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Corrosion Phenomenon and Its Analysis of 6063 Aluminum Alloy in Ethyl Alcohol

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It was found that aluminum alkoxide reaction of aluminum alloy 6063 occurs in ethyl alcohol containing aluminum chloride. The reaction is explained by the superimposition of Al/Al^{3+} reaction as the anodic reaction and ethanol/ethlate reaction as the cathodic reaction. In an environment containing chloride ions, an $Al/AlCl_3$ reaction participates in anodic reaction above and then becomes dominant anodic reaction. Rate of aluminum dissolution by the $Al/AlCl_3$ anodic reaction in ethyl alcohol is accelerated due to the fast system which has low polarization resistance. It is shown that aluminum alkoxide (aluminumtriethoxide) as corrosion product will produce hydrogen peroxide on the way of chain process of productions of ethyl chloride, diethyether and ethyether peroxide. It is also pointed out that the hydrogen peroxide will play a strong cathodic role in further pitting corrosion process. [doi:10.2320/matertrans.L-M2009806]

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1. Introduction

Intensive engineering research and development have been carried out toward the opening of a sustainable society. Development in engineering and technology to prevent global warming are essential, and many efforts have been continued to reduce carbon dioxide emissions.

Attention has been focused on ethyl alcohol (ethanol) as a renewable fuel. The ethanol is a sustainable resource made from plant, since it is rebirthable and will be a potential candidate as environmental friendly fuel. Ethanol is mixed with gasoline fuel known as ethanol-blended gasoline. Engineers in Japan have discussed and taken into consideration an application of the E3 or E20 to automobile fuel.[1]

It has been pointed out that the ethanol may cause corrosion attacks in aluminum fuel parts.[2] JAMA (the Japan Automobile Manufacturers Association) reported that when aluminum and ethanol were mixed and touched together at about 398 K for 100 hours, corrosion occurred on an aluminum pipe. The report said that the corrosion is so-called dry corrosion (alkoxide reaction) which occurs under the conditions of high temperature and pressure.[3]

In the JAMA report there are surface observations of dry corrosion and descriptions of the phenomenon, but the its mechanism has not been clarified in detailed. It is also said that hydrogen generated by the dry corrosion may increase pressure of the inside of pipe. This means that dry corrosion is phenomenon occurred in both high temperature and high pressure conditions. However, the high-pressure condition in the automobile structure is not so common, because a fuel pipe has usually free end to the atmosphere; the delivery pipe for fuel between a fuel tank and an inhaler of engine may be under around atmospheric pressure rather than high pressure above. We predict that another mechanism must be required to explain the occurrence of the dry corrosion.

In this paper, the mechanism for the dry corrosion is discussed from an electrochemical point of view to have the well-accepted mechanism for dry corrosion.

2. Experimental Method

2.1 Specimen

The 6063 Al-Mg-Si alloy in JIS (Japanese Industrial Standard) was used (0.2–0.6% Si, Fe $<$ 0.35%, 0.45–0.90% Mg, Cu $<$ 0.10%, Mn $<$ 0.10%, Cr $<$ 0.10%, Zn $<$ 0.10%, Ti $<$ 0.10%). The 6063 Al-Mg-Si alloy (abbreviated as the 6063 in followings) is used as specimen. The specimen had a width of 15 mm, a length of 100 mm and a thickness of 3 mm, and its surface was masked with insulating tape to employ an exposed surface area of about 4.5 cm^2 for the polarization curve. Pretreatment is necessary to guarantee that experiments must be started under the same surface conditions. This treatment involved dipping the specimens into a 10% NaOH aqueous solution at 343 K for one minute, and washing, soaking in a 30% HNO_3 at room temperature (298 K) for one minute, washing, and air drying.

2.2 Test solution

The solvent used were dehydrated ethyl alcohol (99.5%) in a market, and de-ionized water and anhydrous aluminum chloride as solutes were used. The volume of test solution was 0.3 dm^3. Polarization curves were measured at room temperature (298 K) and 351 K. In order to raise the solution temperature, a hotplate was used. The solution temperature was maintained at a constant temperature by the hotplate with controller.

2.3 Measurement

The electrical conductance and pH of the test solutions were determined by a combined measuring apparatus which has both electrical conductance meter and a pH meter (F-55S, Horiba, Ltd.). An autoclave (NU-4, Nitto Kouatsu Co., Ltd.) was used to confirm an occurrence of the alkoxide reaction of which conditions have been written in the JAMA report. The 6063 specimen with scratch line cut with glass knife in the ethanol was kept in a Teflon container and then set in the autoclave vessel.

Polarization curves were potentiodynamically obtained by an electrochemical measurement system (HZ-5000, Hokuto

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Denko Corporation). A silver-silver chloride reference electrode with bare wire (V vs. SSE) was used as a reference electrode (the V vs. SSE is abbreviated as V unless otherwise stated). A platinum electrode was used as an counter electrode. Polarization curves were measured at a scan rate of 0.5 mV/s. After corrosion test, the surface morphologies were evaluated by an optical microscope and a scanning electron microscope (SEM).

