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Synergistic Effect of Anions in the Corrosion
of High Strength 7075-T6 Aluminum Alloy

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Jia-Dong Yeh

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SYNERGISTIC EFFECT OF ANIONS IN THE CORROSION OF HIGH STRENGTH 7075-T6 ALUMINUM ALLOY

BY

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ABSTRACT

SYNERGISTIC EFFECTS OF ANIONS IN THE CORROSION OF HIGH STRENGTH 7075-T6 ALUMINUM ALLOY.

BY

Jia-dong Yeh

This study is focused on the first steps in the pitting process, the adsorption of chloride ions and the inhibition mechanism of sodium nitrate and sodium nitrite upon 7075-T6 aluminum alloy.

The experimental results support the idea that the corrosion is controlled by the relative rates of the repair and breakdown of the protective aluminum oxide film in the corroding medium. In the presence of chloride ions, the predominent anodic process is the formation of soluble aluminum chloride instead of aluminum oxide. Sodium nitrate is an effective oxidizing passivator, which inhibits corrosion by the adsorption displacement of Cl^- from the surface and formation of a stable, insoluble aluminum oxide film. Finally, a competitive reaction between nitrite anions and chloride anions on the aluminum oxide must be incorporated into aluminum chloride equilibra with the net result of retarding the formation of soluble $AlCl^-_4$ type species due to the enhance adsorption capacity of nitrite ions on the aluminum oxide.

ACKNOWLEDGEMENT

The author wishes to thank Dr. Robert Summitt for this patience, support, guidance and friendship throughout the course of this work.

Special thanks to my family for their love and support without which this work would not have been possible.

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I. Introduction

A. General Introduction

The corrosion behaviors of high strength 7075-T6 aluminum alloy in NaCl, NaCl-$NaNO_3$, and NaCl-$NaNO_2$ solutions have been investigated by weight losses, and chemical analysis measurements. A 14 day alternate immersion method, which utilizes a one hour cycle that includes a 10 minute period in an aqueous solution followed by a 50 minute period out of the solution, was used in this study. In addition, the corrosion products were examined using an optical microscopic to determine the type and extent of attack or inhibition.

B. General Background

High strength 7075-T6 aluminum alloy is often used, when weight and strength are important factors, as in aircraft. However, high strength 7075-T6 aluminum alloy is subject to corrosion in aggressive environments.

Aluminum alloys are extremely susceptible to chloride attack. Therefore, it is important that an inhibitor system be developed that demonstrates the ability for passivation against chloride ion.

The classification of inhibitors[1], which is generally accepted, is as follows : (1) adsorption type (mainly chemisorption); and (2) film forming - passivating (oxidizing and nonoxidizing) ; and (3) precipitation.

A classical example of adsorption type of inhibitor may be found in the pitting corrosion prevention of stainless steels. The protection is related to the adsorption displacement of Cl^- from the surface by inhibiting ions. The study of the adsorption of chlorine ions demonstrates a competing adsorption resulting in Cl^- displacement from the surface in the presence of inhibiting ions[1]. McCafferty[2] has also obtained expermental evidence that the adsorption characteristics of inhibitors are determined by their electron donating ability.

On the other hand, one can cite many examples when, in the inhibiting process, increased corrosion resistance is caused by the emergence of protective film on the alloy surface[1]. An example of this type of inhibitor is the oxidizing inhibitor. Oxidizing inhibitor function by shifting the electrochemical potential of the corrosion metal into a region where a stable, insoluble oxide or hydroxide forms which protects the metal surface. This type of inhibitor is especially effective on steels, although it is also effective on aluminum , copper alloys and certain other alloy systems.

Sodium nitrate is considered to be an oxidizing inhibitor, which is very effective in aqueous systems that contain chloride[3]. These compounds, which are readily reduced, promote the formation of a stable, insoluble metal oxide on the metal surface.

A program was conducted to investigate the corrosion-inhibiting properties of sodium chloride, sodium nitrate, and sodium nitrite in corrosion of aluminum alloy.

II. Theoretical Background

A. Breakdown and Pore Formation of Oxide Film on Metals

When a fresh aluminum surface is exposed to air, it oxidizes rapidly, and, as a result, a compact, adherent protective film of aluminum oxide (alumina) is formed. In aqueous solutions, surface layers, which for the greater part consist of crystalline hydrates of alumina, are developed [4]. Aluminum oxide is relatively inert chemically, and the passive behavior of aluminum depends on this inactivity [5]. If the oxide film dissolves, the metal corrodes uniformly,and Lorking and Mayne [6,7] have shown that corrosion was associated with the initial rate of solution of the anhydrous oxide. On the other hand, when the film is damaged under conditions that prevent normal self-repairing, the same amount of corrosion is located at one particular spot, and extensive damage known as pitting corrosion occurs [8].

The breakdown of passive films by halide ions has been reviewed by Kolotyrkin [9], Hoar [10], Foley [11], and more recently by Galvele [12]. From the many reports in the literature the prevalent explanations for pit initiation may be classified as follows : (1) competitive adsorption, halide ions are adsorbed preferentially to species such as OH^- and H_2O that would passivate the metals, (2) the halide ion penetrates the oxide film, possibly through cracks or fissures, and attacks the bare metal, (3) the halide ion diffuses through the oxide film (lattice diffusion) and attacks the meatl, (4) the halide ions peptize the hydrous oxide film in the colloidal sense, and (5) the halide ions form complexes with aluminum ions to render soluble reaction products that are normally insoluble.

However, there is not as yet a unanimously recognized explanation with respect to the mechanism by which an oxide film loses its protective ability.

Recently, Foley and Nguyen [13] postulated that the initiation of pitting of aluminum in halide solutions proceeds in four consecutive steps : (1) the adsorption of the aggressive anion on the oxide film ,

$$Cl^- \text{ (in bulk solution) } \rightleftharpoons Cl^- \text{ (adsorbed on } Al_2O_3\cdot nH_2O \text{ sites)}$$

(2) the chemical reaction of the adsorbed anion with the Al^{+3} in the oxide lattice;

$$Al^{+3} \text{ (in } Al_2O_3\cdot nH_2O \text{ lattice) } + Cl^- \rightleftharpoons Al(OH)_2Cl$$

or

$$Al^{+3} \text{(in } Al_2O_3\cdot nH_2O \text{ lattice) } + Cl^- \rightleftharpoons Al(OH)_2Cl_2^-$$

(3) the thinning of the oxide film by dissolution;

(4) the direct attack of the exposed metal by the aggressive anion with the formation of transient

complexes which rapidly undergo hydrolysis

$$Al^{+3} + 4\ Cl^- \rightleftharpoons AlCl_4^-$$
$$AlCl_4^- + 2\ H_2O \rightleftharpoons Al(OH)_2Cl + 2\ H^+ + 3\ Cl^-$$

It has been reported [14] that the preferential adsorption sites may be defects or flaws in the oxide film.

Foley and Nguyen also have investigated [15] a reaction scheme for the metal dissolution processes by using scrape potential technique. They concluded that the controlling step is the complexation reaction of the hydrated cation with the anion present. The overall reaction of aluminum with water is usually written as :

$$Al + 3\ H_2O \rightleftharpoons Al(OH)_3 + 3/2\ H_2$$

and the following reactions involving some aluminum species occur during dissolution in the chloride solution :

$$Al \rightleftharpoons Al^{+3} + 3\ e^- \qquad (1)$$
$$Al^{+3} + H_2O \rightleftharpoons H^+ + AlOH^{+2} \qquad (2)$$
$$AlOH^{+2} + Cl^- \rightleftharpoons Al(OH)Cl^+ \qquad (3)$$
$$AlCl^{+2} + 2H_2O \rightleftharpoons Al(OH)_2Cl + 2\ H^+ \qquad (4)$$
$$Al(OH)Cl^+ + H_2O \rightleftharpoons Al(OH)_2Cl + H^+ \qquad (5)$$
$$Al(OH)_2Cl + H_2O \rightleftharpoons Al(OH)_3 + H^+ + Cl^- \qquad (6)$$

$$Al(OH)_3 \text{ (amorphous)} \rightleftharpoons r\ Al_2O_3 \cdot H_2O \qquad (7)$$

B. Mechanism of Pit Growth in The Presence of NaCl Solution.

Rosenfeld [16] has proposed an mechanism in which the metal within the pit suffers anodic attack as a result of restricted oxygen supply, and the external (areated) surface forms a large cathode. Inside the pit, Anodic dissolution, together with hydrolysis of the product metal ion, can cause an increase of hydrogen ion concentration. If the net corrosion reaction plus hydrolysis should lead to an increase of hydrogen ion concentration , the process would occur independently of any other process, and would accelerate with time to a steady state where diffusion out of the pit region would limit the buildup. If the corrosion reaction plus hydrolysis should lead to no net change in H^+ concentration, merely an acid solution in a pit would be created. If the corroding solution contains some chloride ion, these transferred anions may be chloride ions, and acid formed inside the crevice is hydrochloric acid. Pourbaix [17] has claimed that this is one reason why chlorides are particularly harmful in promoting pitting corrosion and stress corrosion cracking.

