The Inhibition of Sodium Oleate for Pitting Corrosion of Aluminum Alloy 2024 in 0.1 mol L\(^{-1}\) NaCl Solution

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The inhibition mechanism of sodium oleate (C\(_{17}\)H\(_{33}\)COONa) for pitting corrosion of aluminum alloy (AA) 2024 in 0.1 mol L\(^{-1}\) NaCl solution was investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) and X-ray photoelectron spectroscopy (XPS). C\(_{17}\)H\(_{33}\)COONa showed good inhibition effect on uniform corrosion of AA2024 in 0.1 mol L\(^{-1}\) NaCl solution by promoting surface passivity of aluminum alloy. But in NaCl solution with high concentration (3.5 wt.% NaCl), C\(_{17}\)H\(_{33}\)COONa could not promote passivity of aluminum alloy. C\(_{17}\)H\(_{33}\)COONa also suppressed the tendency of pitting initiation and reduced the pitting corrosion sensitivity of aluminum alloy. The addition of 0.1 g L\(^{-1}\) C\(_{17}\)H\(_{33}\)COONa showed good inhibition performance but further concentration increase had little effect on the inhibition efficiency. The C\(_{17}\)H\(_{33}\)COO\(^{-}\) groups adsorbed on the surface of aluminum alloy by chemical adsorption effect, which promoted oxidation of the aluminum alloy surface.

**Keywords:** corrosion inhibition, sodium oleate, pitting corrosion, aluminum alloy

**Introduction**

The application of inhibitors is one of the most practical methods for protection against corrosion of metals.\(^1\) Many inhibitors including organic and inorganic compounds have good corrosion inhibition efficiency, but the majority of them are more or less toxic to both human being and the environment.\(^2\) Among various inhibitors, surfactants are widely recognized and well accepted due to their high inhibition efficiency, low toxicity and relatively low price.\(^3,5\) Surfactants can adsorb on the surface of metals and form hydrophobic films that impede the charge or substance exchange which is related to corrosion process. Meanwhile, surfactants can change the charge state of metal surface and the interfacial properties, decrease the surface energy, and increase the activation energy, thus reducing the corrosion rate of metals.\(^6,7\)

Aluminium alloy (AA) 2024 is a commonly used alloy. But it is vulnerable to pitting corrosion when the surrounding environment contains aggressive ions such as chloride ions. Pitting corrosion usually occurs at the edges of intermetallic inclusions such as the Al\(_2\)CuMg particles (S-phase) on the aluminium alloy surface. The S-phase is usually active with respect to the matrix, and Al and Mg would preferentially dissolve and the Cu-rich phases remain. As a cathode Cu can accelerate corrosion of the surrounding Al matrix and cause serious pitting corrosion.\(^8,9\) When the dissolution of the S-phase particles is suppressed, the corrosion of aluminium alloy would be reduced effectively.\(^10\) Sodium oleate (C\(_{17}\)H\(_{33}\)COONa) is an environmental friendly and cheap anionic surfactant and can be derived from saponification of oleic acid which is widely existed in nature.\(^5\) Amin\(^11\) investigated the corrosion inhibition of copper in NaCl solution using sodium oleate as an anionic surfactant, and found that the inhibition process was due to the formation of an adsorbed film on the metal surface that protected the metal against corrosive species. The author also investigated the inhibitory effect of sodium oleate on the corrosion of Al and Al-Cu alloys in H\(_3\)PO\(_4\) solution and reported that the protection efficiency increased with increasing surfactant concentration.\(^12\) Li et al.\(^13\) reported that sodium oleate showed good corrosion inhibition effect for cold rolled steel in 1.0 mol L\(^{-1}\) HCl solution, and the adsorption of sodium oleate on steel surface obeyed the amended Langmuir adsorption isotherm equation. It was pointed out that sodium oleate was a moderate effective corrosion inhibitor for cold rolled steel in 3.0 mol L\(^{-1}\) H\(_3\)PO\(_4\) solution, while incorporation of sodium oleate with rare earth cerium(IV) improved the inhibition...
performance. Wang et al. studied the inhibition effect of sodium oleate on corrosion of Al alloy in 3.5 wt.% NaCl solution, and concluded that sodium oleate is a mixed-type inhibitor but it mainly suppresses the anodic reaction of Al alloy. Zhou et al. investigated the synergistic inhibition effect of sodium oleate and sodium vanadate on the corrosion of pure Al in NaCl solution, and found that these two inhibitors play the major inhibition role at different corrosion stages respectively. At present, most studies have paid attention to the uniform corrosion and there were few studies focused on the effect of sodium oleate on pitting corrosion prevention of aluminum alloy. In this paper, sodium oleate was added into 0.1 mol L\(^{-1}\) NaCl solution and its inhibition effect for pitting corrosion of aluminum alloy 2024 was studied. The related mechanism was discussed.