3. Experimental Results

3.1 Aluminum alkoxide reaction in the autoclave

Dry corrosion of aluminum was reported as aluminum alkoxide reaction[3)] which had occurred in high temperature and pressure conditions. It is necessary to affirm that the reaction will be reproduced and then its corrosion morphology will also be reconfirmed. The relationship between temperature and beginning of the alkoxide reaction was also examined. A specimen (15 mm × 15 mm × 2 mm) and dehydrated alcohol were placed in a Teflon container and then sealed. The temperature was gradually increased in order to enable to plot the variation of temperature with time (Fig. 1). Beginning of the alkoxide reaction was determined by abrupt sign of the continuous pressure gauge being watched by video recorder. The beginning of the alkoxide reaction is shown as the end of the curve in Fig. 1.

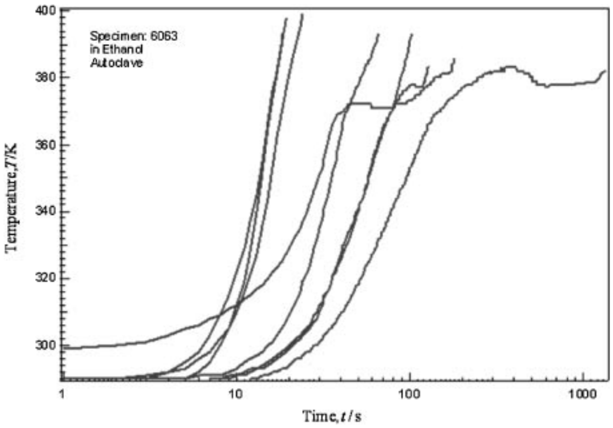

Fig. 1 Relationship between the temperature of aluminum alkoxide reaction and its starting time in ethyl alcohol.

The dT/dt in curve represents the rate of temperature rise. At $dT/dt \fallingdotseq 10\,\mathrm{K/s}$, the dry corrosion starts at about 390 K. At $dT/dt \fallingdotseq 0.06\,\mathrm{K/s}$, the dry corrosion starts at about 380 K. The lower rate of temperature rise is, the alkoxide reaction starts at the lower temperature. Several experiments reveal that the alkoxide reaction was affected by the holding temperature rather than the temperature rising rate. It was found that alkoxide reaction will occurr in almost all the specimens in over 373 K.

Figures 2(a) and 2(b) show the representative surfaces on which the aluminum alkoxide reaction has occurred. Figure 2(a) shows a specimen surface with damages along the scratch lines. Figure 2(b) shows enlarged corrosion area which corresponds to an spot of Fig. 2(a). It characteristically shows gray corrosion surface which may be similar surface of molten aluminum alloy.

3.2 pH and electrical conductivity of ethanol containing aluminum chloride

It is well known that when aluminum is exposured to an environment with chloride ions the aluminum is usually attacked. So aluminum chloride ($AlCl_3$) was added to ethanol (C_2H_5OH, abbreviated as Et-OH), and the pH and electrical conductivity of the solution was measured. Three concentrations of 0.01 M, 0.1 M and 1.0 M $AlCl_3$ were dissolved in Et-OH solvent at temperatures ranging from 298 to 353 K. The changes in pH and electrical conductivity (abbreviated as σ) were shown in Fig. 3 and Fig. 4, respectively.

Before the test, the pH of Et-OH ($AlCl_3$ free) was about 7, and its σ value was 0.04 mS/m. When small amount of the $AlCl_3$ was added to Et-OH, its pH drastically decreased and σ value significantly increased. The pH and σ indicated small differences by variation of temperature: for example, the pH shows almost same value of 0 to 0.5 in Et-OH + 0.1 M $AlCl_3$ solution even at the temperature range of 298 to 351 K. The same σ value of around 70 mS/m also is shown.

3.3 Corrosion behavior of 6063 in Et-OH + $AlCl_3$

Section 3.2 has found that when a little of $AlCl_3$ was added to Et-OH solvent, the pH drastically decreased and the σ significantly increased. This means that an environment of

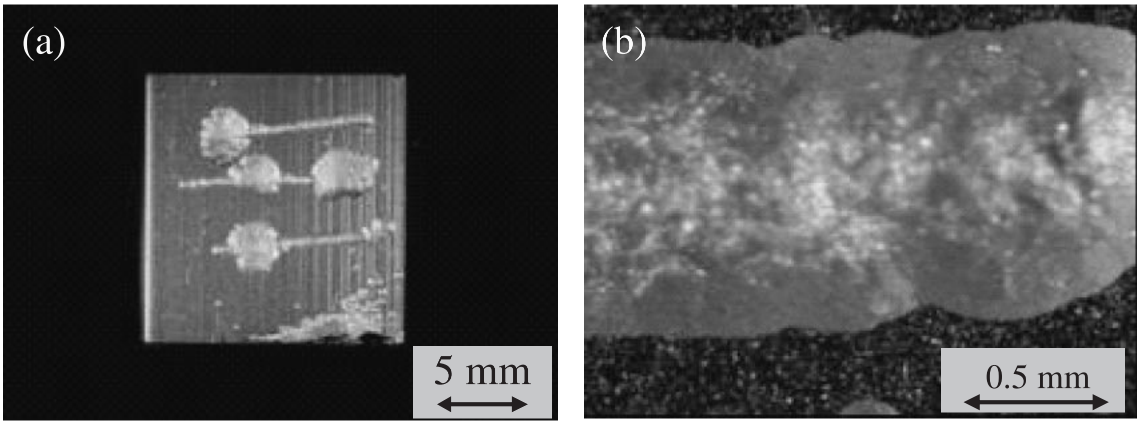

Fig. 2 Surface observation (Fig. 2(a)) and SEM observation (Fig. 2(b)) of aluminum alloy 6063 after the alkoxide reactions of Fig. 1.