Fontana [18] and Greene suggested another mechanism, based on electroneutrality, where chloride ions migrate into the crevice to balance the otherwise increasingly positive charge resulting from metal ion concentration. This gives rise to an accumulation of aggressive anions within the pits.

It has been shown [19] that during the pitting corrosion there was heavy pickup of chloride ions in pits as the aluminum chloride species was trapped in the pits with restricted diffusion. Similar results were obtained more recently by Berzines et al. [19], who measured adsorption isotherms on corroding Al with $^{36}Cl^-$. The adsorption was mainly localized to the corroding pit sites.

Alkire, Hebert and Siitari [20,21] also postulate the importance of Cl^- inside the crack. If accumulation by migration of chloride ions within the crevice is significant, it is possible that activation behavior would depend on Cl^- concentration. The influence of Cl^- concentration on pitting also has been studied by Bogar and Foley [22]. At the higher Cl^- concentration, the following reaction will take place.

$$Al + 4\ Cl^- \rightleftharpoons AlCl_4^- + 3\ e^-$$

$$Al + 4\ Cl^- + 3\ H^+ \rightleftharpoons AlCl_4^- + 3/2\ H_2$$

This action of Cl^- promotes pit growth.

C. Mechanisms of Metals Passivation with Inhibitors.

In considersing the inhibition of the corrosion of aluminum and aluminum alloys by the aggressive anions, the starting point is to examine the steps by which aggressive anions act on aluminum. These steps have been established[1]

(1) Adsorption of halide (e.g. Cl^-) on the aluminum oxide surface,

(2) Complexing of aluminum cation in the oxide lattice with halide to form a soluble $AlCl_4^-$ species,

(3) Soluble species diffuse away from the surface resulting in a thinning the protective oxide film,

(4) At sufficiently thinned sites, the aluminum reacts directly with the electrolyte.

A compound proposed as an inhibitor may be involved in the mechanism in either of the first two steps. The compound may compete for adsorption sites and retard the formation of soluble halide species. Secondly, the compound, as its anion, can compete with Cl^- in the $Al^{+3} + 4\ Cl^- \rightleftharpoons AlCl_4^-$ equilibrium reaction again preventing the formation of soluble halide species. But, in the latter case, if an inorganic anion forms a stable complex ion with the aluminum cation, then dissolution will proceed just as it would with the formation of the aluminum halide species.

Sodium nitrate - this compound is considered to be oxidizing passivators that provide the formation of protective oxide film, which is very effective in aqueous systems that contain chloride [23]. Augustynski [24] has postulated the mechanism of nitrate ions on the corrosion inhibition that nitrate ions presumably enter the oxide lattice, after being adsorbed on the oxide / solution interface, and are successively reduced in a N-type region of the film containing excess metal ions and trapped electrons.

The reduction of nitrate ions :

$$NO_3^- + H_3O^+ + 3\ Al^{+3} + 9\ e^-$$
$$= AlN + Al_2O_3 + 1/2\ H_2 + H_2O \text{ (overall reaction)},$$

which is followed by the hydrolysis of aluminum nitride :

$$2\ AlN + 3\ H_2O = Al_2O_3 + 2\ NH_3$$

must be accompanied by the oxidation of aluminum occuring at the metal / oxide interface :

$$Al = Al^{+3} + 3\ e^-$$

and the diffusion of Al^{+3} ions towards the oxide / solution interface.

III. Apparatus and Experimental Procedure

A. Specimen

For all the measurements, bare rectangular sheets of high strength 7075-T6 aluminum alloys were employed. The chemical analysis for this aluminum alloy is given in Table.1

Table 1

7075-T6 Aluminum Alloy

Element	Zn	Mg	Cu	Cr	Mn
%	5.52	2.76	1.41	0.23	0

B. Preparation of Specimen

The test coupons were fabricated as close to dimension of 4.6 x 1.7 x 0.16 cm as possible, with a 0.26 cm hole near one end for suspension purposes. After fabrication of the coupons. They were cleaned in the conventional manner. The coupon was immersed in NaOH solution (5 g/100 ml) at 75°-80°C for 1 minute at room temperature, and thoroughly rinsed in distilled water and acetone. The coupon were suspended by means of glass hooks to avoid solution contamination[25].

The dimensions of each specimen were carefully measured to determine the surface area (appendix I). In case the specimens were not carefully square, five measurements of each dimension were taken at different points on the specimen and averaged.

Samples were immersed in solution of various salt concentration for periods of 14 days at room temperature. Immediately following the alternate immersion test, the corrosion product was removed with a stripping solution of 20 gm of chromic acid and 32.5 ml of 85% phosphoric acid / liter at 80°C for 1 to 10 minutes, or until clean. If a film remained, the specimen was dipped in concentrated nitric acid for 1 minute at room temperature.

After cleaning, the coupons were rinsed with distilled water and acetone and allowed sufficient time to dry thoroughly. The weight loss reported was the difference in weight of the sample before the test and that after the immersion.

C. Determination of Cl^- Concentration

In this study, we use the Mohr Argentometric Method to determine the chloride ion concentration in the bulk solution. This method uses silver nitrate as the titrant and potassium chromate as the indicator. Silver nitrate first reacts selectively with the chloride ion in the sample to produce insoluble white silver chloride. After all the chloride ion has been consumed, the silver nitrate reacts with the chromate to form an orange-colored silver chromate precipitate, marking the end point of the titration. The indicator blank should be determined by titrating distilled water in the same way. The procedure of titration as follows:

1. Take sample by filling a clean 100-ml graduated cylinder to the 100-ml mark. Pour the sample into a clean 250-ml erlenmeyer flask.
2. Add the contents of one chloride 2 indicator powder pillow and swirl to mix.
3. Titrate the sample with silver nitrate standard solution while swirling the flask until the color changes from yellow to red-brown.
4. calculation as followed:

$$g / l\ Cl^{-} = (\text{ml } AgNO_3 \text{ sample} - \text{ml } AgNO_3 \text{ blank}) \times \text{N. of } AgNO_3 \times 35.46 / \text{ml sample}$$

D. Ultraviolet Spectrophotometric Determination of Nitrate Ions and Nitrite Ions [26]

The nitrate ion in the aqueous solution shows electronic adsorption bands centered at about 301 and 203 nm. with molar absorptivities of about 7,000 and 9,500 l / mole. cm, respectively.

The nitrite ion in the aqueous solution shows electronic adsorption bands centered at about 356, 280 and 210 nm. with molar absorptivities of about 23,000, 9,000 and 47,000 l / mol. cm respectively.

IV. Experimental Results

A. The Corrosion Behaviors of 7075-T6 Aluminum Alloy in NaCl Solutions

The weight losses and adsorption of chloride ions for the various concentration of NaCl solutions are given in Tables 2-3, and the weight loss and adsorption of chloride ions as a function of concentration of NaCl solution are graphically represented in Figures 1-2, The maximum weight losses is observed at 2.0 wt.% NaCl solution. In general, appreciable weight losses were an indication that some pits had formed, so that a plot of weight loss was also an indication of corrosion by pitting. Therefore, the corrosion by pitting exhibited a maximum effect at 2.0 wt.% NaCl solution.

