

A Selective Removal of FeAl₃ Intermetallic Compound Particles on Aluminum by Cathodic Treatment in a Nitric Acid Solution

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It is well known that iron is one of the most common impurity elements found in industrial aluminum. The FeAl₃ are detrimental to corrosion behavior and surface treatment such as anodizing. In order to rid aluminum surface of FeAl₃ exposed, simple and effective electrochemical treatment, by which selective removal of FeAl₃ can proceed, has been developed in trial and error. It is found that FeAl₃-free surface is obtained by the treatment (- 2.0V vs. Ag/AgCl for more than 1000s) in 17mass% HNO₃ solution. It is explained that the selective removal attributes to the simultaneous dissolution of iron and aluminum elements in FeAl₃ and cathodic reactions such as $\text{NO}_2^- + 8\text{H}^+ + 6\text{e} = \text{NH}_4^+ + 2\text{H}_2\text{O}$.

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

1. INTRODUCTION

For the environmental quality or sustainable development, many kinds of technological efforts have been made. One of the most desirable development concepts may be recycle-use for industrial materials. Aluminum is one of the most desirable materials for recycle-use. It is expected that the application of used aluminum will be spread out not only to cast aluminum alloys but also wrought aluminum alloys, because the used aluminum has increased in the recent Japanese market. The recycled aluminum is usually contaminated by many impurity elements such as iron, silicon, copper, titanium and etc. at their collection and the remelting processes. In this paper we focus on iron element.

It is well-known that iron is one of the most common impurities in industrial aluminum [1]. Iron precipitates in the form of intermetallic compounds, such as FeAl₃, in aluminum matrix. The FeAl₃ particles exposed to the surface make aluminum oxide film thin or non-existent. The presence of FeAl₃ is detrimental to the corrosion behaviors or finishing treatment of aluminum, such as anodizing. Mentioning the corrosion problem, the potential differences between the FeAl₃ particles and the aluminum matrix produce the local corrosion cell. This local corrosion cells readily promote the pitting attacks on weakened oxide film in a chloride environment. In the electrochemical point of view, it is desirable that aluminum surfaces have free intermetallic compound particles.

In this paper, we have proposed a technique, which is to remove only FeAl₃ particles on the matrix surface. This technique will be one of

the simple treatments to get a desirable rare-substrate for utilizing of aluminum.

2. Experimental Method

2.1 Specimens

The chemical compositions of the specimens are given in Table 1.

Table 1 Chemical compositions of specimens

Specimen	Chemical composition/mass%						
	Fe	Si	Cu	Mn	Zn	Ti	Al
Al	tr.	tr.	tr.	tr.	tr.	tr.	99.99
F1	0.320	100	0.02	tr.	tr.	0.01	bal.
F3	1.040	100	0.020	0.010	0.010	0.01	bal.
FeAl ₃	40.8	tr.	tr.	tr.	tr.	tr.	bal.
Fe	99.9	-	-	-	-	-	-

Chemical compositions of the specimens used are in the followings: 99.99%Al (specimen 4NA1), Al-0.32%Fe alloy (specimen F1), Al-1.04%Fe alloy (specimen F3), Al-40.8%Fe cast (specimen FeAl₃) and 99.9%Fe plate (specimen Fe). The Al-Fe alloy specimens (specimen F1 and F3) were cast, hot-rolled and cold-rolled into 1mm thick sheet, and then homogenized at 813K for 16h.[2] For comparing and interpreting the polarization behaviors, the high purity aluminum plate specimen(specimen Al), intermetallic compound specimen(specimen FeAl₃) and pure iron plate specimen(specimen Fe) were also used. The intermetallic compound specimen was confirmed to be FeAl₃ by X-ray diffraction analysis. The plate specimens were prepared by cutting coupons of 15x80mm. The exposed surface area of all

plate specimens are 4.5cm^2 by covering with insulating tape. All specimens were cleaned and pickled in a 10% NaOH solution at 353K for 1min. After rinsing with water, they were passivated in a 30% HNO_3 solution at room temperature (about 298K) for 1 min, and subsequently washed and dried.

2.2 Solution

The solution was a HNO_3 solution of de-ionized water. The volume of the solution was always 1 liter. Continuous bubbling of 99.999% N_2 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 5mV/s was selected. The reference electrode was Ag/AgCl in saturated KCl solution. The reference electrode was connected to the measuring cell with a salt bridge and Luggin capillary 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[3] was performed. The specimen was potentiostatically kept at the less noble potential of -2.0 V vs. Ag/AgCl in a HNO_3 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% $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ + 10% H_3PO_4 aqueous solution) at 353K 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. All photos of 3000 magnifications are shown.

