Al alloy towards uniform attack. These findings refer to the acceleration influence of the alloyed copper towards uniform corrosion of Al samples in these solutions. This is also reflected in the polarization curves in which the passive current, \(j_{pass}\), is enhanced upon alloying Al with Cu. Similar trend was observed for the corrosion of Al and Al–Cu alloys in H\(_3\)PO\(_4\) solutions \([41]\). On the other hand, the electrochemical behaviour of Al-6061 alloy is similar to that of Al, where their \(E_{corr}\) values are relatively close to each other (see later). However, the Al-6061 recorded the lowest \(j_{corr}\) and the highest cathodic and anodic overpotentials. The alloying elements
of this alloy therefore increased, as will be shown, its corrosion resistance towards uniform corrosion.

The obtained electrochemical parameters, based on calculations presented in Figure 2a) are collected in Table 1 as a function of the sample composition.

Table 1 – Various parameters derived from Tafel extrapolation and ICP-AES methods recorded for the tested Al samples in 0.5 M KSCN solution at 25 °C.

<table>
<thead>
<tr>
<th>Tested Sample</th>
<th>$\beta_a$ / V dec$^{-1}$</th>
<th>$-\beta_c$ / V dec$^{-1}$</th>
<th>$E_{corr}$ / V(SCE)</th>
<th>$j_{corr}$ / A cm$^{-2}$</th>
<th>$\nu_{Tafel}$ / µm y$^{-1}$</th>
<th>$\nu_{ICP-AES}$ / µm y$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-6061</td>
<td>0.146</td>
<td>0.205</td>
<td>-1.18</td>
<td>0.0005</td>
<td>5.47</td>
<td>6.41</td>
</tr>
<tr>
<td>Al</td>
<td>0.164</td>
<td>0.232</td>
<td>-1.19</td>
<td>0.001</td>
<td>10.93</td>
<td>13.12</td>
</tr>
<tr>
<td>Al-4.5%Cu alloy</td>
<td>0.132</td>
<td>0.170</td>
<td>-1.24</td>
<td>0.0034</td>
<td>37.17</td>
<td>35.95</td>
</tr>
<tr>
<td>Al-7.5%Cu alloy</td>
<td>0.110</td>
<td>0.103</td>
<td>-1.26</td>
<td>0.0049</td>
<td>53.57</td>
<td>51.76</td>
</tr>
</tbody>
</table>

The numerical values of the corrosion current density ($j_{corr}$) were converted into corrosion rates, $\nu_{Tafel}$, in µm y$^{-1}$ (Micrometer per year; the penetration rate of corrosion through a metal) using the expression $^{[42]}$:

$$\nu_{ICP-AES} = 3280 \cdot j_{corr} \cdot (M / nd)$$

where $M$ is the atomic weight of Al (26.98154 g mol$^{-1}$), $n$ the number of electrons transferred in the corrosion reaction ($n = 3$) and $d$ the density of Al (2.70 g cm$^{-3}$). Rates of the uniform corrosion were also included in Table 1 as a function of sample composition at 25 °C.

Data presented in Table 1 reveals that the rate of uniform corrosion increases when Al alloyed with copper. This increase in the rate of uniform corrosion enhances with increasing alloyed copper content. On the other hand, the Al-6061 alloy presented the lowest corrosion rate, reflecting its high corrosion resistance towards corrosion in these solutions. The effect of temperature on the rates of uniform corrosion of Al and its tested alloys was also studied based on Tafel polarization measurements (data not shown here). Generally, the rates of corrosion of the tested Al samples increase with increase in temperature. The apparent activation energies ($E_o^a$) of the corrosion process are calculated for all tested samples (Figure 3) based on Arrhenius equation $^{[43]}$:

$$\ln (\text{rate}) = - (E_o^a / RT) + \ln A$$

The calculated $E_o^a$ values are found to be 32.62, 41.64, 50.22 and 65.02 kJmol$^{-1}$ for Al-7.5%Cu, Al-4.5%Cu, Al and Al-6061, respectively. It is clear that alloying Al with copper decreases the activation energy of the corrosion process to an extent depending on the content of the alloyed copper in the Al sample. These results confirm the high corrosion tendency of Al-Cu alloys. The Al-6061 alloy exhibits the highest activation energy value among the tested samples, confirming its high corrosion resistance. Based on previous findings, the ranking of the rate of the uniform corrosion of these alloys is Al-7.5%Cu > Al-4.5%Cu > Al > Al-6061.
Figure 3 – Arrhenius plots recorded for the tested Al samples in 0.50 KSCN solutions.