At low concentration of sodium chloride solution, adsorption of chloride ions is linear with concentration and, at high concentration, reaches a plateau on which adsorption is independent of concentration. From these results, it can be found that the amount of adsorption of chloride is linear with the amount of weight losses, and it agrees with Berzins' observation[19] that the adsorption of chloride ions were localized to corroding pit sites.

In order to better understand the initial stage of development of a corroding aluminum surface, we used an optical microscopic to study the breakdown of passivating oxide film by chloride ions. The typical pit corrosion of

Table 2 Weight Changes of 7075-T6 Aluminum Alloy After 14 Day Alternate Immersion in Various sodium Chloride Solutions.

NO	ELECTROLYTE	SPECIMEN SURFACE AREA (cm^2)	SPECIMEN WGT. LOSS 10^4 (g/cm^2)
1	0.1 wt% NaCl	10.191	6.869
2	0.5 wt% NaCl	9.963	31.517
3	1.0 wt% NaCl	10.326	49.196
4	2.0 wt% NaCl	10.097	50.708
5	3.0 wt% NaCl	9.921	47.677
6	4.0 wt% NaCl	9.751	28.920
7	5.0 wt% NaCl	10.005	29.785

Table 3 Chloride Concentration Before and After Adsorption. Alternate Immersion Tests with 7075-T6 Aluminum Alloy in Different Concentration of Sodium Chloride Solutions.

SOLUTION	INITIAL Cl^- CONC. (g/l)	FINAL Cl^- CONC. (g/l)	Cl^- ADSORPTION 10^4 (g/l cm^2)
0.1 wt% NaCl	0.636	0.632	3.925
0.5 wt% NaCl	3.219	3.194	25.093
1.0 wt% NaCl	6.401	6.328	70.695
2.0 wt% NaCl	10.601	9.934	69.030
3.0 wt% NaCl	13.286	13.214	72.573

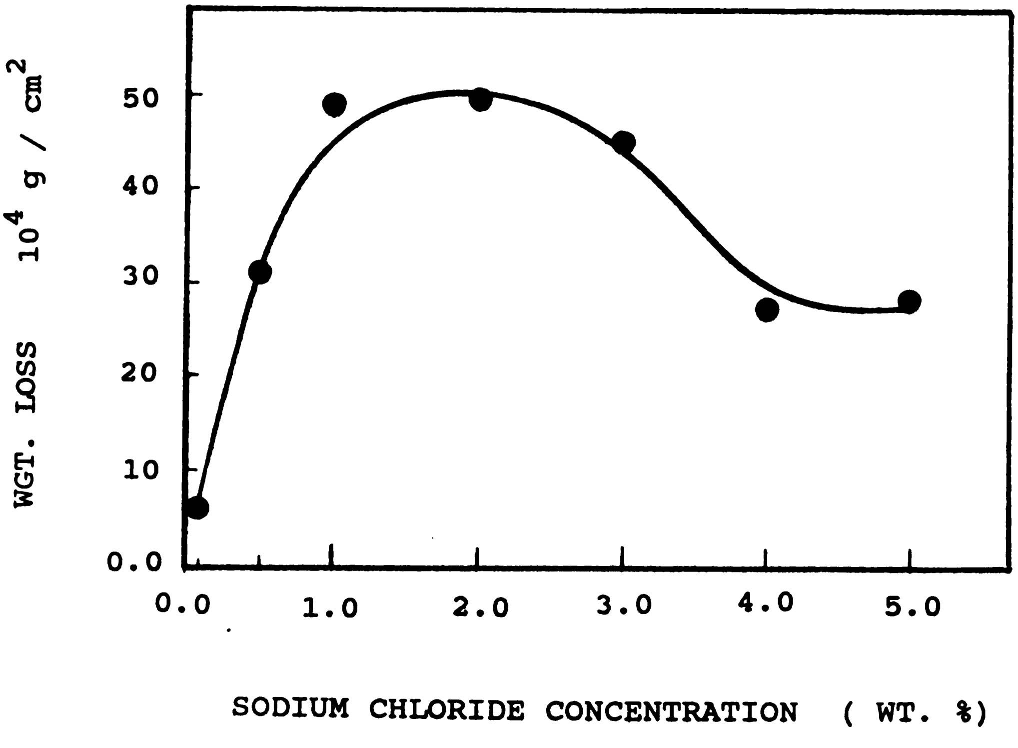


Figure 1 Effect of NaCl on the Corrosion of 7075-T6 Aluminum Alloy after 14 Day Alternate Immersion tests.

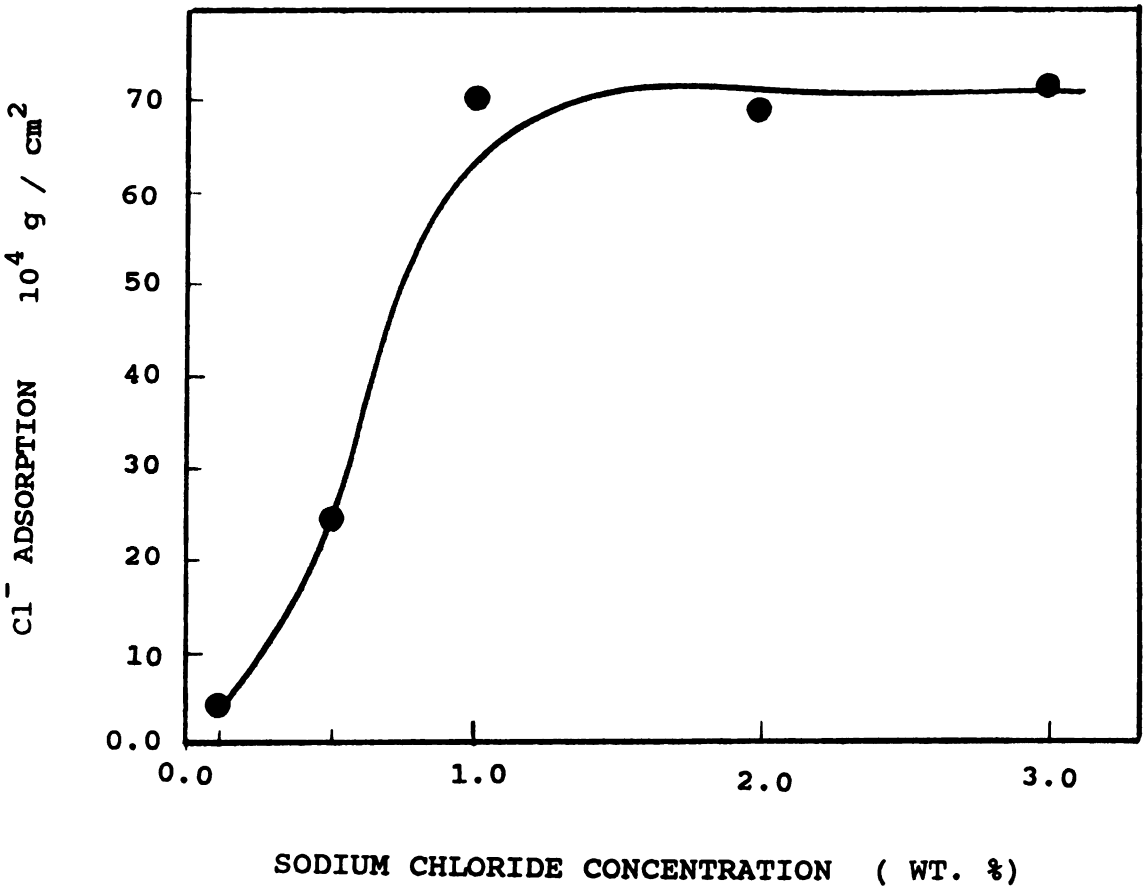


Figure 2 **Adsorption of Chloride on 7075-T6 Aluminum Alloy after 14 Day Alternate Immersion Tests.**

aluminum alloy is shown in Figure 3(a). This investigation is followed by immersing the same specimen in 0.1 wt.% NaCl solution over a period of 72 hours, as shown in Figures 3(b)-(d).It is obvious that a bare aluminum surface site is exposed to the aggressive environment, and results in serious pitting after the breakdown of the protective aluminum oxide film. From Figures 3(a)-(d) we observed the following results : (1) the existence of passivating oxide film, (2) only a few active sites for pitting corrosion, as indicated by arrow, (3) the progressive breakdown of passivating oxide film.