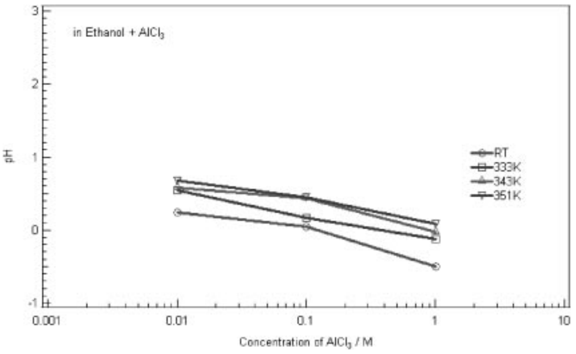

Fig. 3 Relationship between the pH of ethyl alcohol as a solvent and the concentration of aluminum chloride as a solute at various temperatures.

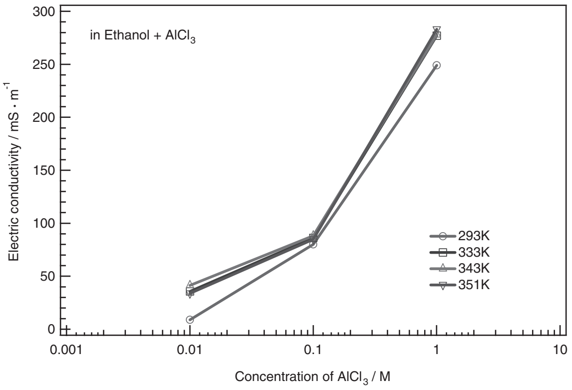

Fig. 4 Relationship between the electrical conductivity of ethyl alcohol and the concentration of aluminum chloride under various temperatures.

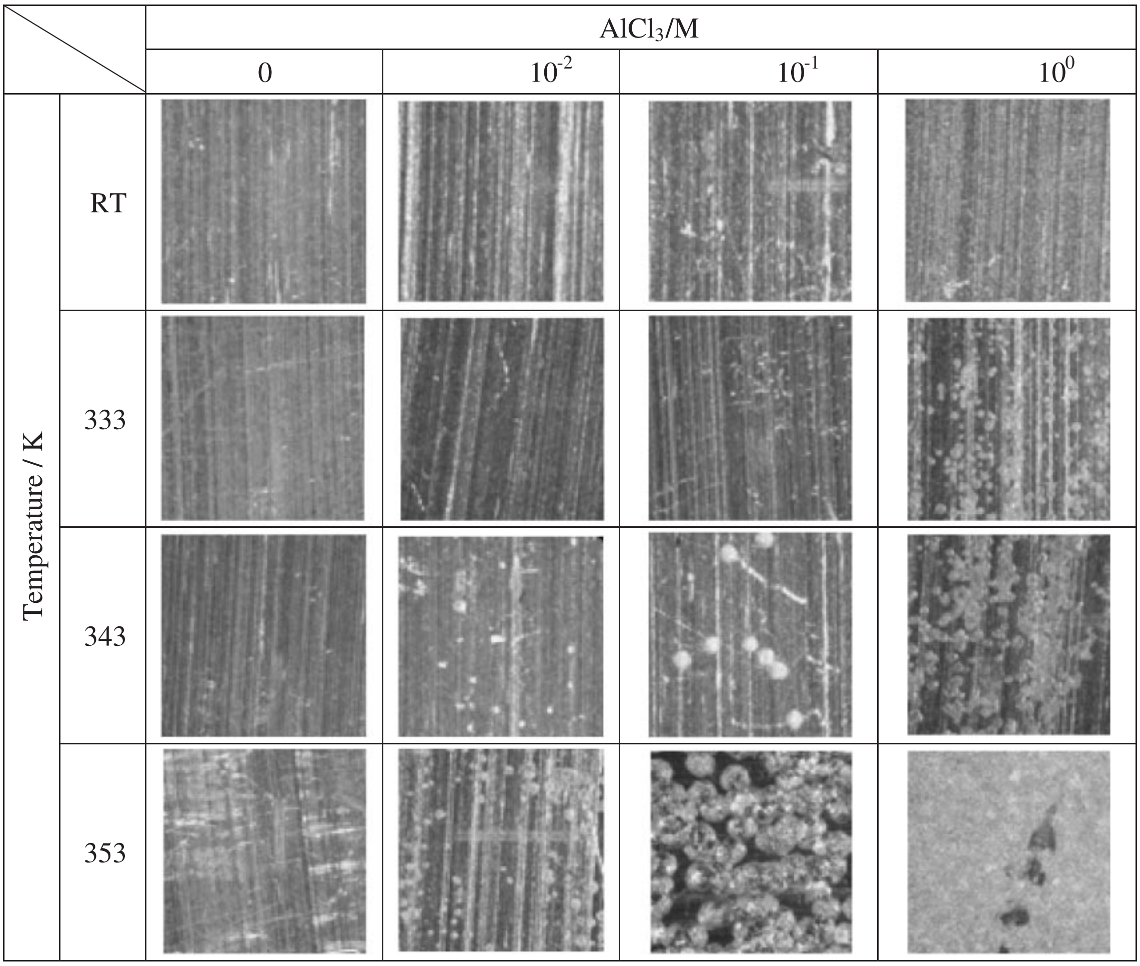

Fig. 5 Surface observations of aluminum alloy 6063 after a corrosion test in combinations of ethyl alcohol with aluminum chloride and solution temperatures.

the Et-OH + AlCl$_3$ solution must be severe corrosion environments. As the test solution, the AlCl$_3$ (0.0 M as blank test, 10^{-2} M, 10^{-1} M and 1.0 M) was dissolved into the Et-OH. The 6063 was immersed in it at solution temperature range from 298 to 353 K for 9 ks. Figure 5 shows the corrosion surfaces after the immersion test.

