CHARACTERISTIC CORROSION NATURE OF ALUMINUM CONTAINING IRON IN NaCl ENVIRONMENTS

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-**ABSTRACT**- Electrochemical measurements and metallurgical observations have been made to clarify the effect of NaCl concentration on the corrosion behavior of the intermetallic compounds such as $FeAl_3$ in aluminum. The preferential dissolution of iron in the intermetallic compounds and subsequently deposition of ferrous iron to metallic iron occurs in the dilute NaCl solution environment (<1.0M NaCl). The intermetallic compounds in the concentrated NaCl solution environment (>3.0M NaCl), however, always provide the cathodic sites at which the well-known oxygen reduction reaction takes places. It is explained that dissolution possibility of the intermetallic compounds is depend on the variation of the corrosion potentials; the pitting potentials are equal to the corrosion potentials related to the concentrations of NaCl solutions.

Keyword: *corrosion, aluminum-iron alloy, NaCl solution, NaCl concentration, pitting attack*

1. INTRODUCTION

Iron is the most common impurity found in industrial aluminum. Iron forms intermetallic second phase (e.g. $FeAl_3$) in aluminum. When particles are present on the surface, the oxide film over them is thin or weak. It is well known that this $FeAl_3$ particle plays a cathodic role to the aluminum matrix in a corrosive environment[1]. In the environment containing chloride ions aluminum is locally attacked. Since the aluminum is usually used in the neutral pH environments, the corrosion problem in common use is confined to the localized corrosion such as pitting at tacks.

Though it is often said that the localized corrosion of aluminum is controlled by the cathodic reduction of dissolved oxygen, it seems that the cathodic role of the oxygen is not so major process in a environment. For instance, it is well observed in a long period of corrosion process that the reduction of dissolved oxygen, which it always takes place on the $FeAl_3$ particles, may be shielded and depressed by forming a bulky or nodular corrosion product[2]. As one of the factors influencing corrosion product, it is pointed out that its adhesive tendency is often depend on the NaCl concentration[3],[4].

In order to obtain the basic concept on the mechanism of pitting attack, the relation between electrochemical behavior of the Al-Fe alloy and NaCl concentration has been investigated.

2. EXPERIMENTAL METHOD

2.1 Specimen

The chemical composition of the specimen is given in Table 1.

Table 1 Chemical composition of specimen

Chemical composition/wt%										
Fe	Si	Cu	Ti	Mn	Mg	Ni	Zn	Cr	V	Al
1.4	0.08	<0.01	0.02	<0.01	<0.01	<0.01	0.01	0.01	<0.01	bal.

The Al-Fe alloy specimen is made by direct-casting a mixture of 99.9% aluminum and 99.9% iron. The cast was homogenized at 873K for 4 hours, and then it was hot-rolled and cold-rolled into 1mm thick sheets. After degreasing by acetone, specimen was pickled in a 10% NaOH solution at 353K for 1 minute. After rinsing with water, specimen was finally passivated in a 30% HNO solution at room temperature (about 298K) for 1 minute.

2.2 Solution

Nine kinds of the test solutions, they are 0.01M, 0.03M, 0.05M, 0.1M, 0.3M, 0.5M, 1.0M, 3.0M and 5.0M (approximately NaCl saturated solution) NaCl were selected. The NaCl (reagent grade) and deionized water were used. The volume of the test solution is always one litter. The solution was deaerated by continues N_2 bubbling through the solution. A moderate agitation by magnetic stirrer kept the solution condition uniform.

2.3 Measurement

The polarization curve has been potentiodynamically measured. A scanning rate of 0.5mV/sec was selected. The reference electrode was Ag/AgCl in saturated KCl solution. The potentials are quoted with respect to the Ag/AgCl unless otherwise stated. A scanning electron microscope (SEM: JSM-T100 of JOEL Co. Ltd., Japan) was utilized for the observation of the specimen surfaces.

