

The Effect of Calcium Nitrite on the Electrochemical Characterization of 3003 Aluminum Alloys in Sea Water

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Abstract: The electrochemical behavior of 3003 aluminum alloys with calcium nitrite in sea water was tested using electrochemical techniques. It was found that calcium nitrite can be used as an inhibitor to protect the 3003 aluminum alloy from corrosion in sea water, if used with a specific volume. Cyclic polarization testing was conducted to investigate the corrosion behavior of the 3003 aluminum alloys at different calcium nitrite volumes. The studies showed that at high volumes (13 ml and up of calcium to 250 ml of sea water) or low volumes (1-7 ml of the calcium nitrite 10 250 ml of sea water), the 3003 aluminum alloy has higher susceptibility to corrosion. When 8ml of the inhibitor used a noticeable difference was observed. Passivation was clear from the cyclic polarization curves. In addition to the cyclic polarization testing, SEM was used to study the surface of the alloys after being exposed to different volumes of calcium nitrite. The results were matched.

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Introduction

Aluminum alloys are well known of their strength, and relatively acceptable corrosion resistance [1]. They are widely used in many industries such as heat exchange systems, food handling, and electronic devices [1, 2]. The corrosion behavior of aluminum alloys in highly corrosive environment depend on the atomic structural of the alloy, chemical composition, the temperature of the solution, the oxygen content, and the effectiveness of the protection method [3]. Many corrosion inhibitors were studied by scientists. The inhibitors can be divided into either organic or inorganic ones [1]. Chromates are one of the major inorganic inhibitors that are still in use. Due to the toxic nature of the chromate, the urge to find an inhibitor that can work as good as chromate but with less toxicants. Citric acid as an inhibitor was studied and it was found that it will protect the aluminum alloys at a specific concentration, while this protection will be decreased as the concentration of the citric acid increased [1].

The effectiveness of the corrosion inhibitors or the corrosion inhibition efficiency is a function of fluid composition, quantity of water, presence of oxygen, and temperatures. With the correct concentration of the fluid and the inhibitor, the inhibition efficiency could increase. One of the mechanisms of the inhibitors effect is the formation of a passive layer that will stop the access of the corrosive substance [4]. Calcium nitrite is an anodic inhibitor, and with anodic inhibitors if too low

concentration used, it will aggravate pitting corrosion, and that was observed in this study [4].

3003H14 aluminum alloys is the focus of the study in this research. 3003 is the most widely used due to the increase of strength over the other types of the aluminum alloys such as 1100 grade [5]. It was found that calcium nitrite is a good corrosion inhibitor for steel in alkaline and concrete environments [6]. In this study the calcium nitrite was tested on 3003 H14 aluminum alloys in 0.5 M NaCl environment. In general aluminum alloys when present in oxygen containing environment such as water or air, they form an oxide layer, which is responsible for the aluminum alloys corrosion resistance property. This property can be affected by many factors, for instance: If the pH of the solution is acidic or basic, continuous temperature change, and the presence of an aggressive ions such as chlorine ions, as the case in this study [7]. It was found in another study that the corrosion rate depend on the pH of the solution, and the Nitrite ions act as anodic inhibitor especially in a highly corroded environment [8]. In this study cyclic polarization measurements and SEM were used to investigate the effect of the calcium nitrite addition to 3003 Aluminum alloys in 0.5M NaCl solution.

2. Experimental procedures

The aluminum alloy used in this study is the bare aluminum panels that are made from 3003 H14. They are 0.025 inches thick. The specimens were 4 by 12 inches. Each sample was cleaned with an alcohol, and air dried for about 15 seconds, before

hooked with the flat cell. After, the samples were placed into a flat electrochemical cell that allowed a 1 cm² area of the sample to be exposed to 0.5 M NaCl solution. The sample was the working electrode; a platinum counter electrode and a saturated calomel reference electrode were placed in the cell. Cyclic polarization technique was used to test the corrosion behavior of the samples, with and without calcium nitrite using a potentiostat. The voltage was scanned from -0.6 mv below the measured open circuit potential up to 1v at a scan rate of 1mv/s while the resulting current was measured and recorded. Calcium nitrite used in this experiment was the standard 30% solution. A pipet was used to deliver different amounts into the 0.5 M NaCl solution, 1ml-15ml. Each test was repeated three times to check the reliability of the test where a new spot on each sample was cleaned as mentioned above for every trial. Each of these samples was then prepared for the SEM.