The characteristics of the progressive breakdown of protective oxide film agree with the mode of adsorption model, as shown in Figure 4.

B. The Corrosion Behaviors of 7075-T6 Aluminum Alloy in NaCl-$NaNO_3$ Solutions.

A series of experiments were carried out to study the inhibitive effect of nitrate ions on the weight losses of aluminum and the adsorption of chloride ions. The results are shown in Tables 4-5, and Figures 5-6. Figures 5-6 show that the weight losses of aluminum and the adsorption of chloride ions were progressively reduced with increasing concentration of sodium nitrate, and the nitrate ions tended to completely inhibit the pitting corrosion in the high concentration of sodium nitrate

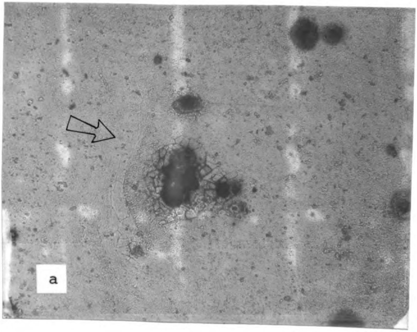
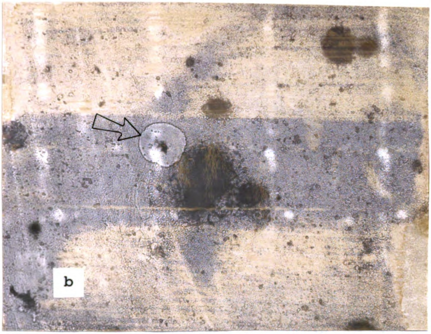
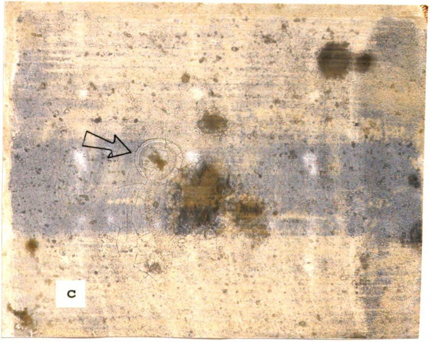


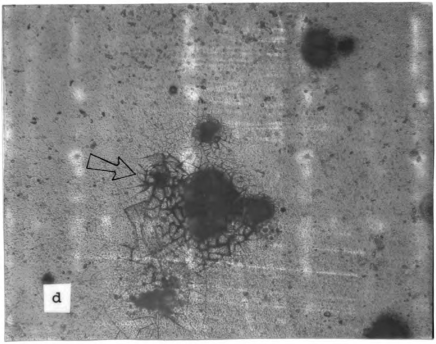
Figure 3 Photomicrographs in Sequence Showing the Surface Appearances of 7075-T6 Aluminum alloy in 0.1 wt.% NaCl - 0.1 wt.% $NaNO_3$ after 14 Day Alternate Immersion Tests (a), Followed by Immersing in 0.1 wt.% NaCl for 24 Hours (b), 30 Hours (c), 72 Hours (d), 200X . The Active Site for Pitting Corrosion is indicated by Arrow.



Immersing in 0.1 wt.% NaCl Solution for 24 Hours.



Immersing in 0.1 wt.% NaCl Solution for 30 Hours.



Immersing in 0.1 wt.% NaCl Solution for 72 Hours.

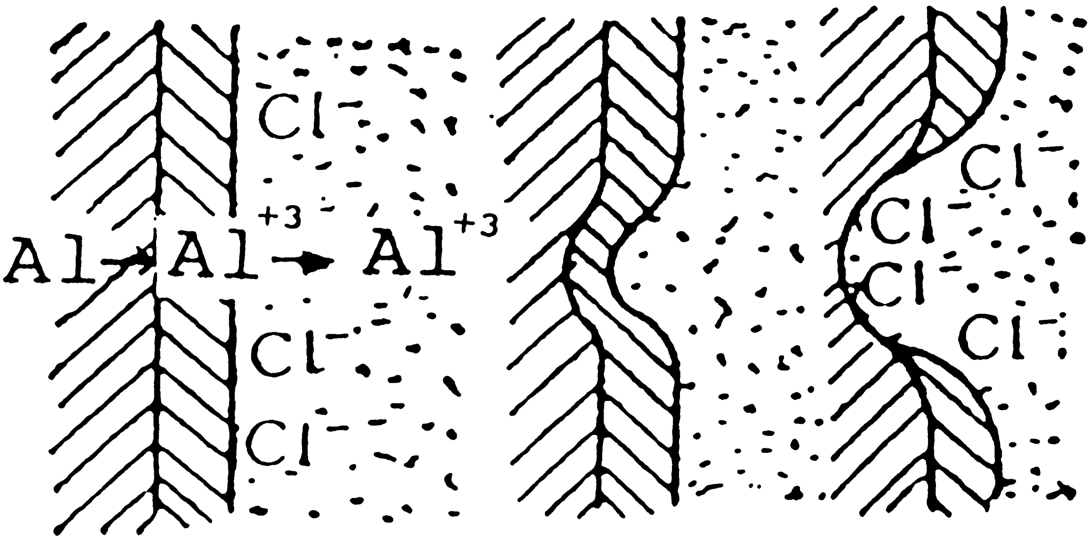


Figure 4 Mode of adsorption Mechanism for Chloride Ions Acting on the Aluminum.

Table 4 Weight Changes of 7075-T6 Aluminum Alloy After 14 Day Alternate Immersion in Salt Solutions of Various Nitrate / Chloride Ratios.

NO	ELECTROLYTE	SPECIMEN SURFACE AREA (cm^2)	SPECIMEN WGT. LOSS 10^4 (g/cm^2)
1	0.1 wt% NaCl / 0.03 wt% $NaNO_3$	9.781	1.431
2	0.1 wt% NaCl / 0.05 wt% $NaNO_3$	10.108	0.890
3	0.1 wt% NaCl / 0.06 wt% $NaNO_3$	10.316	0.679
4	0.1 wt% NaCl / 0.08 wt% $NaNO_3$	10.186	0.589
5	0.1 wt% NaCl / 0.1 wt% $NaNO_3$	10.065	0.497
6	0.1 wt% NaCl / 0.3 wt% $NaNO_3$	10.072	0.397
7	0.1 wt% NaCl / 0.5 wt% $NaNO_3$	10.158	0.295
8	0.1 wt% NaCl / 1.0 wt% $NaNO_3$	10.367	0.096

Table 5 Chloride Ion Concentration Before and After Adsorption. Alternate Immersion Tests with 7075-T6 Aluminum Alloy in Salt Solution of Various Nitrate / Chloride Ratios.