**Experimental**

The experimental material was aluminum alloy 2024. The nominal composition (wt.%) is 3.8-4.9 Cu, 1.2-1.8 Mg, 0.3-0.9 Mn, 0.5 Fe, 0.5 Si, 0.25 Zn, 0.1 Cr, 0.15 Ti, 0.15 others, and balance AI.

The size of the aluminum alloy specimen was 13 mm \(\times\) 13 mm \(\times\) 10 mm. The specimen surface was manually abraded with 240, 600 and 1000 grit silicon carbide papers successively, and cleaned with deionized water and alcohol. Then the working surface was coated with a single-component room-temperature curing silicon rubber to avoid crevice corrosion, leaving an area of 0.09 cm\(^2\) exposed. The samples were kept in a drier before electrochemical tests.

Polarization measurements for aluminum alloy were carried out in 0.1 mol L\(^{-1}\) NaCl solution. The pH value of the original solution was 6.3. Were added into the NaCl solution 0.05, 0.1, 0.2 and 0.4 g L\(^{-1}\) sodium oleate (C\(_{17}\)H\(_{33}\)COONa), respectively. The sodium chloride and sodium oleate were all reagent-grade and all solutions were prepared using deionized water at room temperature, without deaeration. The pH values of the solutions were measured with a pH meter (Ray Magnetic Company, Shanghai, China). In addition, a 0.1 mol L\(^{-1}\) NaCl with 0.2 g L\(^{-1}\) C\(_{17}\)H\(_{33}\)COONa solution was prepared and the pH value was adjusted to 6.3 by using HCl solution. A 3.5 wt.% NaCl with 0.2 g L\(^{-1}\) C\(_{17}\)H\(_{33}\)COONa solution was also prepared to study the effect of NaCl concentration.

Potentiodynamic polarization curves were measured using a CS350 electrochemical workstation (Corrtest Company, China). A three electrode system was used in the test, with the aluminum alloy specimen as working electrode, a platinum electrode as counter electrode, and an Ag/AgCl electrode (SSC) as the reference electrode. Before polarization tests the open circuit potential of the working electrode was monitored in the test solutions for 20 min until it was stable. The polarization test was begun from −0.2 V to the open circuit potential, at a potential scanning rate of 0.1 mV s\(^{-1}\) to anodic direction until the current density reached 200 \(\mu\)A cm\(^{-2}\), then the scanning was reversed to the cathodic direction. The data acquisition rate was 5 times per second. Because of the stochastic characteristic of pitting corrosion, under each experimental condition at least five tests were employed. Corrosion current density \(i_{\text{corr}}\) was obtained by fitting the cathodic polarization curves using CVview software. During the potentiodynamic polarization process the potential from which the current increased continually was denoted as the pitting potential \(E_{\text{p}}\), and the potential at which the reversed polarization curve intersected the positive polarization curve was denoted as the repassivation potential \(E_{\text{rp}}\). Electrochemical impedance spectroscopy (EIS) measurements were performed at the corrosion potentials in the frequency range from 100 kHz to 10 mHz with an AC voltage amplitude of \(\pm10\) mV. The instrument was PARSTAT 2273 system.