It will be generally accepted that when a Et-OH solvent has contained a small amount of AlCl$_3$, the 6063 specimen has severely attacked in the results of being a rough and gray corrosion appearances. For example, when the 6063 was immersed in the solution of Et-OH + 10^{-1} M AlCl$_3$ at 343 K, the gray corrosion appearances have been observed, which were almost the same appearances in Fig. 2. It was found that aluminum alkoxide reaction occurred under atmosphere pressure when the Et-OH contains a small amount of AlCl$_3$.

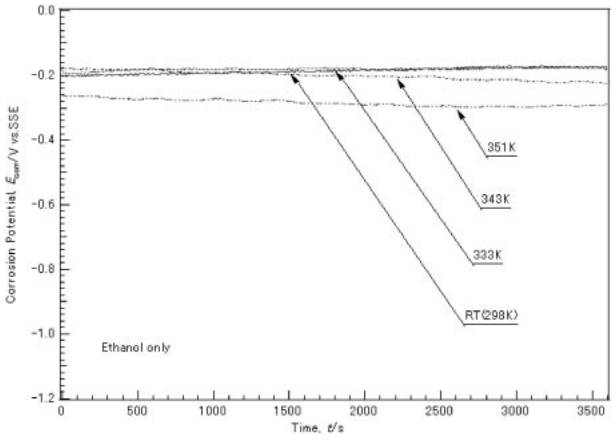

Fig. 6 Variations of corrosion potential with time in ethyl alcohol at various temperatures.

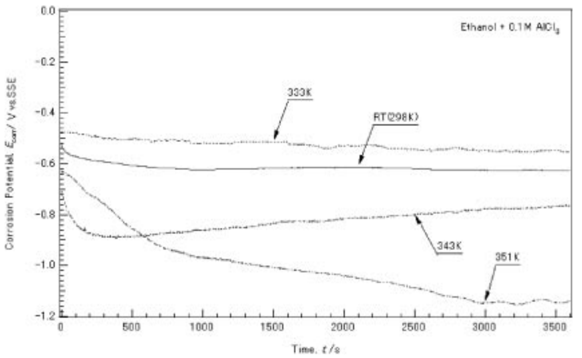

Fig. 7 Variations of corrosion potential with time in ethyl alcohol withs 0.1 M aluminum chloride at various temperatures.

3.4 Variation of corrosion potential with time and the polarization curve of 6063 in Et-OH + $AlCl_3$ solution

The change in spontaneous corrosion potential, E_{corr} and the polarization curves, E-i were measured for obtaining the basic electrochemical information. In several combinations of solution temperature and $AlCl_3$ concentration, the E_{corr} was measured for one hour. Figures 6 and 7 show typical results. Figure 6 shows a result of the Et-OH solvent only as a blank test. In the case of Et-OH itself, E_{corr} at 351 K (Fig. 6) drifted at a slight less noble potential from -0.25 V to -0.3 V. When 0.1 M $AlCl_3$ was added to the Et-OH, the E_{corr} shifted toward a significantly less noble potential (Fig. 7). It was found that the addition of $AlCl_3$ shifts the E_{corr} of the 6063 to less noble potential at the temperature range (298–351 K).

The E_{corr} in Fig. 7 was around -0.6 V at 298 K and then showed about -0.8 V at 343 K at the end of measuring period. The value of E_{corr} in the Et-OH + 0.1 M $AlCl_3$ solution showed -1.15 V after 3.5 ks at 351 K. No order relationship was found between the solution temperature and E_{corr}. It was characteristically noticed that the E_{corr} in the high solution temperature fluctuated in the potential with large magnitude.

The E-i curve was measured to investigate the electrochemical behavior of 6063 in the Et-OH. Figures 8 and 9 show the relation of the solution temperatures (298 and 353 K) and the $AlCl_3$ concentration (0.1 M and 1.0 M).

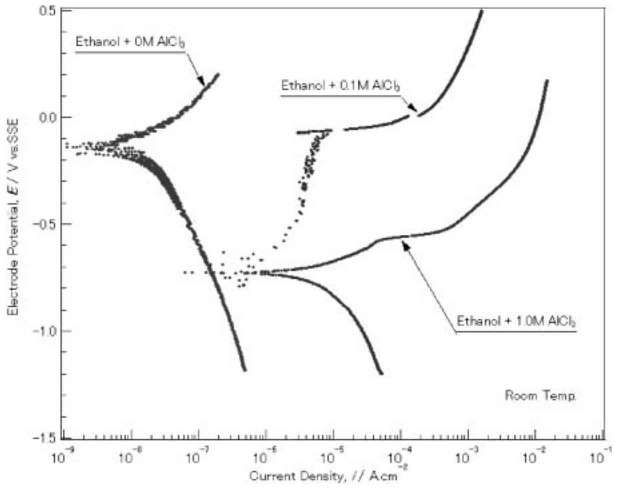

Fig. 8 Polarization curves of aluminum alloy 6063 in ethyl alcohol containing three concentrations (0 M, 0.1 M, 1.0 M) of aluminum chloride at room temperature.