SOLUTION	**INITIAL Cl^- CONC. (g/l)**	**FINAL Cl^- CONC. (g/l)**	**Cl^- ADSORPTION 10^4 (g/l cm^2)**
0.1 wt% NaCl/ 0.03 wt% $NaNO_3$	0.607	0.603	4.090
0.1 wt% NaCl/ 0.05 wt% $NaNO_3$	0.613	0.609	3.960
0.1 wt% NaCl/ 0.06 wt% $NaNO_3$	0.604	0.600	3.877
0.1 wt% NaCl/ 0.08 wt% $NaNO_3$	0.609	0.605	3.927
0.1 wt% NaCl/ 0.1 wt% $NaNO_3$	0.612	0.608	3.974
0.1 wt% NaCl/ 0.3 wt% $NaNO_3$	0.611	0.609	1.986
0.1 wt% NaCl/ 0.5 wt% $NaNO_3$	0.613	0.611	1.969
0.1 wt% NaCl/ 1.0 wt% $NaNO_3$	0.613	0.611	1.929

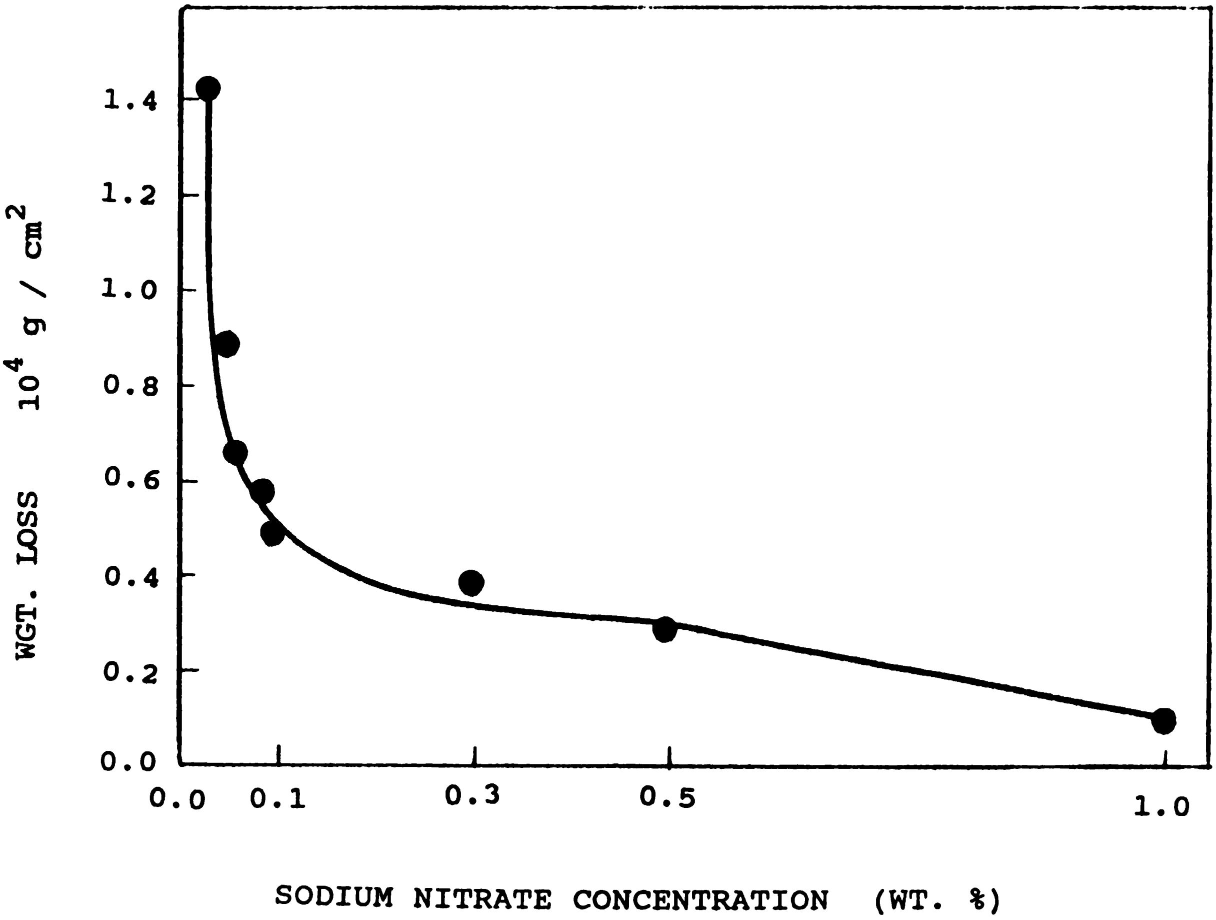


Figure 5 Effect of $NaNO_3$ Addition to 0.1 wt.% NaCl Solution on the Corrosion of 7075-T6 Aluminum Alloy.

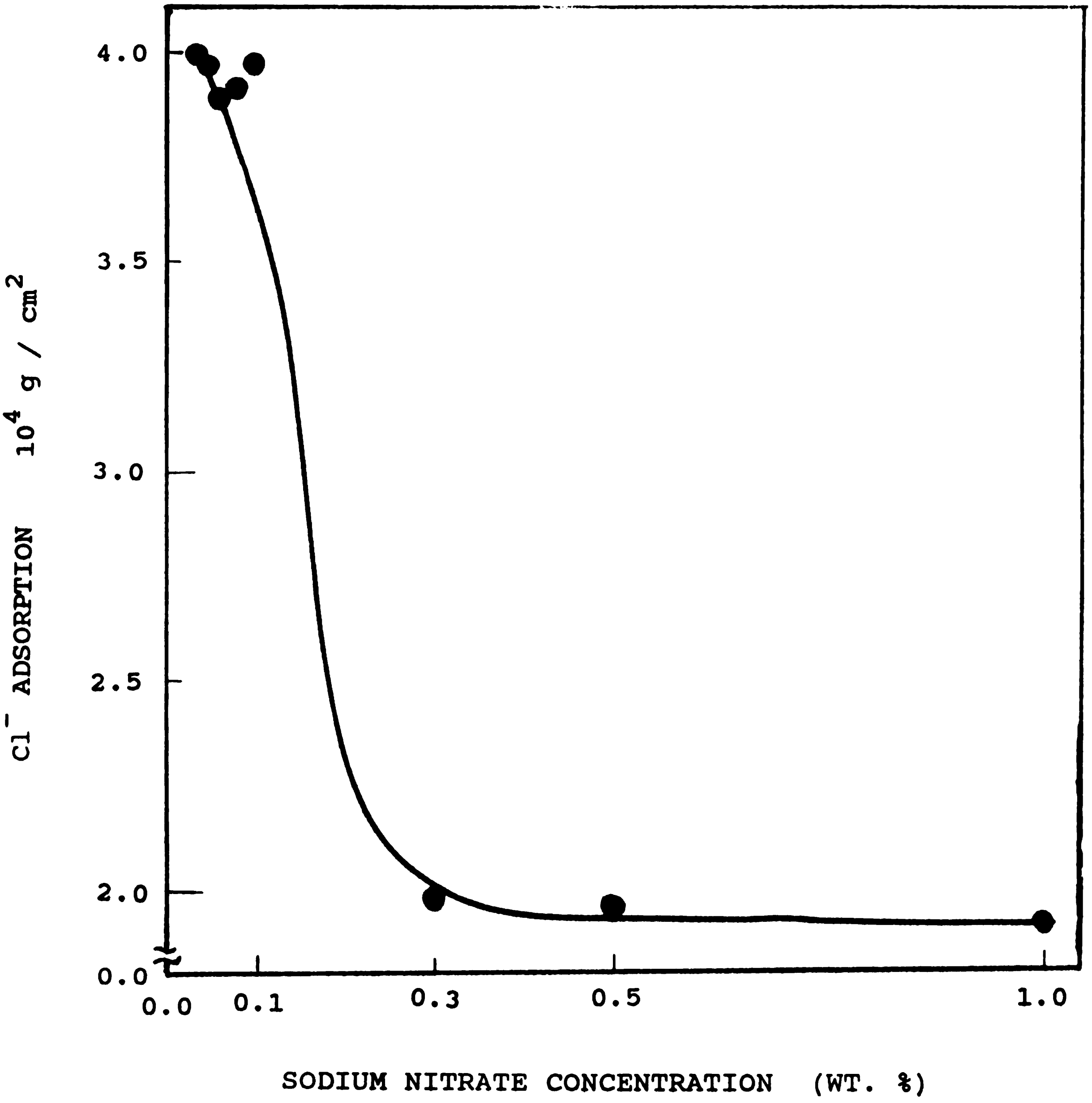


Figure 6 **Adsorption of Chloride Ion on the 7075-T6 Aluminum Alloy in Various $NaNO_3$ Solutions.**

solution. Also, we observed that the amount of adsorption of chloride is linear with the amount of weight losses of aluminum.