Before and after polarization tests in the testing solutions, the surface morphologies of the samples were observed with a scanning electronic microscope (SEM, Hitachi S4700). Energy dispersive spectroscopy (EDS) was used to analyze the composition of the corrosion products on the sample surface.

After the potentiodynamic polarization tests, X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was employed to analyze the corrosion products on the aluminum alloy surface. All the binding energy values were calibrated according to C1s peak at 285 eV. The narrow scan spectra were fitted with XPSPEAK 4.1 software.

**Results and Discussion**

Figure 1 shows the pH values tested after the addition of different concentrations of C\(_{17}\)H\(_{33}\)COONa in 0.1 mol L\(^{-1}\) NaCl solution. Each error bar represents a 95% confidence limit. It can be seen that the pH value of the solution increased with the increase of C\(_{17}\)H\(_{33}\)COONa concentration. The pH increase is because that sodium oleate is a salt with strong acidity and weak alkalinity. C\(_{17}\)H\(_{33}\)COO\(^-\) ions undergo partial hydrolysis in the solutions according to equation 1, producing some OH\(^-\) ions and lead to increased pH value. It was reported that the increase in solution pH could cause the corrosion potential of aluminum alloy move towards negative direction, but have little effect on pitting potential \(E_{\text{p}}\)\(^{10,16}\).

\[
\text{C}_{17}\text{H}_{33}\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_{17}\text{H}_{33}\text{COOH} + \text{OH}^- \quad (1)
\]
Figure 2 shows typical cyclic anodic polarization curves of aluminum alloy 2024 in 0.1 mol L\(^{-1}\) NaCl solution with different contents of C\(_{17}\)H\(_{33}\)COONa. Without C\(_{17}\)H\(_{33}\)COONa, AA2024 showed typical characteristics of active dissolution. When C\(_{17}\)H\(_{33}\)COONa was added, the corrosion potential was obviously shifted to the negative direction, passivity range was observed and pitting corrosion occurred at higher anodic potential. With increasing sodium oleate concentration, the pitting potential increased. However, the concentration of sodium oleate had no effect on the passive current density and the corrosion potential.

Figure 3 shows the Nyquist diagrams for AA2024 in 0.1 mol L\(^{-1}\) NaCl solution in different concentrations of C\(_{17}\)H\(_{33}\)COONa.

Because the addition of sodium oleate resulted in the increase of pH solution. In order to understand if the passivation of aluminum alloy was induced by the pH rising, potentiodynamic polarization behavior of AA2024 in NaCl solutions with 0.2 g L\(^{-1}\) C\(_{17}\)H\(_{33}\)COONa and different pH values was studied. The pH value of 0.1 mol L\(^{-1}\) NaCl with 0.2 g L\(^{-1}\) C\(_{17}\)H\(_{33}\)COONa solution was adjusted to the original pH value of 0.1 mol L\(^{-1}\) NaCl solution (pH 6.3). In Figure 4, it is seen that the passivity state of the aluminum alloy still could be observed and the corrosion potential moved positively, while the pitting potential showed no change. This result indicates that the passivation of aluminum...
alloy was induced not by the increased pH value but by the presence of C\textsubscript{17}H\textsubscript{33}COONa. As an anodic corrosion inhibitor, C\textsubscript{17}H\textsubscript{33}COONa can improve the passivation of aluminum alloy.\textsuperscript{16} The pH solution decrease could cause corrosion potential (E\textsubscript{corr}) to move to the positive direction, which is consistent to the literature results.\textsuperscript{10,16} In addition, in 3.5 wt.% NaCl with 0.2 g L\textsuperscript{-1} C\textsubscript{17}H\textsubscript{33}COONa solution, there was no obvious anodic passive state observed on the polarization curve, which is also consistent with a previous report.\textsuperscript{14} This shows that in solution with high Cl\textsuperscript{-} concentration, 0.2 g L\textsuperscript{-1} C\textsubscript{17}H\textsubscript{33}COONa could not improve the passivity of aluminum alloy.