3. Results and discussion

Figure 1 shows the polarization curves of 3003 Al at different amount of calcium nitrite added as an inhibitor. From the figure, it was noticed that if calcium nitrite added in small quantities it will act as if there is no inhibitor added into the solution. The same trend was observed when more than 8 ml was added to the test solution. The inhibitor addition will increase the passivity of the Al, but as it appears from the graph it is clear that 8 ml of calcium nitrite is providing the lowest corrosion potential if compared when other amounts were added. In addition, the passivity region when 8 ml used was larger compared to the others. SEM was used to look at four different

3003 Al alloy surfaces. Figure 2 shows the surface as the sample received, it is clear that the surface has few scratches from handling the sample and there is no corrosion to begin with. Figure 3, shows the surface with 5ml of calcium nitrite was added. Figure 4 shows the surface when 8 ml of the inhibitor was used, and Figure 5 shows the surface when 15 ml of the inhibitor was used.

It is seen that, calcium nitrite addition, resulted in corrosion potential reduction and formation of passive layer on the Al surfaces with 8 ml Calcium nitrite. The SEM pictures show a match to the cyclic polarization curves, same conclusion reached as when 8ml of calcium nitrite used providing better protection than if other quantities used. Figure 3 and Figure 5 show a rough surface, with deep pitting, while Figure 4 show the surface that was treated with 8ml calcium nitrite, the difference is clear. With the 8ml of the inhibitor a clear protection is obvious; the surface looked as smooth as never touched any corrosive solution, similar to the surface as received. The reason behind these results could be the PH change that the inhibitor will do to the solution, and hence to the samples. The following table shows the PH for different amount of the inhibitor used:

Table 1: The effect of calcium chloride volume and the pH of the solution

ml Calcium Nitrite	PH
5	7.02
8	8.68
15	8.91

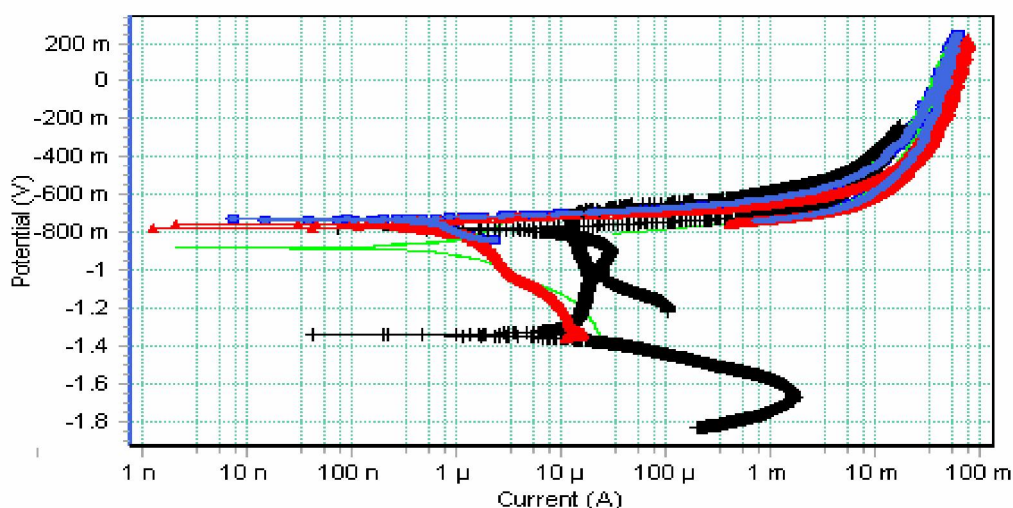


Figure 1: Cyclic polarization curves

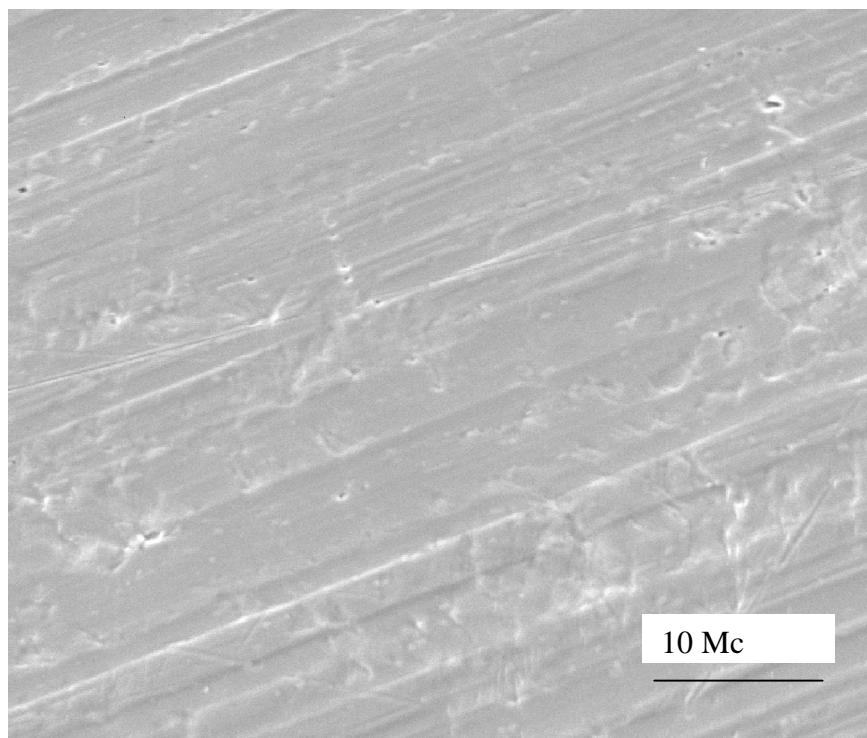


Figure 2 SEM as the sample received

