

Improving of Corrosion Resistance of Aluminum Alloys by Removing Intermetallic Compound

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It is well known that iron is one of the most common impurity elements found in aluminum and its alloys. Iron in the aluminum forms an intermetallic compounds such as FeAl_3 . The FeAl_3 particles on the aluminum surface are one of the most detrimental phases to the corrosion process and anodizing procedure for aluminum and its alloys. Trial and error surface treatment will be carried out to find the preferential and effective removal of FeAl_3 particles on the surfaces without dissolution of aluminum matrix around the particles. One of the preferable surface treatments for the aim of getting FeAl_3 free surface was an electrochemical treatment such as cathodic current density of -2 kAm^{-2} in a 20-30 mass% HNO_3 solution for the period of 300s. The corrosion characteristics of aluminum surface with FeAl_3 free particles are examined in a 0.1 kmol/m^3 NaCl solution. It is found that aluminum with free FeAl_3 particles shows higher corrosion resistance than aluminum with FeAl_3 particles.

Keywords : aluminum, iron, electrochemical treatment, intermetallic compound, selective dissolution

1. Introduction

It is well known that iron is one of the most common impurity elements found in aluminum. The presence of the Al_3Fe intermetallic compound particles, almost insoluble phases in aluminum matrix, affected to corrosion behavior of aluminum and its alloys.¹⁾ Since Al_3Fe particles are electrochemically more noble than the aluminum matrix the cathodic reactions such as oxygen gas and hydrogen ions reduction reactions are readily depolarized at these particles while the matrix suffer localized dissolution.

It was suggested that one of the possible remedies for the corrosion problems is vanishing the particles from the aluminum surface by a controlled electrochemical technique. According to a technique, the particles can be dropped away and separated from the surface matrix. Depending on circumstances, in which no new intermetallic particles are exposed underneath, the technique like this way may prove effective.²⁾ But the above technique has two weak points; (1) in some cases the residual particles are often observed, and (2) over-dissolution of the matrix may accidentally excavate new particles underneath.

The electrochemical behavior of Al_3Fe intermetallic compound particles in various environments has been

studied.³⁾ It happened that after some polarization measurements in a acid solution the particle-free or -less surface have been obtained. This unexpected happening may lead to a new surface treatment that a controlled polarization technique will probably develop to a new surface pretreatment, which provides aluminum matrix with the Al_3Fe -free surface.

The aim of this work is to introduce the new method to get the completely Al_3Fe -free surface, which is found by trial and error experiments, and to investigate its electrochemical characteristics on corrosion of the aluminum. Some of the results obtained by new method are compared with the ordinary surface treatment. The effect of the new surface treatment on surface morphology and structure of the aluminum is examined.

2. Experimental

2.1 Specimens

Chemical compositions of the specimens used are in the followings: 99.99%Al (specimen Al), Al-1.04%Fe alloy (specimen Al-Fe), Al-40.8%Fe cast alloy (specimen Al_3Fe) and 99.9%Fe plate (specimen Fe). The detail chemical compositions of the specimens are given in Table 1.

The Al-Fe alloy specimen was cast, hot-rolled and cold-rolled into 1 mm thick sheet, and then homogenized at 813K for 160h.²⁾ For comparing and interpreting the

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Table 1. Chemical compositions of specimens

Specimen	Chemical composition/mass%						
	Fe	Si	Cu	Mn	An	Ti	Al
Al	-	-	-	-	-	-	99.99
Al-Fe	1.04	0.10	0.02	0.01	0.01	0.01	bal.
Al ₃ Fe	40.8	tr.	tr.	tr.	tr.	tr.	bal.
Fe	99.9	-	-	-	-	-	-

polarization behaviors, the high purity aluminum plate specimen (specimen Al), intermetallic compound specimen (specimen Al₃Fe) and pure iron plate specimen (specimen Fe) were also used. The intermetallic compound specimen was confirmed to be Al₃Fe by X-ray diffraction analysis. The plate specimens were prepared by cutting coupons of 15x80 mm. The exposed surface area of all plate specimens are 4.5 cm² by covering with insulating tape.

All specimens were cleaned and pickled in a 10% NaOH solution at 353 K for 1 min. After rinsing with water, they were passivated in a 30% HNO₃ solution at room temperature (about 298 K) for 1 min, and subsequently washed and dried.

2.2 Solution

The solution was a HNO₃ solution of de-ionized water. The volume of the solution was always 1 liter. Continuous bubbling of 99.999% N₂ gas through the solution permitted a deaerated condition. Moderate agitation was maintained by magnetic mixer for the experiments.