3. EXPERIMENTAL RESULTS

3.1 Weight loss of Al-Fe alloy specimen

The weight loss of the Al-Fe alloy specimen (corroded area is 60cm^2) dipped in aerated nine kinds of solution (0.01, 0.03, 0.05, 0.1, 0.3, 0.5, 1.0, 3.0, 5.0M NaCl) for 1000 hr was measured. The weight loss is scattered in 0.01M-1.0M NaCl solution. It shows approximate value of 15-0 mg/(60 cm^2.10^{3}h). The weight loss in 5.0M NaCl sharply increases. Its value is approximate

100mg/(60 cm^2. 10^{3}h). According to the Faraday's law, 100mg/(60 cm^2. 10^{3}h) of the weight loss corresponds to the anodic current density of 5uA/ cm^2.

3.2 Observation of Al-Fe alloys surfaced

In order to compare the surface morphology, SEM observation of the specimens were carried out and shows in Fig.1(a)-Fig.1(d).

(a):before corrosion test

(b):corroded in 0.05M NaCl solution

(c):corroded in 1.0M NaCl solution

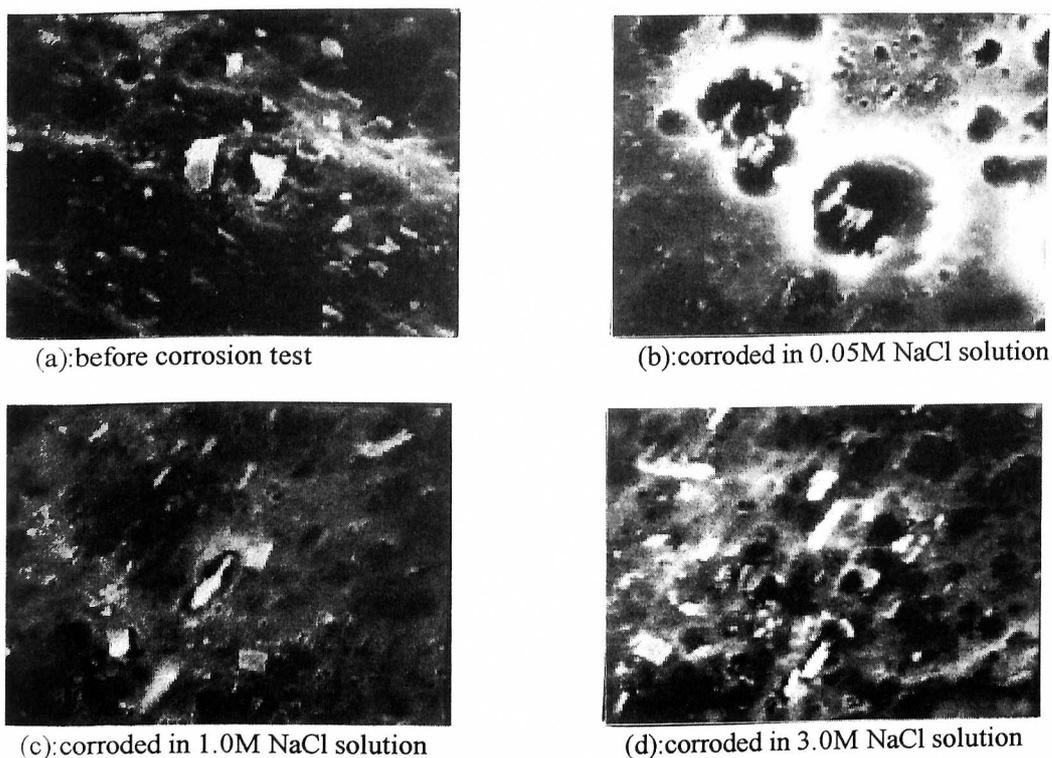(d):corroded in 3.0M NaCl solution

Fig.1   SEM observation of Al-Fe alloy (x2000)

As blank test, Al-Fe alloy specimen surface before corrosion test was observed and shown in Fig.1(a). It is observed that many dispersed intermetallic compounds(probably FeAl$_3$), which show sharp forms of needles and rectangles, were presented on the matrix.

Fig.1(b)-Fig.1(d) shows the corroded specimens. Many crystallographic pitting cavities on all the specimen surfaces, are observed. These photos show also attacked areas without pits. It characteristically shows that concave surroundings of some intermetallic compound particles were observed in the 0.01M-1.0M NaCl solutions. The round shape of FeAl$_3$ particles suggests that the dissolution of FeAl$_3$ has occurred. On the other hand, there is no change in the shape of FeAl$_3$ in the 3.0M and 5.0M NaCl solutions. Their surfaces show almost the same surface of Fig.1(a).