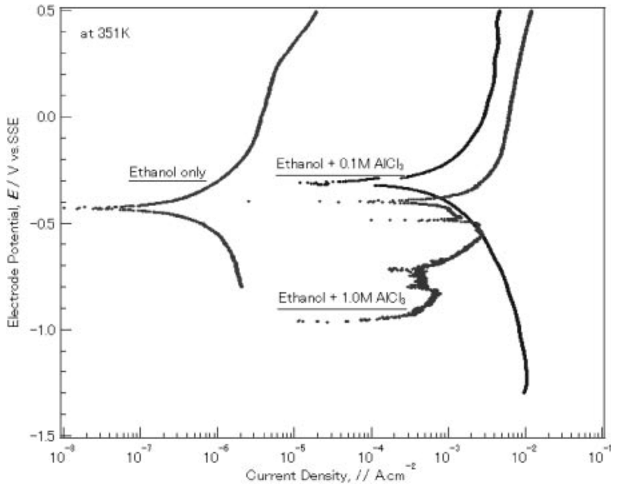

Fig. 9 Polarization curves of aluminum alloy 6063 in ethyl alcohol containing three concentrations (0 M, 0.1 M, 1.0 M) of aluminum chloride at 353 K.

The effect of solution temperature was examined; the difference between the Et-OH (Ethanol + 0 M $AlCl_3$ curve in Fig. 8) and the solution temperature (Ethanol only curve in Fig. 9) was examined. The open circuit potential (E_{corr}) at 298 K is around -0.12 V shown in Fig. 8, but it shifts toward a less noble potential of -0.42 V at 353 K shown in Fig. 9. It is also found that same tendency of the less noble shift has been observed in curves containing $AlCl_3$; when $AlCl_3$ is added to Et-OH, all curves shift to the right direction (Fig. 8 and Fig. 9). On some curves the pitting potential, E_{pit} is observed. For example, room temperature curves indicate that the E_{pit} in Et-OH + 0.1 M $AlCl_3$ shows about -0.1 V and the E_{pit} in Et-OH + 1.0 M $AlCl_3$ shows about -0.6 V. No clear E_{pit} is found at 351 K curves (Fig. 9). It was characteristically shown that the current of Et-OH + 1.0 M $AlCl_3$ fluctuates significantly. It was found that 0.1 M and 1.0 M $AlCl_3$ at high solution temperature accelerated the corrosion current density to large magnitude of order of mA·cm^{-2}.

4. Discussion

4.1 Aluminum alkoxide reaction

Alcohol such as methyl alcohol (CH_3OH) and ethyl alcohol (C_2H_5OH) is a chemical compound in which one hydrogen atom of a hydrocarbon is replaced with hydroxyl group (-OH). The chemical abbreviation for alcohol has often written as R-OH. One of chemical characteristics of R-OH has an occurrence of the alkoxide reaction, which replaces the H in R-OH with metal M in chemical replace reaction. Equation (1) express that R-O-M (often referred to as alkoxide or alcohlate) and hydrogen gas will be produced by the following chemical reaction.

$$2\text{M} + 2\text{R-OH} = 2\text{R-O-M} + \text{H}_2 \tag{1}$$

When the metal M is aluminum, aluminumtetraethoxide, Al(O-Et)$_3$ will form. The reaction is expressed by eq. (2).

$$2\text{Al} + 6\text{Et-OH} = 2\text{Al(O-Et)}_3 + 3\text{H}_2 \tag{2}$$

The changes of the oxidation number leads to that the eq. (2) will be divided into electrochemical reactions: anodic reaction of the following eq. (3) and cathodic reaction of the eq. (4).

$$\begin{cases} \text{Al} = \text{Al}^{3+} + 3\text{e} & (3) \\ 3\text{Et-OH} + 3\text{e} = 3\text{Et-O}^- + 3/2\text{H}_2 & (4) \end{cases}$$

Two reactions occur quickly, which are known as a "*fast system*".[4,5] The relationship between electrode potential, E and anodic internal current density, i_a of eq. (3) is represented by anodic internal polarization curve, E-i_a. In the same manner, the cathodic reaction is represented by cathodic internal polarization curve, E-i_c. They are expressed by the following eqs. (5) and (6):[4]

$$(E \sim i_a)\text{: } E = E^{\emptyset}_{\text{Al/Al}^{3+}} + \frac{RT}{3F}\ln\frac{1}{k_{\text{Al}^{3+}}} + \frac{RT}{3F}\ln i_a \tag{5}$$

$$(E \sim i_c)\text{: } E = E^{\emptyset}_{\text{Et-O}^-/\text{Et-OH}} + \frac{RT}{2F}\ln k^2_{\text{Et-O}^-}\cdot k_{\text{H}_2} - \frac{3RT}{2F}\ln(-i_c) \tag{6}$$

Where, $E^{\emptyset}_{\text{Al/Al}^{3+}}$ and $E^{\emptyset}_{\text{Et-O}^-/\text{Et-OH}}$ denote the standard formal electrode potential (V vs. SHE), F denotes the Faraday constant (96.5×10^3 A·s·mol^{-1}), R denotes gas constant (8.31 J·mol^{-1}·K^{-1}), T denotes the absolute temperature (K), and $k_{\text{Al}^{3+}}$, $k_{\text{Et-O}^-}$ and k_{H_2} denote Al^{3+} ions, Et-O$^-$ ions and hydrogen gas diffusion coefficient (mA·cm·mol^{-1}),[4,5] respectively.

