Research Paper

Studies on the Mechanism of Anodic Oxidation of Aluminum Using Deuterosulfuric Acid System

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Mechanism of anodic oxidation and dissolution of aluminum in 1M-sulfuric acid solution was investigated using the same concentration of deuterosulfuric acid system.

At constant voltage electrolysis, cell voltage was suddenly reduced from 11 volt to 8 volt, for instance, the recovery of current in sulfuric and deuterosulfuric acid systems was simultaneously recorded by an electromagnetic oscillograph. Furthermore exchange effect of the electrolyte in which samples were anodically formed and allowed to recover was investigated, that is, samples were formed in sulfuric acid solution, then allowed to recover in deuterosulfuric acid solution and vice versa, wherefrom the effect of protons was interpreted.

The rate of chemical dissolution of oxide films immersed in the sulfuric or deuterosulfuric acid solution was determined by a gravimetric method. The exchange effect mentioned above was also tested.

From these experiments the effect of protons on anodic oxidation of aluminum in the sulfuric acid electrolyte was found to be predominant in the process of chemical dissolution rather than in the process of anodic oxidation.

1 Introduction

In the previous paper\(^1\), comparison of the sulfuric and deuterosulfuric acid electrolyte for anodizing aluminum under galvanostatic conditions was made and differences in the anodizing bath voltage and film capacitance were discussed. According to Murphy et. al., protons liberated from the following reactions may be retained at the oxide/electrolyte interface forming the so called "protonic space charge", which regulates formation and dissolution of anodic oxide films.

\[
\begin{align*}
2\text{Al}^{3+} + 3\text{H}_2\text{O} & = \text{Al}_2\text{O}_3 + 6\text{H}^+ & (1) \\
2\text{Al}^{3+} + 3\text{OH}^- & = \text{Al}_2\text{O}_3 + 3\text{H}^+ & (2) \\
2\text{Al}^{3+} + 3\text{HSO}_4^- & = \text{Al}_2(\text{SO}_4)_3 + 3\text{H}^+ & (3)
\end{align*}
\]

Michelson\(^1\) has recently reported, that on abrupt changes of the applied bath voltage, rearrangement of the cell structure must occur. The time required from the initial to final state is schematically indicated in Fig. 1, and is called the recovery period. From experimental results, he concluded, that recovery must proceed by dissipation of a protonic space charge and hence the colloidal gel model proposed by Murphy et. al., was preferable rather than the single geometric pore model.

Diggle et. al.,\(^5\) on the other hand, sustained the latter in the course of the capacitance measurement. They concluded, that the processes involving the film thinning of slow chemical dissolution and of rapid field-assisted dissolution can be distinctly separated in the recovery period. During the slow chemical dissolution, ionic current through the barrier layer is nearly zero while the film capacitance increased steadily. When the film thinning approached to the limiting barrier thickness, where the appreciable ionic current
can flow, sudden increases of both current and film capacitance were observed, suggesting the field-assisted film thinning now occurs. The purpose of this study is to determine effect of protons on the recovery period in anodizing aluminum by using deuterosalicylic acid as electrolyte.

2 Experimental

Since deuterium in heavy water tends very readily to exchange with hydrogen in atmospheric moisture, all the equipment should be free from the air, but to facilitate to exchange samples easily, following apparatus was developed. (Fig. 2) The electrolyte was found in the bottom of the cell and heavy non-reactive gas (CO₂) was introduced from the inlet, covering the electrolyte surface and separating it from the atmospheric moisture.

![Fig. 1 Schematic diagram of the current recovery effect](image)

The purpose of this study is to determine effect of protons on the recovery period in anodizing aluminum by using deuterosalicylic acid as electrolyte.

![Fig. 2 Apparatus for measuring recovery effect](image)

To compare with sulpheric and deuterosalicylic acid systems, two identical cells were prepared and all the measuring circuits were composed of twin systems as shown in the figure. Two voltage stabilizers, one is for high voltage and the other for low voltage, were preliminarily adjusted to the required cell voltage (E₁ and E₂), and were connected to the electrolytic cells via switch S. Changes in cell current were recorded simultaneously on the recording paper of an electromagnetic oscillograph, the sensitivity of each element being adjusted quite identical. The electrolytic cells were immersed in a water bath maintained at constant temperature.