The corrosion current density (i\textsubscript{corr}) was determined by fitting the cathodic part of the potentiodynamic polarization curves using Tafel extrapolation and the inhibition efficiency (\eta) was calculated. Table 1 shows the changes of i\textsubscript{corr} and \eta with C\textsubscript{17}H\textsubscript{33}COONa concentration. It can be seen that after 0.05 g L\textsuperscript{-1} C\textsubscript{17}H\textsubscript{33}COONa was added, i\textsubscript{corr} apparently decreased and \eta showed a high value. With the C\textsubscript{17}H\textsubscript{33}COONa concentration further increasing, both i\textsubscript{corr} and \eta remained basically stable, indicating that C\textsubscript{17}H\textsubscript{33}COONa has good corrosion inhibition effect for aluminum alloy in the whole studied concentration range.

Table 1. Effects of C\textsubscript{17}H\textsubscript{33}COONa concentration on corrosion current density (i\textsubscript{corr}) and inhibition efficiency (\eta)

<table>
<thead>
<tr>
<th>Concentration / (g L\textsuperscript{-1})</th>
<th>i\textsubscript{corr} / (μA cm\textsuperscript{-2})</th>
<th>\eta / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.4950</td>
<td>–</td>
</tr>
<tr>
<td>0.05</td>
<td>0.2569</td>
<td>95.32</td>
</tr>
<tr>
<td>0.1</td>
<td>0.3739</td>
<td>93.20</td>
</tr>
<tr>
<td>0.2</td>
<td>0.5750</td>
<td>89.54</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4791</td>
<td>92.26</td>
</tr>
</tbody>
</table>

Figure 5 shows the influence of C\textsubscript{17}H\textsubscript{33}COONa concentration on the corrosion potential (E\textsubscript{corr}), the pitting potential (E\textsubscript{b}) and the repassivation potential (E\textsubscript{p}) of AA2024 in 0.1 mol L\textsuperscript{-1} NaCl solution. The addition of sodium oleate raised E\textsubscript{b}, apparently, but when the concentration was higher than 0.1 g L\textsuperscript{-1}, E\textsubscript{b} remained basically stable. With the increase of C\textsubscript{17}H\textsubscript{33}COONa concentration, the separation between the corrosion potential and the pitting potential increased, which is indicative of improved passivity and decreased tendency for pit initiation.\textsuperscript{16} The main reason of the decrease in E\textsubscript{corr} may be ascribed to the increase of OH\textsuperscript{-} concentration in solution. According to Nernst equation:

\[
E_{\text{O}H^- / O_2} = 1.229 - 0.0591 \text{ pH} \tag{2}
\]

the pH variation from 6.3 (0.1 mol L\textsuperscript{-1} NaCl solution) to 9.5 (0.2 g L\textsuperscript{-1} C\textsubscript{17}H\textsubscript{33}COONa with 0.1 mol L\textsuperscript{-1} NaCl solution) would lead the equilibrium potential of the cathodic reduction reaction to move about 0.19 V negatively thereby the corrosion potential would decrease accordingly. The above results indicate that, considering both uniform corrosion and pitting corrosion, the lowest inhibition concentration of C\textsubscript{17}H\textsubscript{33}COONa for aluminum alloy 2024 in 0.1 mol L\textsuperscript{-1} NaCl solution is about 0.1 g L\textsuperscript{-1}.

As an anionic surfactant, the molecule of sodium oleate is composed of both polar hydrophilic group and nonpolar hydrophobic group. The polar group adsorbs on the surface of aluminum alloy to form a barrier film which shows hydrophobicity and can retard or block direct adsorption of the aggressive ions on aluminum alloy surface,\textsuperscript{13} so as to inhibit the onset of pitting attack. In addition, the variation of the repassivation potential (E\textsubscript{p}) with C\textsubscript{17}H\textsubscript{33}COONa concentration shows that the addition of sodium oleate had little effect on the repassivation process of the pits already occurred. This result is consistent with the result in Figure 4, showing that sodium oleate had no apparent inhibition effect in high salty and acidic environments, such as the condition within developed pits.