Since the surface of aluminum is usually covered with an oxide film, the polarization curves obtained in real experiments will be expressed by a following eq. (7) which has oxide film resistance term of $\rho^{\text{Al}_2\text{O}_3}l$.

$$(E \sim i_a)\text{: } E = E^{\emptyset}_{\text{Al/Al}^{3+}} + \frac{RT}{3F}\ln\frac{1}{k_{\text{Al}^{3+}}} + \frac{RT}{3F}\ln i_a + i_a\cdot\rho^{\text{Al}_2\text{O}_3}l \tag{7}$$

Where, $\rho^{\text{Al}_2\text{O}_3}$ denotes the resistivity of aluminum oxide film (Ω·cm), and l denotes the thickness of the oxide film (cm).

Hence, the polarization curve, E-i will be obtained when the following simultaneous eq. (8) are satisfied:

$$\begin{cases} i = i_a + i_c \\ E = E^{\emptyset}_{\text{Al/Al}^{3+}} + \frac{RT}{3F}\ln\frac{1}{k_{\text{Al}^{3+}}} + \frac{RT}{3F}\ln i_a + i_a\cdot\rho^{\text{Al}_2\text{O}_3}l \\ E = E^{\emptyset}_{\text{Et-O}^-/\text{Et-OH}} + \frac{RT}{2F}\ln k^2_{\text{Et-O}^-}\cdot k_{\text{H}_2} - \frac{3RT}{2F}\ln(-i_c) \end{cases} \tag{8}$$

As the alkoxide reaction in spontaneous corrosion state is the eq. (2), the following regulation is needed.

$$i = 0 \quad \text{or} \quad i_a = -i_c \tag{9}$$

In a case of rough relation for Fig. 8 can be simulated, an outline of E-i curve will be plotted. The numerical values[6] were used for estimation. It is assumed that the diffusion layer thickness is 0.01 cm and the diffusion coefficient of all chemical species is 10^{-5} cm^2·s^{-1}. The resistivity $\rho^{\text{Al}_2\text{O}_3}$ of oxide film depends on its electric insulating properties. Three simulation values of resistivity are employed to calculate: they are 10^7, 10^9 and 10^{11} Ω·cm. The l is 10^{-7} cm which roughly corresponds to the thickness of barrier layer of aluminum oxide film. Figure 10 shows the results of the relationship between the three curves of E-i_a ($\rho^{\text{Al}_2\text{O}_3}l$: 10^4 Ω·cm^2, 10^2 Ω·cm^2, 10^0 Ω·cm^2) and one E-i_c curve at room temperature (298 K).

The intersections ($i_{\text{corr}}, E_{\text{corr}}$) between three $E \sim \log i_a$ curves and one $E \sim \log|i_c|$ curve means spontaneous corrosion states which have satisfied the eq. (8) and eq. (9). Point (①, ②, ③) indicate the corrosion potentials, E_{corr} and corrosion current densities, i_{corr}. For instance, at point ① ($\rho^{\text{Al}_2\text{O}_3}l = 10^4$ Ω·cm^2) a corrosion current of 2 μA·cm^{-2} flows at the corrosion potential of −0.4 V. It is shown that the degradation of the oxide film coincided with the increase of corrosion current: point ② (0.01 A·cm^{-2}) to 0.7 A·cm^{-2} (point ③). It was confirmed that the corrosion current has large dependence on quality of the oxide film by the superimposition of the E-i_a curve and E-i_c curve. This leads to that the aluminum alkoxide reaction has oxide-film dependence.

It is necessary to discuss the effect of temperature on the polarization curves. Figure 11 shows the results. As an example, the change in the $E \sim \log i_a$ curves of $\rho^{\text{Al}_2\text{O}_3}l = 10^4$ Ω·cm^2 with the temperatures of 298 K and 351 K is estimated. The $E \sim \log|i_c|$ curve shifts significantly toward

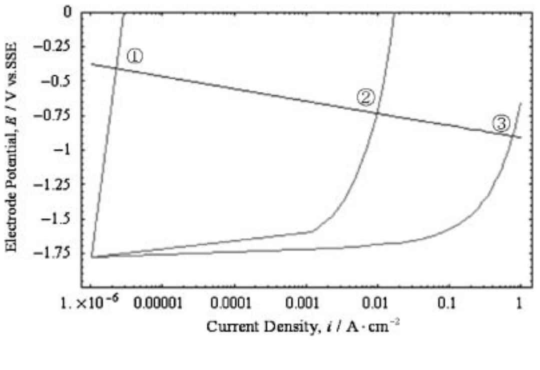

Fig. 10 Schematic representation of the superimposition of anodic polarization curves of aluminum alloy 6063 with various oxide film resistances, and the cathodic polarization curve of ethyl alcohol at room temperature.

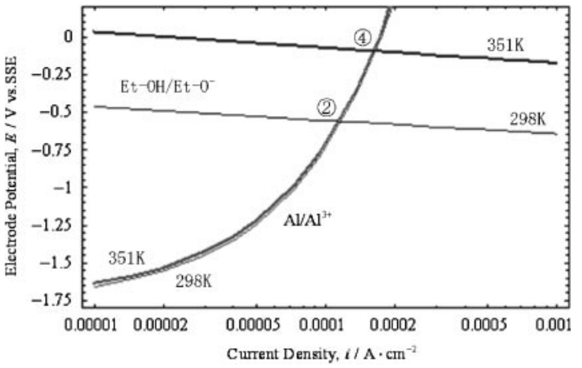

Fig. 11 Schematic representation of the superimposition of anodic polarization curves of aluminum alloy 6063 with an oxide film resistance value of $10^4\,\Omega\cdot\text{cm}^2$ and the cathodic polarization curve of ethyl alcohol at temperatures of 298 K and 351 K.