2.3 Electrochemical surface treatment

The polarization curves have been potentiodynamically measured. A scanning rate of 5 mV/s was selected. The reference electrode was Ag/AgCl in saturated KCl solution. The reference electrode was connected to the measuring cell at the distance of 5 mm from the specimen. The platinum counter electrode and working electrode were placed in the same solution. After trial and error experiments have been carried out, a cathodic treatment was successfully performed.^{4,5)} The specimen was galvanostatically kept at cathodic current density of -200 mA/cm² in a HNO₃ solution for 1000s. The corrosion product adhered after the above treatments must be removed to get clear surface morphology. For this end, the specimens were dipped into the cleaning solution (4% Na₂CrO₄·4H₂O+10% H₃PO₄ aqueous solution) at 353 K for 4 min. For assessment of the treated surfaces, SEM (JSM-T100, JOEL Co., Japan) was routinely used to observe the morphology of the treated surfaces.

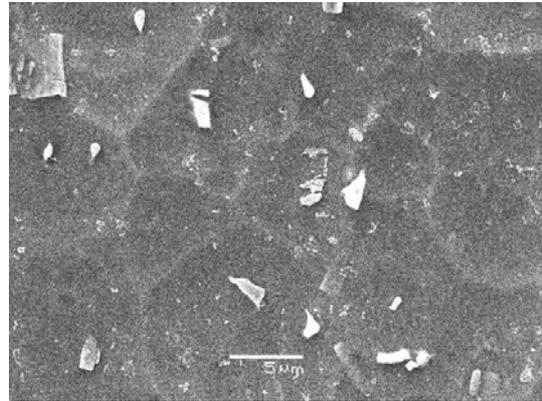


Fig. 1. Observation of surface of original Al-Fe alloy specimens (Al-Fe specimen, before test)

3. Results

3.1 Observation of alloy specimens

For comparing the degree of surface treatment, it is necessary to observe the original surface of the Al-Fe specimen. Fig. 1 shows a typical example surfaces. The dispersed intermetallic compound particles of a few micrometers are observed. These are probably Al₃Fe.

3.2 Cathodic surface treatment

The trial and error efforts have been made to find out the suitable electrochemical conditions that the preferential or selective dissolution of Al₃Fe particles will only occur in an effective manner and the dissolution of aluminum matrix will hardly occur. First of all, the effects of concentration of HNO₃ solution on the surface finishing of the specimen were investigated. The Al-Fe alloy specimens were cathodic-treated at the condition of -200 mA/cm² and 1000 s in the various concentration of HNO₃ solution. The

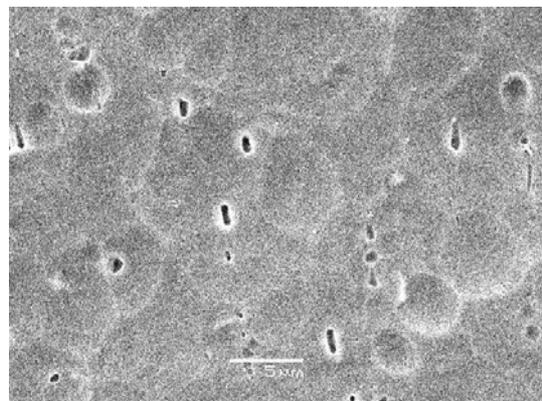


Fig. 2. Observation of Al-Fe alloy specimens in 1/4conc.(17%) HNO₃ solution

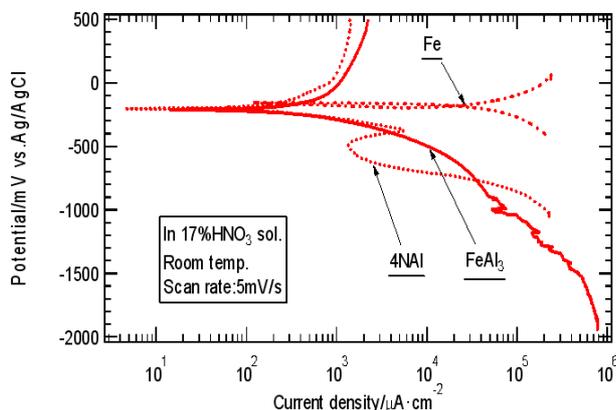


Fig. 3. Polarization curves of pure aluminum, intermetallic compound and pure iron specimens in a 17% HNO₃ solution

result of 1/4 conc. (17%) HNO₃ solutions is excellent and its surface is shown in Fig. 2 as the typical example.

Although the appreciable aluminum surfaces with Al₃Fe particle free is obtained (Fig. 2, treated in 17% HNO₃ solution), but on the surface by treated in other concentration of HNO₃ solution some residual Al₃Fe particles are observed. It is found out that a suitable HNO₃ concentration for the cathodic treatment above exists, and it may be 17% HNO₃ solution.

3.3 Polarization curves of components

The polarization curves of pure aluminum specimens (specimen Al), intermetallic compound specimen (specimen Al₃Fe) and pure iron specimen (specimen Fe) in a 17% HNO₃ solution are shown in Fig. 3.