3. Results

3.1 Observation of the surface of Al-Fe alloys

For comparing the degree of surface treatment, it is necessary to observe the original surface of the F1 and F3. Figure 1 shows a typical example of Al-Fe alloy (F3 specimen) surfaces. The dispersed intermetallic compound particles of a few micrometers are observed. These are probably FeAl_3 . The more FeAl_3 particles are observed on the surface of F3 than that of F1, because of Al-Fe alloy specimen F3 has larger iron content (1.04%Fe) than F1 (0.32%Fe).

3.2 Surface treatment

The trial and error efforts have been made to find out the electrochemical conditions that the preferential or selective dissolution of FeAl_3 particles will effectively occur and the dissolution of aluminum matrix will hardly occur. As a fundamental electrochemical condition, constant potential of -2.0V vs. Ag/AgCl and HNO_3

solutions was selected. At first step, the effects of concentration of HNO_3 solution on the surface finishing of the specimen were investigated. The Al-Fe alloy specimens were cathodic-treated at the condition of -2.0V vs. Ag/AgCl and 1000s in the various concentration of HNO_3 solution. The results of conc.(68%) HNO_3 and 1/4conc.(17%) HNO_3 solutions are shown in Figure 2(a) and (b) as the typical example.

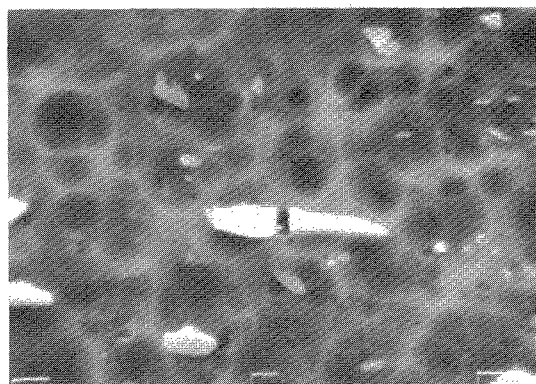


Fig.1 Observation of surface of original Al-Fe alloy specimens (F3 specimen, before test)



Fig.2(a) Observation of of Al-Fe alloy specimens (F3 specimen) in conc.(68%) HNO_3 solutions

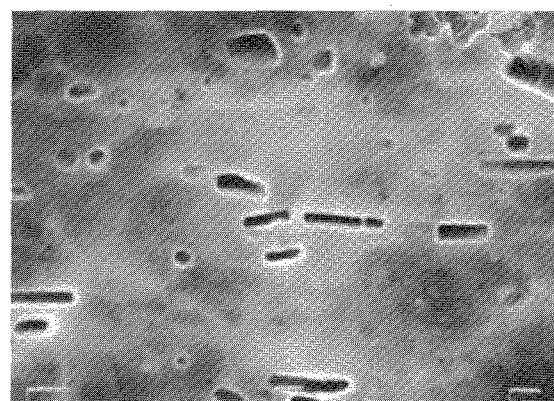


Fig.2(b) Observation of Al-Fe alloy specimens (F3 specimen) in 1/4conc.(17%) HNO_3 solution

After surface treatment, the each surface of specimen is observed by SEM. Appreciable

aluminum surfaces (Fig.2(b), treated in 17% HNO_3 solution) with FeAl_3 -free is obtained, but on the surface (Fig.2(a), treated in 68% HNO_3 solution) some FeAl_3 particles are observed.

At second step, the effect of immersion period of time is investigated. The Al-Fe alloy specimens were cathodic-treated at the condition of -2.0V vs.Ag/AgCl and in 17% HNO_3 solution in various immersions of times. The results of 200s and 2000s are shown in Figure 2(c) and (d), as the typical example.

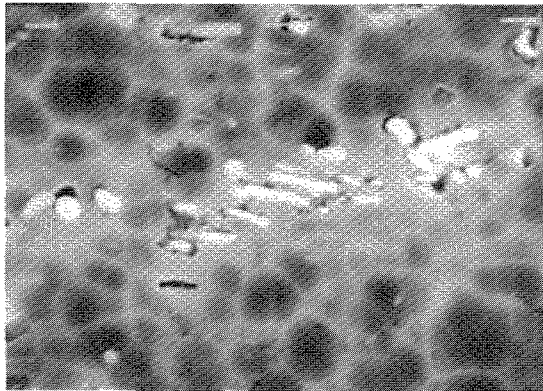


Fig.2(c) Observation of Al-Fe alloy specimens (F3 specimen) in 17% HNO_3 solution for the period of 200s.