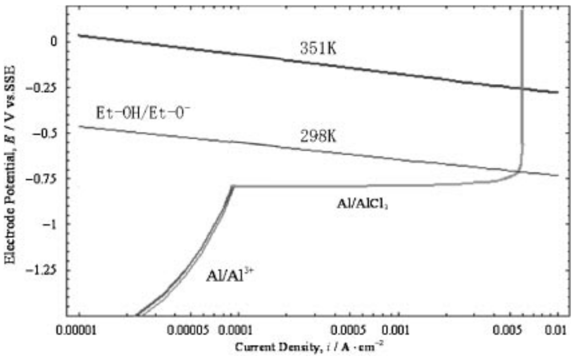

Fig. 12 Schematic representation of anodic polarization curves of aluminum alloy 6063 under pitting attack by chloride ions, and the cathodic polarization curve of ethyl alcohol at room temperature (298 K) and 351 K.

the noble potential direction when the solution temperature rises. On the other hand, the $E \sim \log i_a$ curves show almost same shape at 298 and 351 K: the corrosion current density increases from $0.13\,\text{mA}\cdot\text{cm}^{-2}$ (point ②) to $0.17\,\text{mA}\cdot\text{cm}^{-2}$ (point ④) along with the temperature increased from 298 to 351 K. It is emphasized that the temperature dependence of aluminum alkoxide reaction is responsible for the temperature dependence of the cathodic reaction.

When $AlCl_3$ is added to the Et-OH, the chloride ions which have been dissociated from $AlCl_3$ accelerate the corrosion reaction of aluminum. In this case it may be assumed that a following anodic reaction will occur:

$$\mathrm{Al} + 3\mathrm{Cl}^- = \mathrm{AlCl_3} + 3\mathrm{e} \tag{10}$$

This equation is also well known as a fast system. Its E-i_a curve will be expressed by the following:[4,5)]

$$E = E^{\emptyset}_{\mathrm{Al/AlCl_3}} + \frac{RT}{F}\ln k_{\mathrm{Cl^-}} + \frac{RT}{F}\ln\frac{1}{(i_{\mathrm{Cl^-,L}} - i_a)} \tag{11}$$

where $E^{\emptyset}_{\mathrm{Al/AlCl_3}}$ denotes the standard formal electrode potential (V vs. SHE), $k_{\mathrm{Cl^-}}$ denotes the diffusion coefficient of $\mathrm{Cl^-}$ ions ($\text{mA}\cdot\text{cm}\cdot\text{mol}^{-1}$), and $i_{\mathrm{Cl^-,L}}$ denotes the diffusion-limited current density ($\text{mA}\cdot\text{cm}^{-2}$).

When the $AlCl_3$ exists in the Et-OH, an expression of the E-i curve is equivalent to the following eq. (12).

$$\begin{cases} i = i_a + i_c \\ E = E^{\emptyset}_{\mathrm{Al/Al^{3+}}} + \dfrac{RT}{3F}\ln\dfrac{1}{k_{\mathrm{Al^{3+}}}} + \dfrac{RT}{3F}\ln i_a + i_a\cdot\rho^{\mathrm{Al_2O_3}}l \\ E = E^{\emptyset}_{\mathrm{Et\text{-}O^-/Et\text{-}OH}} + \dfrac{RT}{2F}\ln k^2_{\mathrm{Et\text{-}O^-}}\cdot k_{\mathrm{H_2}} - \dfrac{3RT}{2F}\ln(-i_c) \\ E = E^{\emptyset}_{\mathrm{Al/AlCl_3}} + \dfrac{RT}{F}\ln k_{\mathrm{Cl^-}} + \dfrac{RT}{F}\ln\dfrac{1}{(i_{\mathrm{Cl^-,L}} - i_a)} \end{cases} \tag{12}$$

Substitution of the numerical values into eq. (12) leads to the graphical relationship between $E \sim \log i_a$ and $E \sim \log|i_c|$ curves. In an example of the $AlCl_3$ concentration of $0.1\,\text{mol}\cdot\text{dm}^{-3}$, the $i_{\mathrm{Cl^-,L}}$ is expressed as following.

$$\begin{aligned} i_{\mathrm{Cl^-,L}} &= k_{\mathrm{Cl^-}}[\mathrm{Cl^-}]_{\mathrm{bulk}} \simeq (0.02\times10^3\,\text{A}\cdot\text{cm}\cdot\text{mol}^{-1}) \\ &\quad\times(0.3\,\text{mol}\cdot10^{-3}\,\text{cm}^{-3}) \\ &= 0.006\,\text{A}\cdot\text{cm}^{-2} \end{aligned} \tag{13}$$

Figure 12 shows graphical plotting of the $E \sim \log i_a$ and $E \sim \log|i_c|$ curves. The anodic diffusion-limited current density of $i_{\mathrm{Cl^-,L}}$ characteristically appears in the E-i_a curves, due to the diffusion term of chloride ions which is shown as vertical $i_{\mathrm{Cl^-,L}}$ of $0.006\,\text{A}\cdot\text{cm}^{-2}$ on E-i_a curves in Fig. 12.