In order to better understand the inhibition of pitting by NO_3^-, a sequence of experiments was carried out to study the surface appearances by using optical microscopic . Figure 7(a)-(b) shows the surface appearances of aluminum exposed in 0.1 wt.% NaCl solution for 2 hours,7(a) then exposed in distilled water for 12 hours ,7(b). Figures 7(a)-(b) show effects of distilled water upon the pitting corrosion 7075-T6 aluminum alloy. It shows that the surface appearances are unchanged after immersing the same specimen in the distilled water. However, it appears that the oxide was repaired, as indicated by arrow, after immersing the previous specimen in 1.0 wt.% $NaNO_3$ over a period of 24 hours as shown in Figures 7(c)-(d). We, again, observed that the protective oxide film was breakdown, and aluminum alloy resulted in serious pitting after immersing the specimen back in to 0.1 wt.% NaCl solution in Figure 7(e)-(f). The characteristics of the film repair is simply represented in figure 8.

C. The Corrosion Behavior of 7075-T6 Aluminum alloy in NaCl-$NaNO_2$ Solutions.

A series of experimentals were carred out to study

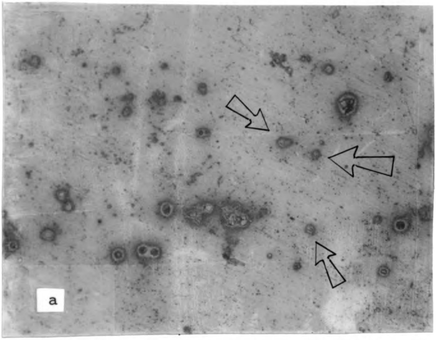
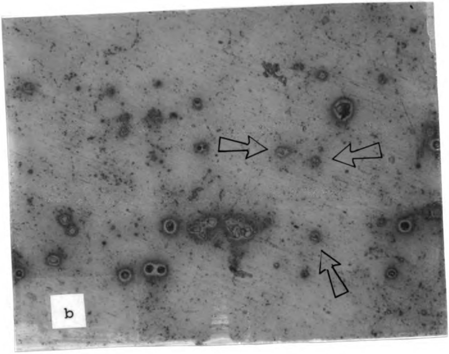
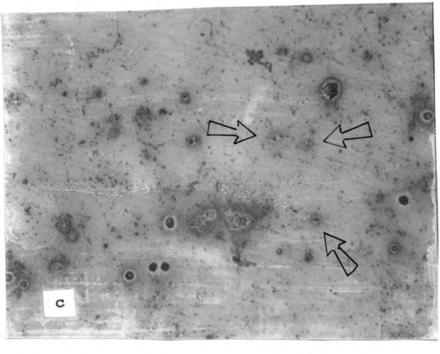


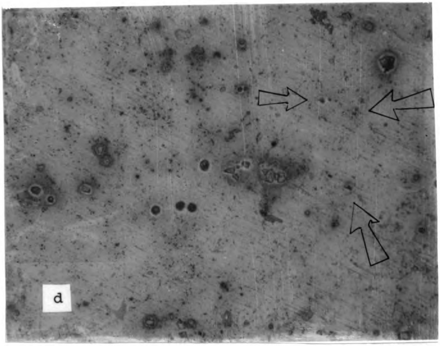
Figure 7 Photomicrographs in Sequence Showing the Surface Appearances of 7075-T6 Aluminum Alloy in 0.1 wt.% NaCl for 2 Hours (a), then Exposed in Distilled Water for 12 Hours (b), Followed by Immersing in 1.0 wt.% $NaNO_3$ for 12 Hours (c), for 24 Hours (d), and then 1.0 wt.% NaCl for 1 Hour (e), for 2 Hours (f), 500X . The Repair and Breakdown of oxide film is indicated by arrows.



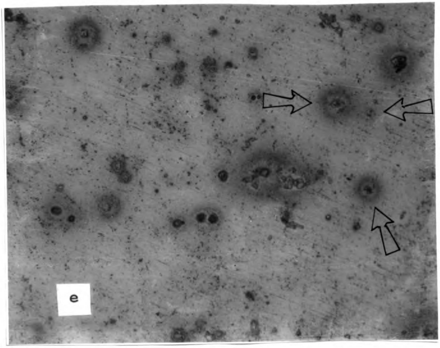
Exposed in Distilled Water for 12 Hours



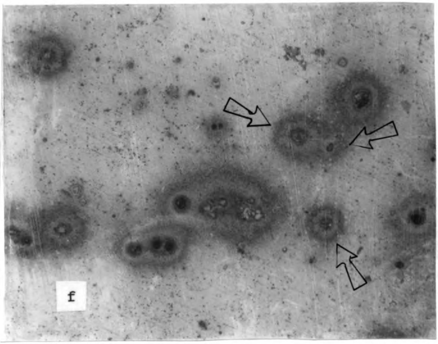
Immersing in 1.0 wt.% $NaNO_3$ Solution for 12 Hours



Immersing in 1.0 wt.% $NaNO_3$ Solution for 24 Hours



Immersing the Specimen Back in to 1.0 wt.% NaCl for 1 Hour



Immersing the Specimen Back in to 1.0 wt.% NaCl for 2 Hours

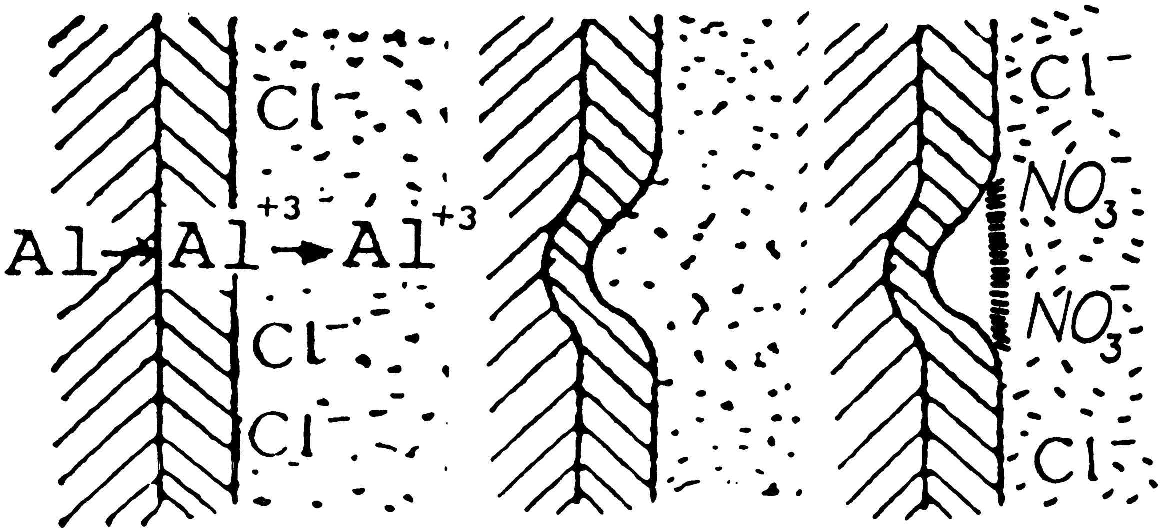


Figure 8 **Mode of Repair of Oxide Film by $NaNO_3$**

the inhibitive effect of aluminum and the adsorption of chloride ions. The results show that the weight losses of aluminum and the adsorption of chloride ions appear to be independent of nitrite ion concentration, as shown in Tables 6-7 and Figure 9. It shows that the surface appearances are unchanged after immersing the same specimen in 1.0 wt.% sodium nitrite solution, as shown in Figures 10(a)-(b). The characteristics of inhibitive effect of nitrite ions are simply represented in Figure 11.

The concentration change of nitrate and nitrite ions are too small to be detected by using Ultraviolet Spectrophotometric Determination, so we fail to get the information about the adsorption of nitrate and nitrite ions.