This order is reversed, with Al-6061 alloy being the most corrosion resistant, considering the rate of the pitting corrosion process. This will be discussed later after the mechanism of the anodic and cathodic processes has been presented (vide infra).

The mechanism of Al or Al alloys corrosion in neutral solutions is based on the dissolution of Al atoms from the active sites or flawed regions of the naturally formed barrier oxide film. It represents an irreversible coupled reaction, the anodic part of which is the metal dissolution and the cathodic counter part of which is the reduction of water or dissolved oxygen yielding OH\(^-\), based on the following cathodic processes \[^{[44]}\]:

\[ \text{H}_2\text{O}(s) + e^- \rightarrow \text{H} + \text{OH}^- \] ..........................

and

\[ \text{H} + \text{H}_2\text{O}(s) + e^- \rightarrow \text{H}_2\uparrow + \text{OH}^- \] ..........................

In oxygen rich solutions (naturally aerated or oxygen saturated), the cathodic part occurs through oxygen reduction:

\[ \frac{1}{2}\text{O}_2 + \text{H}_2\text{O}(s) \rightarrow \text{OH}^\text{ads} + \text{OH}^- \] ..........................

\[ \text{OH}^\text{ads} + e^- \rightarrow \text{OH}^- \] ..........................

The anodic reactions are:

\[ \text{Al} + \text{OH}^- = \text{AlOH}^\text{ads} \rightarrow \text{AlOH}^\text{ads} + e^- \] ..........................

\[ \text{AlOH}^\text{ads} + \text{OH}^- \rightarrow \text{Al(OH)}_2^\text{ads} + e^- \] ..........................

\[ \text{Al(OH)}_2^\text{ads} + \text{OH}^- \rightarrow \text{Al(OH)}_3^\text{ads} + e^- \] ..........................

The formation of the adsorbed \text{Al(OH)}_3, which transforms to \text{Al}_2\text{O}_3, 3\text{H}_2\text{O} in neutral media, may account for the observed passivity in these solutions. The resulting
OH’ ions may also induce Al dissolution with the generation of aluminate species [Al(OH)₄]⁻ [45]:

\[
\text{Al(OH)}_{3\text{ads}} + \text{OH}^- \rightarrow [\text{Al(OH)}_4]^{-}_{\text{aq}} \quad \text{..................................................................................................................(12)}
\]

SCN’ anions may also cooperate with OH’ to damage the protective alumina layer. This could be explained on the basis of the coordination chemistry of SCN’. It is well-known that SCN’ is an ambidentate ligand, i.e., can be bonded with metal ions either via nitrogen, sulphur or both. Coordination of a SCN’ ligand with metal ions has been considered in several books and journals [46-48]. Sasic et al. [49] studied the interaction between Al(III) and SCN’ anion in aqueous solutions using Raman Spectroscopy. Authors in this study showed that SCN’ ligand can displace water molecules in Al(H₂O)₆³⁺ binding through nitrogen in aqueous solutions. They revealed the presence of two soluble complex species, namely Al(NCS)(H₂O)₅²⁺ and Al(NCS)₂(H₂O)₄⁺.

The anodic dissolution of Al in KSCN solutions therefore could be explained as a series of adsorption reactions involving catalysis by SCN’ anion at active surface sites following the equations:

\[
\text{Al} + \text{NCS}^- \rightarrow \text{AlNCS}_{\text{ads}} + e^- \quad \text{..................................................................................................................(13)}
\]

\[
\text{AlNCS}_{\text{ads}} + n\text{H}_2\text{O} \rightarrow \text{Al(H}_2\text{O)}_n^{3+} + \text{NCS}^- + 2e^- \quad \text{..................................................................................................................(14)}
\]

Where Eq. 14 is the dissolution step and Al(H₂O)₆³⁺ represents the solvated Al³⁺ ion. Generally, if the rate of oxide film formation is faster than the rate of its dissolution, film healing (passivation) predominates. The converse causes uniform corrosion to dominate.