3.3 E_{corr} -time curves of Al-Fe alloy

The variation of corrosion potential, E_{corr} with time in the same environment above was measured. It is convenient to classify these complicated curves into 3 categories. The 1st group are curves in rather dilute NaCl solutions; E_{corr} (0.01M NaCl), E_{corr} (0.03M NaCl), E_{corr} (0.05M NaCl) and E_{corr} (0.1M NaCl). These have tendencies of transferring to less noble potential direction. For instance, E_{corr} behavior in 0.01M NaCl solution shows the value of -0.53V at 10^{-1}h, and then 0.80V at 10^3h. The following relation is obtained in curves of 1st group:

$$E_{corr} \ (0.01M\text{-}0.1M \ NaCl, \ 10^{-1}h) > E_{corr} \ (0.01M\text{-}0.1M \ NaCl, \ 10^3h) \qquad (1)$$

The 2nd group are curves in concentrated NaCl solutions; E_{corr} (3.0M NaCl) and E_{corr} (5.0M NaCl). These have been shifted to noble potential direction with all the time. For instance, E_{corr} behavior in 5.0M NaCl solution shows the value of -0.81V at 10^{-1}h, and then -0.74V at 10^3h. The following relation is obtained:

$$E_{corr} \ (3.0M\text{-}5.0M \ NaCl, \ 10^{-1}h) < E_{corr} \ (3.0M\text{-}5.0M \ NaCl, \ 10^3h) \qquad (2)$$

The 3rd group are curves of E_{corr} (0.3M NaCl), E_{corr} (0.5M NaCl) and E_{corr} (1.0M NaCl). These show mixed behaviors of 1st group and 2nd group. Namely, these have fluctual change that the E_{corr} of these curves move to noble potential direction at early corrosion time and then to less-noble potential direction at late corrosion time. For instance, E_{corr} in 1.0M NaCl solution shows value of 0.74V at 10^{-1}h, then -0.71V at 5h and -0.76V at 10^3h. The following relations are obtained:

$$E_{corr} \ (0.3M\text{-}1.0M \ NaCl, \ 10^{-1}h) > E_{corr} \ (0.3M\text{-}1.0M \ NaCl, \ 10^3h)$$
$$E_{corr} \ (0.3M\text{-}1.0M \ NaCl, \ 10^{-1}h) < E_{corr} \ (0.3M\text{-}1.0M \ NaCl, 5h) \qquad (3)$$

3.4 Solution pH-time curves

The variation of bulk solution pH in the same environments with time was measured. There is no apparent and large differences among all the kinds of NaCl solution. The only thing to be clear is that the solution pH increase with time in all kinds of NaCl solutions.

4. DISCUSSION

4.1 Determination of possible chemical species

In order to obtain roughly-estimated information about possible chemical species produced in this experiment, examination of the E-pH equilibrium diagram was made, which are shown as the superimposition of E-pH diagrams of aluminum and iron. The 1st group of E_{corr}, which is in 0.01M-0.1M NaCl solutions, indicates that the stable electrochemical forms at early time must be ferrous ions, Fe^{2+} and aluminum hydroxide, $Al(OH)_3$. Then the next stable forms may be metallic

iron, Fe and Al(OH)$_3$ at late time. The 2nd group of E$_{corr}$, which is in 3.0M -5.0M NaCl solutions, indicates that the stable electrochemical forms must be both Fe and Al(OH)$_3$ for all the time of corrosion process. The 3rd group of E$_{corr}$, which are in 0.3M-1.0M NaCl solutions, shows a mixture of the 1st group and 2nd group. The stable electrochemical forms may be Fe^{2+} or Fe and Al(OH)$_3$

The mention above leads to the important aspect that none of the FeAl$_3$ particles in 3.0M and 5.0M NaCl solution (2nd group) dissolve. The experimental observation leads to another aspect that the adhesive ability of corrosion product become more weak when the specimens are corroded in more concentrated NaCl solution environments; the corrosion product free surface of the FeAl$_3$ particles provide the cathodic sites on which the oxygen reduction can always occur. These aspects explain the experimental fact that the concerted value of the weight loss approximately equals to the oxygen diffusion limiting current density; value of 5-8uA/ cm^2 which is obtained in the cathodic polarization curve.