Table 6 Weight Changes of 7075-T6 Aluminum Alloy After 14 Day Alternate Immersion in Salt Solution of Various Nitrite / Chloride Ratios.

NO	ELECTROLYTE	SPECIMEN SURFACE AREA (cm^2)	SPECIMEN WGT. LOSS 10^4 (g/cm^2)
1	0.1 wt% NaCl / 0.03 wt% $NaNO_2$	10.050	0.696
2	0.1 wt% NaCl / 0.05 wt% $NaNO_2$	9.679	0.723
3	0.1 wt% NaCl / 0.06 wt% $NaNO_2$	10.126	0.691
4	0.1 wt% NaCl / 0.08 wt% $NaNO_2$	10.315	0.679
5	0.1 wt% NaCl / 0.1 wt% $NaNO_2$	9.817	0.611
6	0.1 wt% NaCl / 0.3 wt% $NaNO_2$	9.986	0.600
7	0.1 wt% NaCl / 0.5 wt% $NaNO_2$	10.098	0.594
8	0.1 wt% NaCl / 1.0 wt% $NaNO_2$	9.920	0.605

Table 7 Chloride Ion Concentration Before and After Adsorption. Alternate Immersion Tests with 7075-T6 Aluminum Alloy in Salt Solutions of Various Nitrite / Chloride Ratios.

SOLUTION	INITIAL Cl^- CONC.(g/l)	FINAL Cl^- CONC.(g/l)	Cl^- ADSORPTION 10^4 (g/l cm^2)
0.1 wt% NaCl/ 0.03 wt% $NaNO_2$	0.614	0.610	3,980
0.1 wt% NaCl/ 0.05 wt% $NaNO_2$	0.618	0.614	4.133
0.1 wt% NaCl/ 0.06 wt% $NaNO_2$	0.609	0.605	3.950
0.1 wt% NaCl/ 0.08 wt% $NaNO_2$	0.615	0.611	3.878
0.1 wt% NaCl/ 0.1 wt% $NaNO_2$	0.612	0.608	4.075
0.1 wt% NaCl/ 0.3 wt% $NaNO_2$	0.618	0.615	3.004
0.1 wt% NaCl/ 0.5 wt% $NaNO_2$	0.617	0.614	2.971
0.1 wt% NaCl/ 1.0 wt% $NaNO_2$	0.621	0.617	4.032

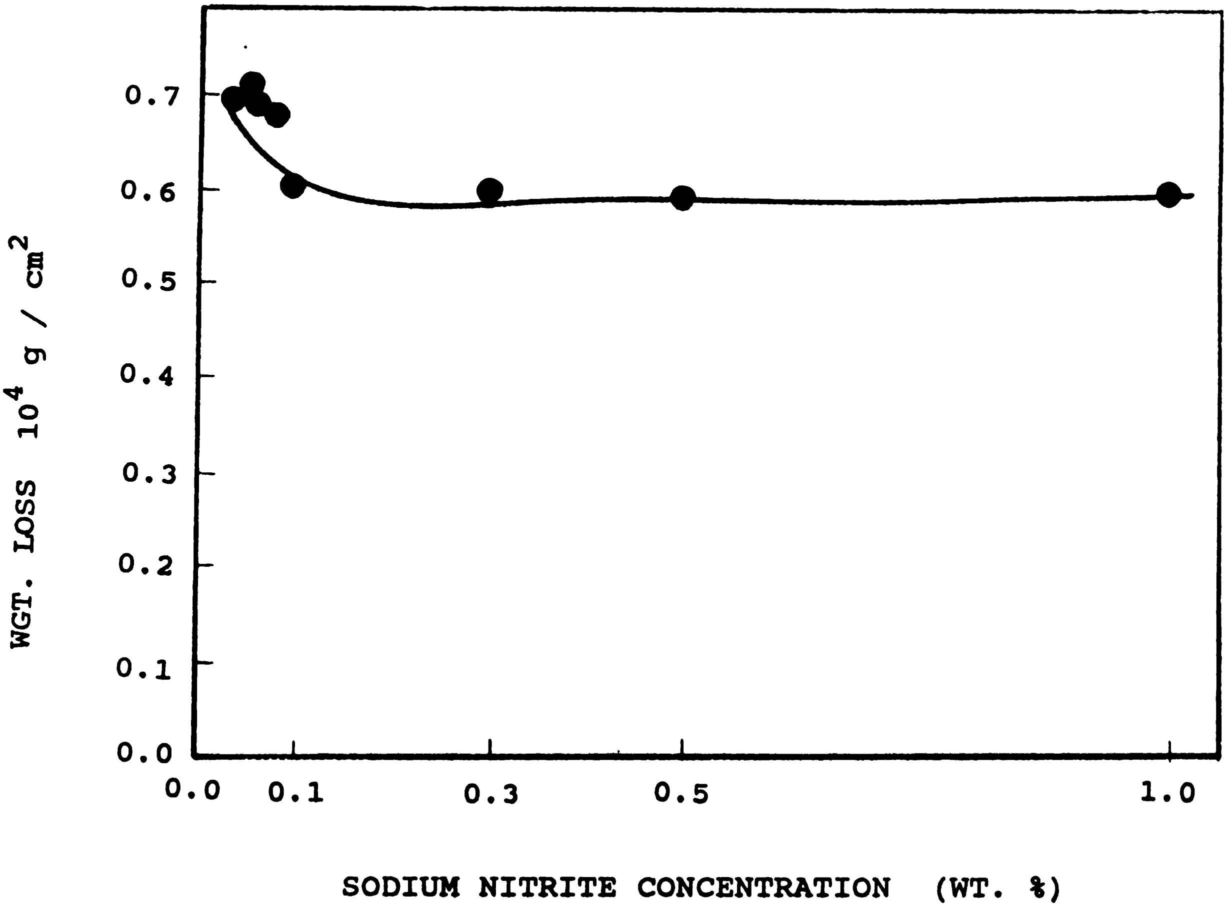


Figure 9 Effect of $NaNO_2$ Addition to 0.1 wt.% NaCl Solution on the Corrosion of 7075-T6 Aluminum Alloy.

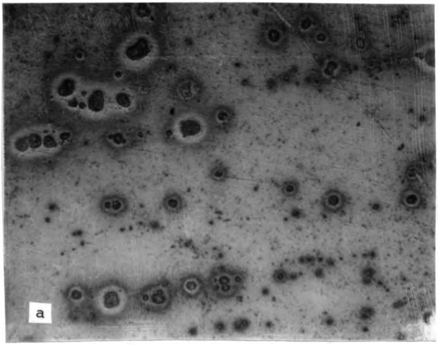
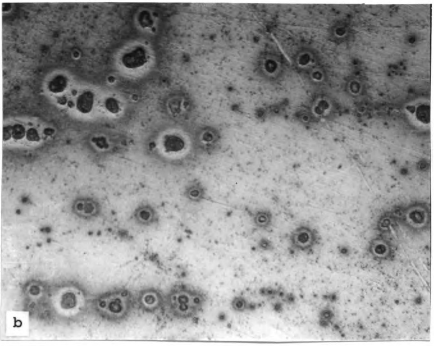


Figure 10 Photomicrographs in sequence Showing the Surface of 7075-T6 Aluminum Alloy Exposed in 0.1 wt.% NaCl for 2 Hours (a), Followed by Immersing in 1.0 wt.% $NaNO_2$ for 5 Days (b), 500 X. The Surface Appear Unchanged.