It is noted that the anodic reaction of eq. (3) will compete with the one of eq. (10), and then the superimposition of E-i_a curves eq. (3) and eq. (10) reveals which reaction will become more dominant anodic reaction on the E-i_a curves.

The anodic reaction of aluminum alkoxide phenomena is limited by diffusion chloride ions. The cathodic reaction shows solution temperature dependence. The anodic reaction of eq. (10) and cathodic reaction of eq. (4) are both fast systems, meaning that the alkoxide reaction may be significantly affected by the solution temperature and the diffusion condition such as solution stirred. This may be possible explanation for the large fluctuation by temperature variation and chloride concentration which have experimentally been observed in Fig. 9.

4.2 Ethanol and corrosion of 6063[7)]

In an realistic circumstances, there are many chances that the aluminum alkoxide produced by dry corrosion dissolves into water. Then hydrolysis reaction of aluminumalkoxide will occur. So aluminum hydroxide and ethanol are produced.

$$\mathrm{Al(O\text{-}Et)_3} + 3\mathrm{H_2O} = \mathrm{Al(OH)_3} + 3\mathrm{Et\text{-}OH} \tag{14}$$

The following substitution reaction between hydrogen ions of Et-OH and chloride ions of HCl will produce ethyl chloride, Et-Cl and water.

$$\mathrm{Et\text{-}OH} + \mathrm{HCl} = \mathrm{Et\text{-}Cl} + \mathrm{H_2O} \tag{15}$$

The ethyl chloride in the above reaction reacts with aluminum alkoxide, then would form diethylether, Et-O-Et and $AlCl_3$.

$$\mathrm{Al(O\text{-}Et)_3} + 3\mathrm{Et\text{-}Cl} = 3\mathrm{Et\text{-}O\text{-}Et} + \mathrm{AlCl_3} \tag{16}$$

This diethylether reacts with the oxygen gas in atmosphere to form peroxide (diethylperoxide, Et-O-O-Et).

$$2\mathrm{Et\text{-}O\text{-}Et} + \mathrm{O_2} = 2\mathrm{Et\text{-}O\text{-}O\text{-}Et} \tag{17}$$

The diethylperoxide will hydrorize to produce hydrogen peroxide, H_2O_2 and ethyl alcohol.

$$\text{Et-O-O-Et} + 2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2\text{Et-OH} \qquad (18)$$

The chain reactions from eq. (14) to eq. (18) will be taken place in natural and spontaneous manner. The hydrogenperoxide produced in the chain process must play a strong cathodic role on the way of aluminum corrosion process, even if temperature decreases.

It must be kept in mind that even if the H_2O_2 occurs in samll volume at a place of the corrosion products or in the pitting cavities, the stay of H_2O_2 will strongly stimulate and promote the corrosion attacks of aluminum. The Et-OH is repeatedly involved in a chain of corrosion reactions above, which means that corrosion will be readily evolved even without a sufficient supply of Et-OH.

It is also important to note that the risk of pitting attacks is always present when the aluminum alkoxide reaction have once occurred. The more over, it will be notified that this risk steadily increases when weak oxide film such as a pitting cavity and a crevice is present on the aluminum surface. Again above explanation emphasizes that once alkoxide reaction occurs, the pitting attack will be never stopped.

5. Conclusion

The alkoxide reaction in the 6063 Al-Mg-Si alloy is explained by electrochemical reactions of $\text{Al} = \text{Al}^{3+} + 3\text{e}$ as anodic reaction and $2\text{Et-OH} + 2\text{e} = 2\text{Et-O}^- + \text{H}_2$ as cathodic reaction. The polarization curve (E-i) of alkoxide reaction can be interpreted as the superimposition of the two internal polarization curves of the anodic reaction (E-i_a) and cathodic reaction (E-i_c). When the 6063 Al-Mg-Si alloy reacts with ethyl alcohol with aluminum chloride, the alkoxide reaction will be accelerated. We graphically discussed how addition of aluminum chloride ions stimulates and accelerates the aluminum alkoxide reaction. It is pointed out that the formation of aluminum alkoxide will produce hydrogen peroxide. We also discussed how the chain processes produce the hydrogen peroxide, and how the pitting attacks continue even if temperature decreases and little ethanol is present.

REFERENCES

1) Y. Daisho, Mitsui & Co., Ltd.: Forefront of bioethanol (illustrated description), (Kogyo Chosakai Publishing, Inc. 2006) pp. 189–228.
2) http://www.mlit.go.jp/jidosha/alcohl/alcohl.html
3) http://www.mlit.go.jp/jidosha/alcohl/01/08_3.pdf
4) G. Charlot, J. Badoz-Lambling and B. Tremillon: Electrochemical Reactions, (Elsevier Publishing Company, 1962) pp. 46–89.
5) O. Seri: *Kinzoku no Fushoku to Bohshoku no Kiso* (The foundations of corrosion and corrosion protection for metal materials), (Seizando Book Store, 2006) pp. 92–122.
6) D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall: J. Physical and Chemical Reference Data, supplement No. 2, vol. 11 (1982).
7) M. Ohki, T. Ohsawa, M. Tanaka and H. Chihara: *Encyclpedic Dictionary of Chemistry*, (Tokyo-kagaku-Dohjin Co. Ltd. 1989).