Based on the above arguments, the uniform corrosion of Al and its tested alloys in KSCN solutions may result from the cooperative aggressive attack of OH’ (reaction 12) and SCN’ anions (reaction 14). The formed soluble species of Al, namely [Al(OH)₄]⁻ and Al-NCS complex species are expected to move into the solution and hydrolyze, leaving bare active sites available for uniform attack.

This increase in the rate of uniform corrosion of Al with the increase in alloyed copper content was further confirmed chemically using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). This method of chemical analysis involves determination of the dissolved Al³⁺ ions as a function of immersion time (up to 30 days) and alloy composition (Figure 4). The slope of each line (mass, in mg, of Al dissolved as Al³⁺ per unit area per unit time; mg cm⁻² h⁻¹) represents the corrosion rate of Al at the specified conditions. It is obvious that the rate of uniform corrosion increases with the percentage of the alloyed copper in the sample. The numerical values of these slopes were converted into the corresponding corrosion current densities (jcorr) using Faraday’s law. The obtained jcorr values were introduced into Eq.3 to get the corrosion rate \(\nu_{\text{ICP-AES}}\) in \(\mu\text{m y}^{-1}\) (see table 1). The rates of corrosion obtained from the ICP method are relatively close to those calculated from the Tafel extrapolation method.
The Al-6061 alloy exhibited, as usual, the lowest rates of corrosion among the tested samples (inspect again table 1).

The acceleration influence of the alloyed copper towards uniform corrosion could be explained adopting previous study of Badawy et al. [50]. They investigated the corrosion and passivation characteristics of Al, Al-6061 and Al-Cu alloys in neutral solutions based on XPS and SEM examinations of the electrode surface. The XPS survey spectra of the Al-Cu alloy obtained by Badawy et al. [50] showed clear peaks of copper even after the surface etching process. The presence of copper on the alloy surface increases the number of the flawed regions and initiates cathodic areas [50,51]. Initiation of the cathodic areas on the Al-Cu alloy surface may be the reason for the high rates of uniform corrosion recorded for this alloy in the present work compared with Al and Al-6061 alloy.

Badawy et al. also reported that the XPS spectra of Al-6061 are very similar to those of Al (Al 2p at 75.5 eV, Al 2s at 120.0 eV, O 1s at 532.5 eV). The XPS spectra of Al-6061 did not show the pronounced peak of Mg (Mg 1s at 1305 eV). This result supports the conclusion that Mg is present mainly as the Mg2Si phase in the bulk of the alloy or migrates rapidly to the solution through the film [50]. Badawy et al. [50] used this trend of the Mg2Si phase to explain why the Al-6061 alloy surface behaves in a very similar manner to the Al surface. This similar behaviour between Al-6061 and Al was observed in the present work too. This is clearly seen from the polarization plots of figure 2b, where the values of $E_{corr}$ obtained for Al-6061 alloy and Al are close to each other.

![Figure 4](image_url)  
**Figure 4** – Corrosion-time plots, obtained by ICP-AES method of chemical analysis, for the tested Al samples in 0.50 KSCN solutions at 25 °C.
Pitting corrosion process (cyclic polarization measurements)

Figure 5 shows the cyclic polarization plots of Al and its tested alloys in 0.50 M KSCN solutions at a scan rate of 0.50 mV s\(^{-1}\) at 25 °C. It is obvious from figure 5 that the obtained plots had the familiar form for Al and Al alloys showing a well-defined corrosion potential, \(E_{\text{corr}}\), followed by a passive region. The passive region results due to the formation of a protective barrier oxide film. The extent of the passive region depends on sample composition. In all cases, this passive region is limited at the breakdown potential \((E_b)\) by pitting as a result of the aggressive attack of SCN\(^-\) anions \([29]\). Passivity breakdown and initiation of pitting are evident by a sudden increase in the passive current density \(j_{\text{pass}}\) at \(E_b\) (pit propagation). Microscopic examinations revealed Al passivity and its breakdown followed by initiation and propagation of pits as has been previously shown \([29]\).

![Cyclic polarization curves for the tested Al samples in 0.50 KSCN solutions at a scan rate of 0.50 mV s\(^{-1}\) at 25 °C.](image)

Figure 5 – Cyclic polarization curves for the tested Al samples in 0.50 KSCN solutions at a scan rate of 0.50 mV s\(^{-1}\) at 25 °C.