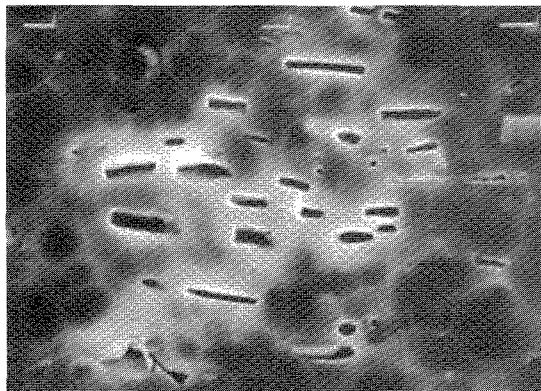


Fig.2(d) Observation of Al-Fe alloy specimens (F3 specimen) in 17% HNO_3 solution for the period of 2000s.

Perfect FeAl_3 -free surface (Fig.2(b) and Fig.2(d)) is obtained in the case of 2000s, but some FeAl_3 surface (Fig.2(c)) is observed in the case of 200s.

It is found that suitable concentration of HNO_3 and immersion time to obtain the FeAl_3 particle-free surface of Al-Fe alloy specimen exists. They are around 17% HNO_3 solution and more than 1000s of the immersion time.

3.4 Polarization curves of Al-Fe alloy specimens

The polarization curves of Al-Fe alloy specimens (specimen F1 and F3) in the 17% HNO_3 solution in Fig.3. The E_{corr} of specimen F1 is about -0.28V vs.Ag/AgCl, and F3 is -0.30 V vs.Ag/AgCl. The more iron content in the Al-Fe

alloy specimen, the larger anodic and cathodic current densities are observed. Roughly speaking, the polarization curves of F1 and F3 specimens show almost the same electrochemical behavior.

3.5 Polarization curves of pure aluminum, intermetallic compound and pure iron specimens

The polarization curves of pure aluminum specimens (specimen 4NAI), intermetallic compound specimen (specimen FeAl_3) and pure iron specimen (specimen Fe) in 17% HNO_3 solution are shown in Fig.4.

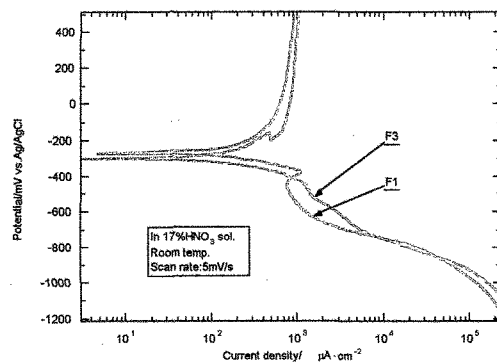


Fig.3 Polarization curves of Al-Fe alloy specimens (specimen F1 and F3) in 17% HNO_3 solution.

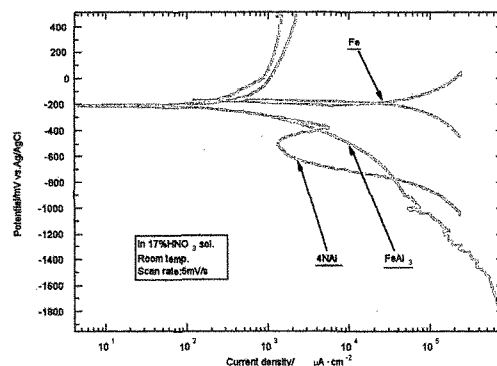


Fig.4 Polarization curves of pure aluminum, intermetallic compound and pure iron specimens in 17% HNO_3 solution.

The E_{corr} of specimen 4NAI is -1.1V vs.Ag/AgCl, and FeAl_3 is -0.20 V vs.Ag/AgCl, and Fe is -0.18V vs.Ag/AgCl. The anodic current value of at the potential of 0.0 V vs.Ag/AgCl shows about 1mA/cm² for 4NAI, 1.3mA/cm² for FeAl_3 and 0.25A/cm² for Fe, respectively. It is characteristically shown that the current of specimen Fe is restricted to narrow potential range of 0V~-0.4V vs.Ag/AgCl due to its rapid dissolution behavior.

4. Discussion

4.1 Metallurgical phase aspect of aluminum containing iron

According to the aluminum-iron phase diagram,

there is a eutectic phase of the Al-FeAl₃ system at 938K at the aluminum end. The equilibrium solid solubility is in the range of 0.03-0.05%Fe at eutectic temperature (938K). The solid solubility decreases to the order of 0.00x%Fe at 700K[2]. 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 matrix shows the value of more than 99.99%Al or more at room temperature. Phases in the Al-Fe alloy specimen used may be treated as a mixture of intermetallic compound particles designated as FeAl₃ (specimen matrix FeAl₃ particles in Table 1) and high purity aluminum specimen Al in Table 1).

4.2 HNO₃ concentration and weight loss of aluminum and iron

Relationships between HNO₃ concentrations and weight loss of aluminum and iron are shown in Fig.5.