The open circuit potential of specimen Al is -0.2 V, and the Al₃Fe is -0.20 V and the Fe is -0.18 V vs. Ag/AgCl. The anodic current value of at the potential of 0.0 V vs. Ag/AgCl shows about 1 mA/cm² for Al, 1.3 mA/cm² for Al₃Fe and 0.25 A/cm² for Fe, respectively. It is characteristically shown that the current of specimen Fe is restricted to narrow potential range of 0 V ~ 0.4 V vs. Ag/AgCl due to its rapid dissolution behavior.

4. Discussion

4.1 Metallurgical phase in aluminum containing iron

According to the aluminum-iron phase diagram, there is a eutectic phase of the Al-Al₃Fe system at 938 K at the aluminum end. The equilibrium solid solubility is in the range of 0.03-0.05% Fe at eutectic temperature (938 K). The solid solubility decreases to the order of 0.00x% Fe at 700 K.¹⁾ The solid solubility of iron in the matrix is considered to be negligibly small at room temperature. This leads to the possibility that the purity of the aluminum

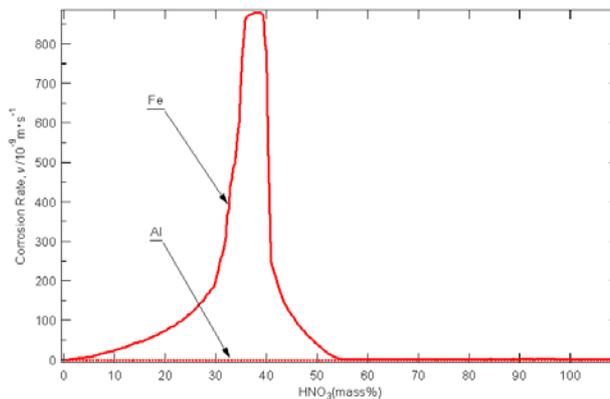


Fig. 4. Relationship between corrosion rate of aluminum and iron in various concentration of HNO₃ solution

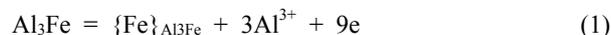
matrix shows the value of more than 99.99% Al or more at room temperature. Phases in the Al-Fe alloy specimen used here may be treated as a mixture of intermetallic compound particles designated as Al₃Fe (specimen Al₃Fe in Table 1) and high purity aluminum (specimen Al in Table 1).

4.2 HNO₃ concentration and weight loss of aluminum and iron

By relationships between HNO₃ concentrations and weight loss of aluminum and iron, in all range of HNO₃ concentrations the weight loss of aluminum is negligibly smaller than that of iron. The weight loss of iron shows maximum value in the range of 37~40% HNO₃ solutions, and drastically decreases in the range of more than 55% HNO₃ solution. It is due to the passivation of iron. The main reason why a cathodic treatment gives us Al₃Fe-free surface is derived from the experimental data that the dissolution rate of each phase of aluminum and Al₃Fe composed of Al-Fe alloy specimen is different in a 17% HNO₃ solution. The Al₃Fe particles which contain iron element dissolve in faster manner than that of aluminum matrix.

4.3 Selective removing

The iron component of the Al₃Fe particles is dissolved in the following possible anodic reactions;

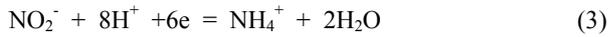


$$E(\text{Al}_3\text{Fe} / \text{Al}^{3+}) = -1.56 + 0.02 \log\{\text{Al}^{3+}\} \quad (2)$$

where, $E(\text{Al}_3\text{Fe}/\text{Al}^{3+})$: Equilibrium potential between Al₃Fe and aluminum ions (V vs. SHE), $\{\text{Fe}\}_{\text{Al}_3\text{Fe}}$: iron in Al₃Fe (-).

It is known that many electrochemical reactions concerning nitric acid may exist.⁴⁾ For instance, it is pointed

out that the following reactions are the most possible reactions, because ions-ions reaction is possible and quick-electron-consuming reaction.



The experimental results that selective dissolution of Al_3Fe particles occurs in a HNO_3 solution may be mainly responsible for the preferential anodic reaction of (1) and ions-ions cathodic reactions of (3) and (4), because of thermodynamic restriction and observations. The residual Al_3Fe particles has enriched-iron surface. The hydrogen evolution reaction of (4) occurs on the iron-riched surface more than on the aluminum matrix. It will be explained that the Al_3Fe particles has been physically activated during the vigorous hydrogen evolution, and then dropped away from the aluminum matrix.

5. Conclusions

The effective surface treatment has been proposed. The selective or preferential dissolution of Al_3Fe particles from the aluminum surface was carried out. The proposed surface treatments is in an electrochemical condition that be kept in a 17% HNO_3 solution for more 1000s of immersion time. Appreciable aluminum surface without Al_3Fe particles was obtained.

References

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