All aluminum samples were Super Raffina (99.999 %), 25 × 10 mm in size and 1 mm in thickness. Prior to the experiment, samples were degreased with benzene, electrolytically polished for 5 minutes, rinsed with water, dried and weighed. Immediately before the experiment, samples were boiled with chromic-phosphoric acid mixture to remove thin air-formed oxide film and then rinsed and dried. As counter electrode large surface of zirconium foil (70 × 70 mm) was used, which is quite resistant against the electrolyte. The electrolytes were prepared from the reagent grade sulpheric or deuterosalicylic acid, of which isotopic purity was more than 99.7 %.

3 Results

3.1 Recovery effect

Applied bath voltages were arbitrarily chosen as follows:

<table>
<thead>
<tr>
<th>Initial state (volt)</th>
<th>Final state (volt)</th>
<th>Potential difference (volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>8.0</td>
<td>2.0</td>
</tr>
<tr>
<td>10.5</td>
<td>8.0</td>
<td>2.5</td>
</tr>
<tr>
<td>11.0</td>
<td>8.0</td>
<td>3.0</td>
</tr>
<tr>
<td>9.0</td>
<td>7.0</td>
<td>2.0</td>
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<tr>
<td>9.5</td>
<td>7.0</td>
<td>2.5</td>
</tr>
<tr>
<td>10.0</td>
<td>7.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Although the trace of recovery current on the oscillograph must ideally be shown as Fig. 1, the actual trace was always found to be apart from the ideal shape, as Fig. 3 for instance, in which the bath voltage was reduced from 10.5 volt to 8.0 volt at 30℃. In the initial stages, the current flow was always lower in the deuterated system than the protonated one, and longer recovery period was observed in the former. It was previously reported, that under galvanostatic conditions, bath voltage was higher in the deuterated sys-

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*H₃PO₄: 70%, H₂SO₄: 20%, CrO₃: 10 wt.%, 96℃
**H₃PO₄: (85%) 35 ml, CrO₃: 20 g, H₂O 1 l
tem than in the protonated one, and present experiment is in good agreement with the previous report.

In all the experiments, the same type of the oscillographic traces were obtained, from which the recovery periods were summarized in Figs. 4 and 5. Since the potential difference is related to the difference in barrier thickness according to the equation

\[
\text{barrier thickness} = 12 \text{ Å}/\text{volt}
\]

for sulfuric acid film, recovery periods should be proportional to the potential difference if the film thinning would proceed at a constant rate. The result suggests, that the rate of the dissolution of oxide films is not uniform but forming time- and forming potential-dependent.

The ratio of the recovery period of the deuterated to the protonated system is shown in Fig. 6. The ratio ranged from 1.1 to 1.4, being higher when the potential difference is small. The ratio of about two expected from their ionic mobilities was not obtained in these cases.

\[
\Delta E
\]

Fig. 6 Relation between abrupt change of the applied voltage and the ratio of the recovery period (\(\text{D}_2\text{SO}_4/\text{H}_2\text{SO}_4\))

Fig. 7 shows the temperature dependence of the recovery periods, from which apparent activation energy of the recovery process including the chemical and electrochemical dissolutions of alumina film was calculated. Difference in the activation energy between the protonated and deuterated system was not able to recognized.

\footnote{Since the ionic mobility of \(\text{OH}^-\) and \(\text{OD}^-\) ions in aqueous solution was reported to be 197 and 119 cm²/s cm⁻¹, respectively, and since the ionic mobility of \(\text{H}^+\) and \(\text{D}^+\) ions in the oxide film was not known, we assume roughly that the ratio of the ionic mobility \(\mu_{\text{H}^+}/\mu_{\text{D}^+}\) is about two. According to J.F. Murphy et. al., current recovery is originated from the neutralization of the protonic space charge, of which diffusion rate would be correlated with its ionic mobility. Therefore, rough estimation of ratio of the recovery period (about two) would be acceptable without considerable error.}
3.2 Exchange effect

In order to clearly if the recovery process is mainly affected by the film constituents itself or by the electrolyte allowed to recover, the following exchange test was examined.