Figure 6 shows the surface morphology of aluminum alloy 2024 after polarization test in 0.1 mol L\textsuperscript{-1} NaCl solution with 0.2 g L\textsuperscript{-1} C\textsubscript{17}H\textsubscript{33}COONa. There are some micro-pits on the sample surface with deposits similar to corrosion products around the pits. Some pits are open but most of them are covered or partially covered with the products. Figure 7 shows a scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) analysis of selected areas A and B in Figure 6. Chlorine element is detected at both site A and B, revealing that the deposits are the build-up of the corrosion products. It was reported
that in alkaline solutions containing Cl\(^-\), Al(OH)\(_2\)Cl and Al(OH)Cl\(_2\), species would exist on aluminum alloy surface,\(^ {17} \) which is consistent with the EDS analysis result in Figure 7. For aluminum alloy 2024, pitting corrosion is usually associated with the intermetallic particles Al\(_2\)CuMg. Al and Mg are selectively dissolved, leaving Cu-rich remnants. Accompanying the dissolution process, Cu may migrate to the vicinity of the pits to form larger cathodic areas, which would accelerate corrosion of the surrounding aluminum alloy matrix and therefore result in the formation of more pits around the Cu-rich areas.\(^ {9,18-21} \) The EDS analysis in Figure 7a shows that Cu is present in the corrosion products around the pit. Above results indicate that the addition of sodium oleate increased the pitting potential of aluminum alloy, but the initiation mechanism of pitting on aluminum alloy was unchanged.

Figure 8 shows the X-ray photoelectron spectroscopy (XPS) spectra for AA2024 surface after polarization exposure in 0.1 mol L\(^{-1}\) NaCl solutions with and without \(\text{C}_{17}\text{H}_{33}\text{COONa}\). Figures 8a and 8b show the O1s and Al2p spectra without \(\text{C}_{17}\text{H}_{33}\text{COONa}\), and Figures 8c and 8d are the O1s and Al2p spectra with \(\text{C}_{17}\text{H}_{33}\text{COONa}\) respectively. In Figure 8a, the peaks at 532.6, 531.6 and 533.8 eV could be respectively ascribed to Al(OH)\(_3\), Al\(_2\)O\(_3\) and H\(_2\)O adsorbed on aluminum alloy surface.\(^ {22,23} \) In Figure 8c, the peaks at 533.8, 531.9 and 532.6 eV may be attributed to –COO– or adsorbed H\(_2\)O, Al\(_2\)O\(_3\)–OCO–, and Al(OH)\(_3\) or Al–O–CO–.\(^ {22-24} \) The changes of O1s and Al2p peaks indicate that after the addition of \(\text{C}_{17}\text{H}_{33}\text{COONa}\), the peak intensity of Al(OH)\(_3\) and Al\(_2\)O\(_3\) increased. Therefore, sodium oleate promoted the formation of the aluminum oxide/hydroxide on the surface, thereby enhancing the passivity. In Figure 8d, the binding energy of Al2p corresponds to the Al matrix at 72.1 eV and the binding energy of Al2p corresponds to Al\(_2\)O\(_3\) at 74.1 eV.\(^ {13} \) Comparing the Al2p peak at 71.8 eV in Figure 8b and the literature values,\(^ {25} \) there is a 0.3 eV shift for the binding energy of Al after addition of \(\text{C}_{17}\text{H}_{33}\text{COONa}\). The reason probably is that when \(\text{C}_{17}\text{H}_{33}\text{COO}^-\) is adsorbed on the alloy surface, the action between O in the –COO– group and Al would induce the outer electron density of the Al atoms to decrease, leading to increase binding energy. This means that \(\text{C}_{17}\text{H}_{33}\text{COO}^-\) groups could adsorb on aluminum.