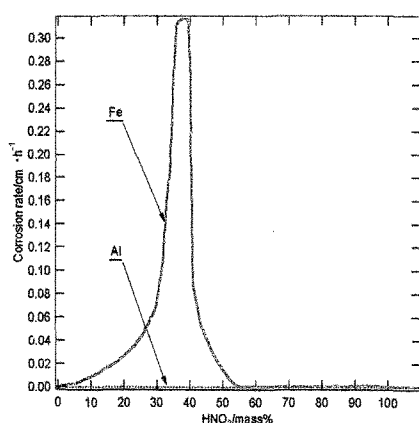
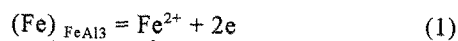


Fig.5 Relationships between HNO₃ concentrations and weight loss of aluminum and iron

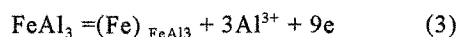
In all range of HNO₃ concentrations the weight loss of aluminum is negligibly smaller than that of iron. The weight loss of iron shows maximum value in the range of 37~40% HNO₃ solutions, and drastically decreases in the range of more than 55% HNO₃ solution. It is due to the passivation of iron. The main reason why a cathodic treatment gives us FeAl₃-free surface is derived from the experimental data that the dissolution rate of each phase (aluminum and FeAl₃) of Al-Fe alloy specimen is far different in a HNO₃ solution. The FeAl₃ particles which contain iron element dissolve in faster manner than that of aluminum matrix.

4.3 Selective dissolution

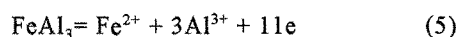
The FeAl₃ particles are dissolved in the following possible reactions;



$$\begin{aligned} E_{\text{eq}}(\text{FeAl}_3/\text{Fe}^{2+}) \\ = -0.41 + 0.03 \log(a_{\text{Fe}^{2+}}/a_{(\text{Fe})\text{FeAl}_3}) \\ = -0.41 + 0.03 \log a_{\text{Fe}^{2+}} \end{aligned} \quad (2)$$



$$\begin{aligned} E_{\text{eq}}(\text{FeAl}_3/\text{Al}^{3+}) \\ = -1.60 + 0.007 \log((a_{(\text{Fe})\text{FeAl}_3} a_{\text{Al}^{3+}}^3)/a_{\text{FeAl}_3}) \\ = -1.60 + 0.002 \log a_{\text{Al}^{3+}} \end{aligned} \quad (4)$$



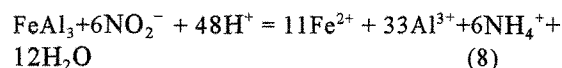
$$\begin{aligned} E_{\text{eq}}(\text{FeAl}_3/\text{Fe}^{2+}, \text{Al}^{3+}) \\ = -1.38 + 0.005 \log((a_{\text{Fe}^{2+}} a_{\text{Al}^{3+}}^3)/a_{\text{FeAl}_3}) \\ = -1.38 + 0.005 \log(a_{\text{Fe}^{2+}} a_{\text{Al}^{3+}}^3) \end{aligned} \quad (6)$$

where, $E_{\text{eq}}(\text{FeAl}_3/\text{Fe}^{2+})$: Equilibrium potential between FeAl₃ and ferrous ions (V vs.SHE), $(\text{Fe})_{\text{FeAl}_3}$: Iron in FeAl₃, $a_{\text{Fe}^{2+}}$: Activity of ferrous ions, $E_{\text{eq}}(\text{FeAl}_3/\text{Al}^{3+})$: Equilibrium potential between FeAl₃ and aluminum ions (V vs.SHE), $E_{\text{eq}}(\text{FeAl}_3/\text{Fe}^{2+}, \text{Al}^{3+})$: Equilibrium potential between FeAl₃, aluminum ions and ferrous ions (V vs.SHE)

It is known that many cathodic reactions concerning nitric acid exist [4]. For instance, the following reaction is one of the most possible reactions, because ions-ions reaction is easy moving reaction and quick-electron-consuming reaction.



The experimental results that preferential dissolution of FeAl₃ particles occur in HNO₃ concentrations are mainly responsible for the simultaneous anodic reaction of (5) and ions-ions cathodic reaction of (7), because both reactions are very rapid reactions. Then overall major reaction may be written in following:



Reaction shows that the last product contains NH₄⁺ ions, which are the last stable chemical forms of HNO₃ in the cathodic treatment.

5. Conclusion

The effective surface treatment has been proposed. The selective or preferential dissolution of FeAl₃ particles from the aluminum surface was carried out. The proposed surface treatments is in the electrochemical condition that be kept in 17mass% HNO₃ solution for more than 1000s of immersion time. Appreciable aluminum surface without FeAl₃ particles was obtained.

6. Reference

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