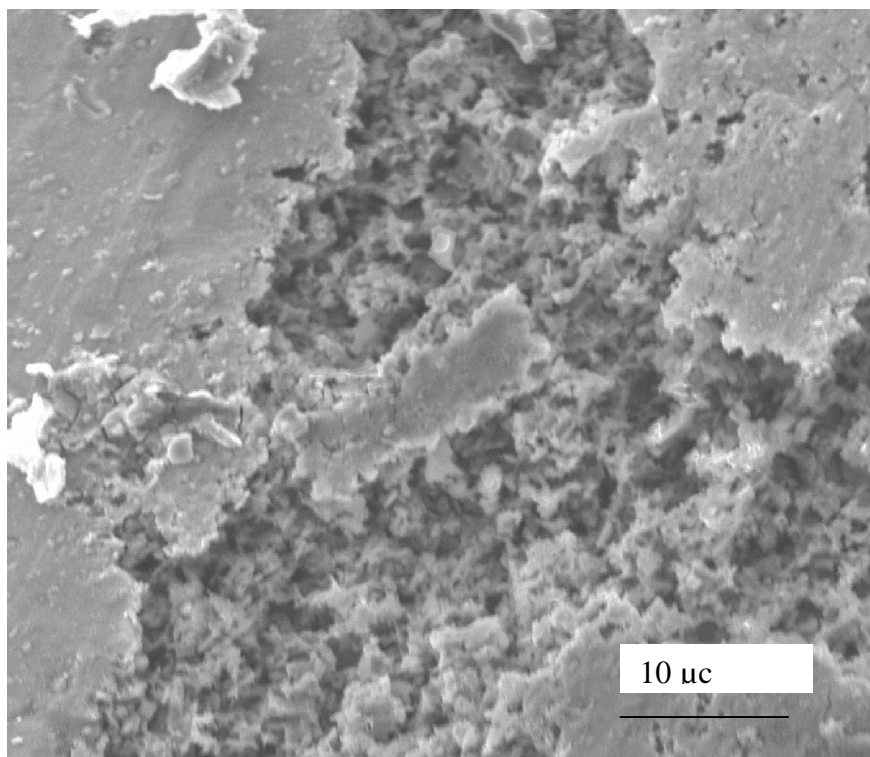


Figure 3 SEM when 5 ml $\text{Ca}(\text{NO}_2)_2$ used

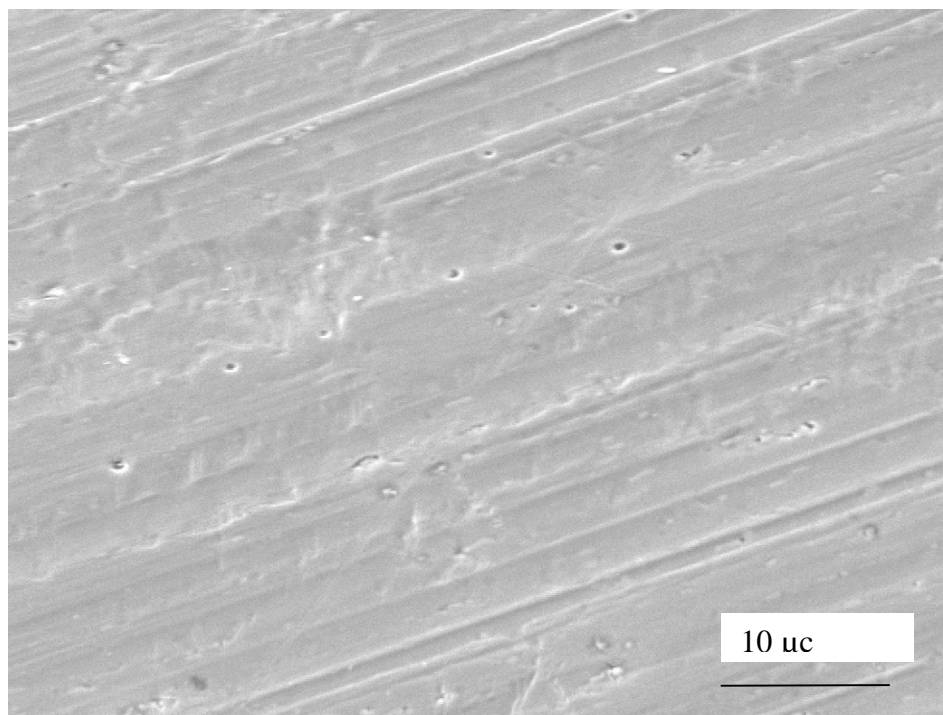


Figure 4 SEM when 8 ml $\text{Ca}(\text{NO}_2)_2$ used

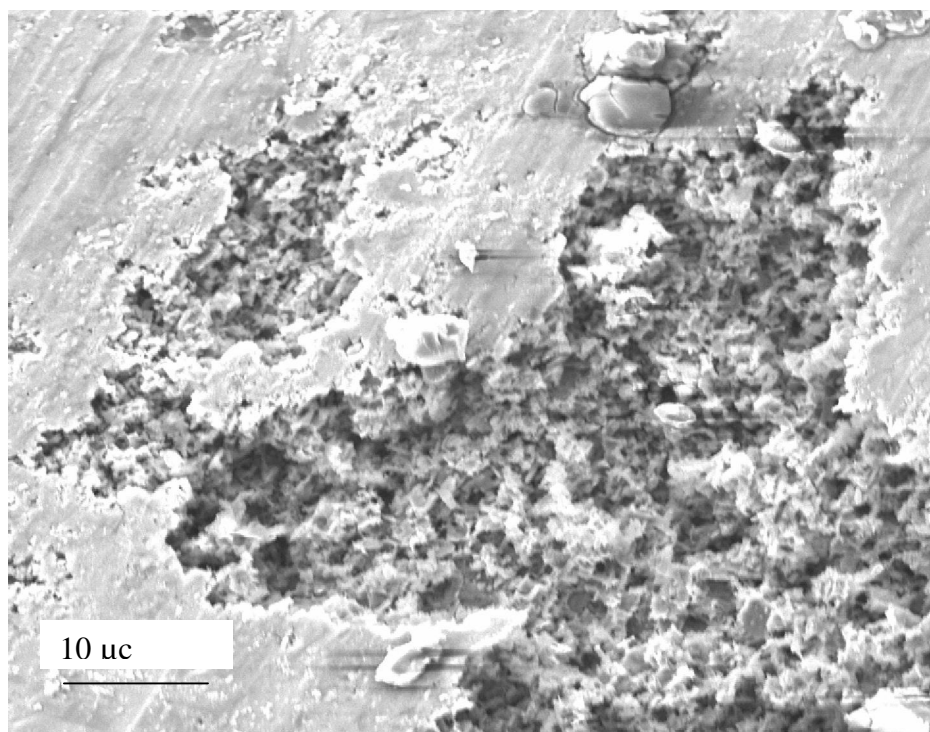
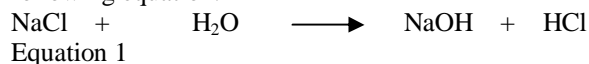
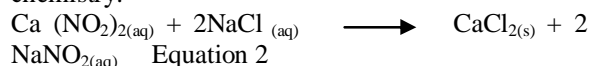