4.2 Corrosion process of Al-Fe alloy in a NaCl environment

Pitting attacks initiate at the aluminum matrix adjacent to the FeAl$_3$ particles, which provide a poor oxide film. The cathodic and anodic reactions of the pitting initiation are as follows:

$$O_2 + 2H_2O + 4e = 4OH^- \tag{4}$$
$$Al + 3H_2O = Al(OH)_3 + 3H^+ + 3e \tag{5}$$

It is important character that the aluminum hydroxide experimentally shows more adhesive behavior in a dilute NaCl solution(1st group) than in a concentrated NaCl solution(2nd group). It is also pointed out that the aluminum hydroxide containing ferrous or ferric hydroxide(1 st group) has well adhesive character[5].

In order to explain the corrosion mechanism of aluminum, it is convenient to divide the corrosion behavior into 2 groups. One is the behavior of group(1), which is already mentioned in 3.3, its corrosion process is in a dilute NaCl solution: up to 0.1M NaCl solution environments. Other is the behavior of group(2), in which pitting attacks occur in a concentrated NaCl solution: more than 3.0M NaCl solution environments. The dissolved oxygen reaction of group(1) is depressed, because the oxygen reduction on the FeAl$_3$ particles covered by corrosion product such as Al(OH)$_3$ and Fe(OH)$_2$ or Fe(OH)$_3$ is almost always depressed. This leads to that the occluded cell, in which pit cavities with FeAl$_3$ particles are shielded with corrosion product from the bulk solution, is formed. To maintain electroneutrality, the migration of chloride ions proceeds. The decease in pH and increase in chloride ion concentration stimulate the dissolution of FeAl$_3$ particles which is always observed in active pit cavities. The ferrous ions produced by the dissolution of FeAl$_3$ can deposit on the active aluminum surface or the newly exposure FeAl$_3$ particles underneath. The E$_{pit}$ becomes less-noble as the resulting of entrance of chloride ions into the pitting cavities. The electrons

released are accepted by the H^+ on the deposited iron in the pitting cavities. Hydrogen evolu[...] easily occurs on the deposited iron due to its low hydrogen overvoltage. The aluminum matrix in [...] pit solution, which was coupled with the deposited iron or newly exposed $FeAl_3$ particles. [...] vigorously and autocatalytically dissolve[6]. These reactions in steady state are as follows:

$$2H^+ + 2e = H_2 \tag{6}$$
$$Al = Al^{3+} + 3e \tag{7}$$

In corrosion behavior of group(2), it is easy to understand that the oxygen reduction reaction [...] the $FeAl_3$ particles is main cathodic reaction during all of the corrosion process, because [...] adhesive ability of $Al(OH)_3$ in a concentrated NaCl solution is poor. This corrosion mechanism [...] already schematically shown by G.Wranglen[6].

5. CONCLUSION

The corrosion behavior of aluminum containing 1.4% iron in various kinds of NaCl solution w[...] analyzed by using the electrochemical measurements and metallurgical observation. It is conven[...] to classify the corrosion behavior into 2 groups. One is in the dilute NaCl solution environme[...] (<0.1M NaCl). The iron in the intermetallic compounds dissolves to ferrous ions. The ferrous io[...] deposit to metallic iron inside the pitting cavities. This iron provides an effective cathodic sites [...] hydrogen evolution reaction. The ferrous ions outside the cavities oxidize into ferrous hydrox[...] and then finally into ferric hydroxide. Another is in the concentrated NaCl solution environme[...] (>3.0M NaCl). Since the corrosion potentials coincided with the pitting potentials shows les[...] noble potential, the electromotive force is not enough to take place the preferential dissolution [...] the iron in the intermetallic phase. The existence of $FeAl_3$, enriched iron, always provides th[...] effective cathodic sites for dissolved oxygen reduction reaction. This is already shown b[...] G.Wranglen.

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