Upon reversing the potential scan, a current hysteresis loop, characteristic of pitting corrosion phenomena, appears. The existence of a hysteresis loop in a cyclic potentiodynamic polarization curve indicates a delay in repassivation of an existing pit when the potential is scanned in the negative direction. The larger the hysteresis loop, the more difficult it becomes to repassivate the pit \([52]\). This loop allows the repassivation potential \((E_{\text{rp}})\) to be determined \([52]\). In the present work, \(E_{\text{rp}}\) is defined as the potential at which the reverse anodic current intersects the forward scan. The pitting current in the reverse scan decreases and completely suppressed at \(E_{\text{rp}}\), where pit growth is arrested.
Further inspection of figure 5 reveals that alloying Al with copper shifts $E_b$ to more positive potentials. This positive shift of $E_b$ increases with copper content in the sample (curves 2 and 3). These findings indicate that an increase of alloying copper, will cause the rate of pitting corrosion of the alloy to decrease. It was proposed previously [53] that the reason why Al–Cu alloys have good anti-pitting properties, compared with Al, is mainly due to the effect of the alloying element (Cu). Uniform and localized corrosion processes will preferentially dissolve Al and leave the surface enriched in Cu species (supposed to be unreactive based on the aqueous thermodynamic behaviour of Cu [54]). The presence of such alloying element in the $\text{Al}_2\text{O}_3$ matrix, rather than in the bulk, was confirmed in previous studies [50,55-58]. The incorporation of copper species into the passive film repairs the film defects (i.e., the active sites are blocked) and precludes significant dissolution of the oxide film [59]. This makes the migration of the aggressive SCN$^-$ anions through the oxide film rather difficult. Alloyed copper would as a result increase the difficulty of soluble film formation required for film rupture to occur [60].

The alloying element may also slow down the rate of metal dissolution by reducing the amount of free metal ions in the pit solution resulting in a decrease in diffusion of SCN$^-$ anions into the pit and reduction in diffusion of metal cations out of the pit [60]. All these effects caused by the alloyed copper decreased the rate of pitting corrosion and made the applied anodic potential raise even higher ($E_b$)alloy to re-activate pitting at the less favourable sites. As the alloyed copper content is increased, copper atoms will appear with greater frequency. Therefore, dissolution processes will be retarded until increasingly higher potentials are reached. Therefore, ($E_b$)alloy must increase with alloyed copper content.

Among the investigated materials, Al-6061 has the highest corrosion resistance towards uniform and pitting corrosion processes. This is clearly seen, as previously shown, from the lower value of the uniform corrosion rate (Table 1) and the higher positive shift of $E_b$ as compared with Al and the two Al-Cu alloys. Al-6061 contains 1.0% Mg and 0.60% Si, which is a combination that leads to the formation of the Mg$_2$Si phase in a heat treatable alloy [61]. The formation of this compound is the base of precipitation hardening. Either in solid solution or as submicroscopic precipitate, it seems that Mg$_2$Si phase has a little influence on the electrode potential as the $E_{corr}$ values of Al and the Al-6061 alloy are close to each other. Similar results were previously obtained [50].

**Conclusion**

The electrochemical behaviour of Al and some of its alloys, namely Al-6061, Al-4.5%Cu and Al-7.5%Cu have been studied in 0.50 M KSCN solution based on OCP, Tafel extrapolation method, ICP-AES method of chemical analysis and cyclic polarization measurements. Results obtained showed that:
(i) OCP vs. time measurements revealed that the tested Al samples tend to be passive in KSCN solutions at longer immersion times to an extent depending on sample composition. Al and Al-6061 were found to passivate faster than the two tested Al-Cu alloys.

(ii) Tafel polarization and ICP measurements showed that alloyed copper accelerates the uniform corrosion to an extent depending on the alloyed copper content in the sample. On the other hand, cyclic polarization measurements revealed that the susceptibility of Al towards pitting attack was suppressed when the percentage of alloyed copper in Al was increased.

(iii) The numerical values of the apparent activation energies of the tested Al samples, based on Tafel extrapolation method, showed that the ranking of the uniform corrosion rates of these alloys follows the order: Al-7.5%Cu > Al-4.5%Cu > Al > Al-6061. This order is reversed for Al and the two Al-Cu alloys regarding the pitting attack of the SCN⁻ anions.

(iv) The Al-6061 alloys presented the highest corrosion resistance towards uniform and pitting corrosion processes in KSCN solutions.

References