Figure 5 SEM when 15 ml $\text{Ca}(\text{NO}_2)_2$ used

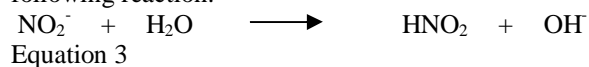
All the above samples were tested under the same conditions of temperatures, room temperature of 25 C was assumed. From the table, when small amount of the inhibitor used, the solution acts neutral, because NaCl when added to water produces a solution with a pH of 7, as both ions are neutral. Na⁺ is the conjugate acid of a strong base, and Cl⁻ is the conjugate base of a strong acid, according to the following equation:



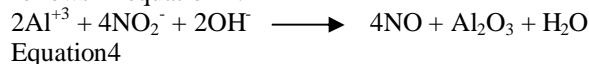
The products will have to effect on the PH of the solution; the solution will corrode the sample due to the presence of the chlorine ions, which is the usual reason for corrosion of the Aluminum alloys. The addition of a small amount of the inhibitor will have no positive or negative effect on the surface of the alloy, the alloy will be have as if there is no inhibitor been added, and the chlorine ion will still attack the surface.. With 15 ml calcium nitrite, the surface as it was shown in Figure 4 was attacked aggressively, and it is clear from the above table, the PH of the solution shows a basic behavior, which could explain the reason for the corrosion. The following molecular equation can explain the chemistry:



NaNO₂ is a soluble compound; its pH is greater than 7. The NO₂⁻ is basic as its conjugate base of a weak acid. The Na⁺ ion is neutral as it is the conjugate acid of a strong base. The basic NO₂⁻ ion will raise [OH⁻] in the solution through the following reaction:



Increasing the [OH⁻] increases the pH of the solution, which will have a corrosive effect on the surface if it exceeded a certain amount. If compared to Figure 3, which shows the effect of adding 8 ml of the inhibitor into the solution. The difference is clear that at this stage calcium nitrite is acting as an inhibitor to corrosion, as the nitrite ion in the presence of the hydroxide and aluminum ions will produce the barrier layer of aluminum oxide, as it follows in equation 4.



4. Conclusions

The inhibitor used for this experiment was the calcium nitrite. It was found that the amount of the inhibitors has to be used with care. From the results, it was clear that using a small amount of the

inhibitor compared to the total sodium chloride solution, will have no inhibition effect on the aluminum alloy surface. In addition it was found with exceeded amount of the inhibitor in the sea water, the inhibitor can actually act as a corrosive material, and it will accelerate corrosion. Hence, there is a higher susceptibility to pitting corrosion with either small or large amount of the inhibitor. Using just right amount, will actually help in forming the barrier protective oxide layer on the surface of the aluminum alloys, and minimize the pitting corrosion as it was clear from the SEM pictures.

The increase in the amount of the inhibitor will not result in more corrosion protection, it will increase the susceptibility to pitting corrosion.

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