Immersing in 1.0 wt.% $NaNO_2$ Solution for 5 Days

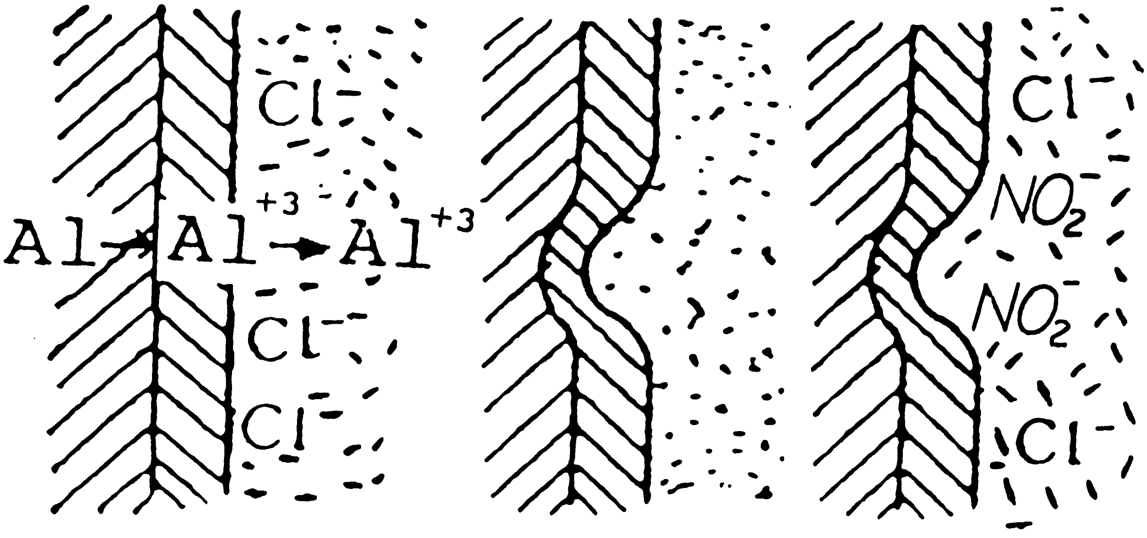


Figure 11 Mode of Competing Adsorption Between NO_2^- and Cl^-

V. Discussion

It is universally accepted that the corrosion resistance of aluminum and aluminum alloys depends on the maintenance of aluminum oxide film in the corroding media. In aqueous sodium chloride, the breakdown of the protective aluminum oxide film is due to the facts that chloride ions are adsorbed preferentially to species such as OH^- and H_2O that would passivate the metals, and the reaction of chloride with aluminum cation in oxide lattice results in a soluble $AlCl^-_4$ complex ion species. After the breakdown, a bare aluminum surface site is exposed to the aggressive medium, and leads to serious pitting.

The most probable reactions mechanism accompanying the initial stage of the corrosion process of 7075-T6 aluminum alloy in NaCl solution is shown in Figure 12.

The formation of protective oxide film can be caused by either the hydration of aluminum hydroxide cation, or the hydration of aluminum cation. However, the breakdown of the protective oxide film can be caused by either the complexation reaction of aluminum hydroxide cation with chloride anions or the reaction of aluminum oxide with chloride anions. Aluminum will directly react with chloride anions after complete breakdown of the protective oxide film.

Bogar and Foley[22] found that the following reaction will take place at the higher Cl^- concentration .

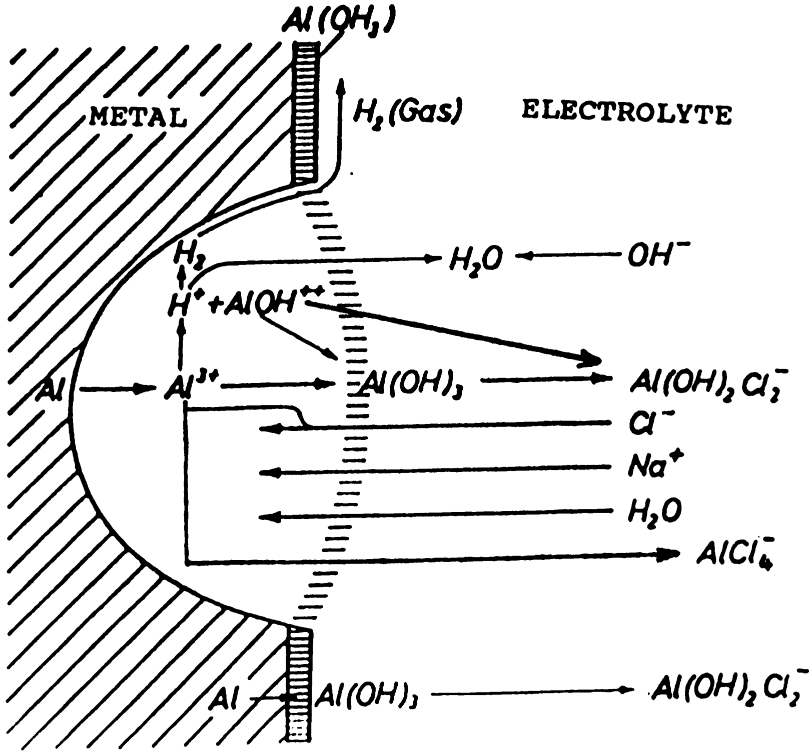


Figure 12 Reaction Scheme for the Aluminum Dissolution Processes in the presence of Sodium Chloride.

$$Al + 4\,Cl^- \qquad\qquad\qquad AlCl^-_4 + 3\,e^-$$

This action of Cl^- promotes pit formation and growth.

Therefore, at the lower concentration (0.1 - 1.0 wt.% NaCl), the weight loss of aluminum is linear with the concentration of sodium chloride in the bulk solution. While the rate of aluminum cation formation reaches a maximum value , the weight losses of aluminum remain constant at the higher concentration (1.0 - 3.0 wt.% NaCl). At the highest concentration (> 3.0 wt.% NaCl) the excess of chloride must change the boundary structure between electrolyte and aluminum. Therefore, The weight loss is dramatically reduced to a limiting value.

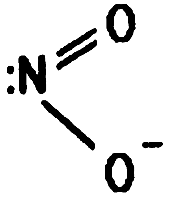
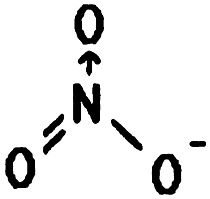
The total weight losses of aluminum are an indication of the total volume of pits resulted in the aluminum, and it is found that the adsorption was localized to corroding pit sites. Therefore, it is obvious that the amount of adsorption of chloride ions is proportional to the weight of aluminum losses.

Sodium nitrate is a effective oxidizing inhibitor due to its high oxidation state, as shown in Table 8. In $NaCl-NaNO_3$ solution, nitrate ions can promote the formation of stable, insoluble aluminum oxide on the aluninum surface. The rate of formation of the aluminum oxide film is larger than the rate of breakdown, and thin, more protective oxide film are formed at higer sodium nitrate concentration. Therefore, the weight of aluminum lost and the adsorption of chloride ions were a dramaticlly decreased to a limiting value with increasing addition of sodium nitrate for a fixed sodium chloride concentration in the bulk solution.

Sodium nitrite has enhanced adsorption capacity to aluminum oxide due to its electron donating ability, as shown in Table 8. In NaCl - $NaNO_2$ solution, nitrite ions compete with chloride ions for adsorption on the aluminum oxide, and retard the formation of the soluble $AlCl^{-}_{4}$ complex species.

Since sodium nitrite has less effect to repair the oxide film, the surface appearances of aluminum appear unchanged in the NaCl - $NaNO_2$ solution. Therefore, the adsorption of chloride is independent of nitrite concentration.

Table 8

Formula	Name	oxidation state	structure
NO^{-}_{2}	nitrite ion	+3	
NO^{-}_{3}	nitrate ion	+5	

VI. Conclusion

1. The corrosion is controlled by the relative rates of the repair and breakdown of the protective aluminum oxide film in the corroding medium.

2. Sodium nitrate is an effective oxidizing passivator, which inhibits the corrosion by the adsorption displacement of Cl^- from the surface and formation of a stable, insoluble aluminum oxide film due to its high oxidation state.

3. Sodium nitrite competes with chloride for adsorption on the aluminum oxide , and retards formation of the soluble $AlCl^-_4$ complex ion species due to its enhanced adsorption capacity.

Appendix 1

Surface Area of Specimen (cm^2)

$$A = 2\ lt + 2\ wt + dt - 2\ (d/2)^2$$

where l = length.
t = thickness.
w = width.
d = hole diameter.

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