Samples were anodized in the H₂SO₄ electrolyte first, then transferred to the D₂SO₄ electrolyte to be allowed to recover by applying the lower anodizing voltage, and vice versa. In order to avoid contamination of the electrolyte by light water, exchange of the samples was done after careful and quick rinse and drying.

Experimental conditions were as follows:

1) formed in H₂SO₄ electrolyte at 12 volt, allowed to recover in D₂SO₄ electrolyte at 8 volt.
2) formed in D₂SO₄ electrolyte at 12 volt, allowed to recover in H₂SO₄ electrolyte at 8 volt.

The results were shown in Fig. 8, comparing the non-exchange tests. The recovery period was always shorter than that of the non-exchange tests, although the final steady current was limited by the solution being allowed to recover. It seems therefore, that proton built in the oxide film played less important roles than that existing in the electrolyte. It must be noted that the time of the interruption by the exchange process was excluded and this period without external applied voltage would have a complex effect on the recovery process. This effect must be further investigated.

3.3 Chemical dissolution

Under applied external voltage condition, anodic oxide film dissolves by both chemical and electrochemical (field-assisted) processes. To distinguish the pure chemical process, dissolution rate of the anodic oxide film in the electrolyte without external applied voltage was measured by a gravimetric method. Samples were at first anodized in either H₂SO₄ or D₂SO₄ electrolyte for 60 min. at the current density of 20 mA/cm² at 25°C. The weight of samples was measured, then immersed in the respective electrolyte. The samples were weighed at intervals until no weight loss of samples was observed and final steady state was obtained. Fig. 9 shows the weight loss of samples. The theoretical film weight* shown in the figure by dotted line was calculated from the charge passed (20 × 3600 × 10⁻¹⁵ coulomb/cm²), from which coating ratio for 1M-H₂SO₄, and 1M-D₂SO₄, electrolyte was found to be 1.26 and 1.41, respectively.

![Graph showing theoretical film weight and dissolution rate](image)

Theoretical film weight was calculated from the charge passed and film dissolution during anodization was assumed to be nil

Fig. 9 Rate of the chemical dissolution in the same electrolyte

From the slope of these curves, rate of the film dissolution in the H₂SO₄ electrolyte was found to be 4 mg/h·cm², while that in the D₂SO₄ electrolyte was initially ca. 1.5 mg/h·cm² and finally ca. 4 mg/h·cm², average dissolution rate being 2.7 mg/h·cm². Change...
in the dissolution rate in the case of the D₂SO₄ electrolyte is presumably due to the effect of rinse at intervals. During this process the exchange reaction between protons and deuterons would have partially occurred. As tested in the case of the recovery effect, exchange of the forming and dissolving solution was done. Result was shown in Fig. 10. Evidently the rate of the film dissolution in the H₂SO₄ electrolyte is presumably due to the effect of rinse at intervals. During this process the exchange reaction between protons and deuterons would have partially occurred. As tested in the case of the recovery effect, exchange of the forming and dissolving solution was done. Result was shown in Fig. 10. Evidently the rate of the film dissolution in the H₂SO₄ electrolyte was faster than that in the D₂SO₄ one. The film formed in the D₂SO₄ electrolyte dissolved in the H₂SO₄ one at the rate of ca. 2 mg/h·cm² initially, however the rate became eventually to 4.4 mg/h·cm² during the course of dissolution. The film formed in the H₂SO₄ electrolyte dissolved in the D₂SO₄ one at the rate of ca. 1.6 mg/h·cm². The ratio of these dissolution rates was ca. 2.7, being greater than 2.0 which is expected from the ionic mobility. The chemical dissolution is therefore mostly depending upon the solution allowed to stand rather than that being formed.