Figure 6. Scanning electron microscopy (SEM) morphology of pitting corrosion for AA2024 after corrosion in 0.2 g L\(^{-1}\) \(\text{C}_{17}\text{H}_{33}\text{COONa}\) with 0.1 mol L\(^{-1}\) NaCl solution: (a) morphology; (b) enlarged view around a pit.

Figure 7. Electron microscopy spectrum for selected areas A and B in Figure 6: (a) area A; (b) area B.
Figure 8. X-ray photoelectron spectra for AA2024 surface exposure in 0.1 mol L$^{-1}$ NaCl solution with and without C$_{17}$H$_{33}$COONa. Spectra without C$_{17}$H$_{33}$COONa (a) O1s and (b) Al2p; and with C$_{17}$H$_{33}$COONa (c) O1s and (d) Al2p.

Figure 9. Effects of immersion time on electrochemical impedance of AA2024 in 0.1 mol L$^{-1}$ NaCl solutions containing 0.1 g L$^{-1}$ C$_{17}$H$_{33}$COONa. The decrease of impedance by immersion time is probably related to the orientation change of the adsorbed oleate ions or oleic acid over the immersion time. That is, when more C$_{17}$H$_{33}$COO$^{-}$ ions adsorb on the surface, interaction between tails of C$_{17}$H$_{33}$COO$^{-}$ will occur through van der Waals force. The hydrocarbons chains of many adsorbed ions leave the surface and aggregate to form hemimicelles, causing the reduction of the effective area covered by C$_{17}$H$_{33}$COO$^{-}$ ions to some extent.  

Figure 10 shows the influence of the solution temperature on the impedance spectra of AA2024 in 0.1 mol L$^{-1}$ NaCl solution containing 0.1 g L$^{-1}$ C$_{17}$H$_{33}$COONa. It is seen that the diameter of the capacitance loops reduces by...
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Conclusions

In conclusion, the corrosion inhibition of C\textsubscript{17}H\textsubscript{33}COONa for aluminum alloy in 0.1 mol L\textsuperscript{-1} NaCl solution includes two sides: on one side, C\textsubscript{17}H\textsubscript{33}COO\textsuperscript{-} ions are partially hydrolyzed in solutions to produce OH\textsuperscript{-}, increasing the cathodic reaction rate and enhancing the Al(OH)\textsubscript{3} formation on the alloy surface. On the other side, C\textsubscript{17}H\textsubscript{33}COONa adsorbed on the aluminum alloy surface through electrostatic adsorption or chemisorption form barrier films, preventing the corrosion process and impeding the adsorption and ingress of chloride ions. With the two parts working together, C\textsubscript{17}H\textsubscript{33}COONa could facilitate the passivity of aluminum alloy surface effectively and inhibit the initiation of pits, thereby showing good inhibition effects for both uniform corrosion and pitting corrosion.

In 0.1 mol L\textsuperscript{-1} NaCl solution, surfactant sodium oleate as an anodic inhibitor could promote the passivity of aluminum alloy and shows good inhibition for uniform corrosion of aluminium alloy. While in high concentration of Cl\textsuperscript{-} solution (3.5 wt.% NaCl) sodium oleate could not promote the passivity of aluminium alloy.

For aluminum alloy in 0.1 mol L\textsuperscript{-1} NaCl solution, sodium oleate suppresses the pitting initiation tendency and reduces the sensitivity of pitting corrosion. The addition of 0.1 g L\textsuperscript{-1} C\textsubscript{17}H\textsubscript{33}COONa shows good inhibition performance but further concentration increases has little impact on the inhibition efficiency. For the pits which have already developed, the addition of C\textsubscript{17}H\textsubscript{33}COONa has little effect on the repassivation process.

Besides electrostatic forces, the polar hydrophilic group in sodium oleate may chemically adsorbs on aluminum alloy surface, which would promote oxidation of the aluminum alloy surface.

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