Theoretical film weight was calculated from the charge passed and film dissolution during anodization was assumed to be nil. Fig. 10 Rate of the chemical dissolution in the exchanged solution

3.4 Effect of mixing H₂SO₄ and D₂SO₄ electrolytes

From the experiments mentioned above, it was supposed, that the effect of deuterons was predominant in the solution rather than in the oxide film. The ratio of the dissolution rate is 1.2~1.4 for the recovery periods, while 2.7 for the chemical dissolution. To determine what concentration of the sulfuric acid solution corresponds to the 1M–deuterosulfuric acid solution in the ability of recovering, the effect of variation in the acid concentration on the recovery periods was investigated. The result showed that the H₂SO₄ concentration of ca. 0.57 mol was comparable to the 1M-D₂SO₄ electrolyte in obtaining the same recovery period. It might be therefore considered, that the ability of recovering is doubled to the D₂SO₄ electrolyte. When these two solutions were mixed in various mole fractions, the recovery period varies from that of the pure state. Fig. 11 shows the variation, indicating that the recovery period lowered steeply with increasing protonic mole fraction until the mole fraction of about 0.6 was attained, then change became slight. Non-linearity of the curve suggest, that the ability of recovering in mixed system was not simply additive but more complicated.

4 Discussion

There have been two different concepts in the recovery phenomenon. One is proposed by Murphy et al., in which the current recovery occurs during the diffusional neutralization of protonic space charge at the oxide/electrolyte interface. The other is presented by Diggle et al., in which the current recovery involves at least two processes: In the initial stage, it is slow film thinning by chemical dissolution, during which the field strength is insufficient to flow the ionic current, and in the later it is rapid film thinning accelerated by the strong electric field. If we take the former concept, the recovery period of the deuterated system would be about doubled to that of the protonated system, since the rate of diffusion and reactivity of deuterons is about a half of the proton. In fact, the ratio of the recovery period ranged from 1.2 to 1.4, being smaller than 2.0. Taking into consideration of the case of unhydrous ferric sulfate, however, the ratio of exactly 2 was reported, from which Lieser et al. has concluded, that the rate-determining step of the dissolution of ferric
sulfate is a reaction involving proton.

We should therefore discard the mechanism in which diffusion of the protonic space charge is in the recovery period rate-determining step. Furthermore, the exchange effect of the recovery period suggested, that protons or deuterons in the electrolyte being allowed to recover played an important role on the recovery process. The results are just opposite to that of Michelson’s in which recovery period was determined by the forming electrolyte. Exchange reaction may proceed by following steps:

\[ D^+ (Al_2O_3) + H^+ \rightarrow H^+(Al_2O_3) + D^+ \]

\[ D^+ + HSO_4^- \rightarrow H^+ + DSO_4^- \]

Since DSO_4^- ion is less ionizable than HSO_4^- ion, concentration of D^+ ion in the solution is small, thus the exchange reaction at the oxide/electrolyte interface proceeds further, and the rate of dissolution became fast as if the oxide film had been formed in the H_2SO_4 electrolyte.

The rate of the chemical dissolution determined by immersion is slow in the case of the D_2SO_4 electrolyte indicating that the dissolution is limited by the solution allowed to dissolve. In this case the ratio of the dissolution rate is more than 2.0. The fact suggests that the chemical dissolution of the oxide film is governed by complex effect of H^+ ion and HSO_4^- ion.

If we assume, that the effect of H^+ ion would be about 2 times of D^+, while that of HSO_4^- would be 1.35 times of DSO_4^- then resulting complex effect should be 2.7 times. Thus it is concluded, that dissolution of oxide films in the sulfuric acid electrolyte without external applied voltage is controlled by both H^+ and HSO_4^- ions.

5 Summary

Effect of deuterons on anodic formation and dissolution of oxide films was determined and results were as follows:

1. Current recovery period after abrupt change of external applied voltage was longer in the deuterated system than that in the protonated system, the recovery period being mainly affected by the solution allowed to recover.

2. The dissolution rate without external applied voltage is faster in the protonated system than that in the deuterated system—[the ratio being ca. 2.7]

3. Effect of protons was predominant in the electrolyte allowed to dissolve rather than in the forming electrolyte, and results were not consistent with that of Michelson's.

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Literatures:
1) N. Baba, This Journal 38 (No. 4), 282 (1970).
5) M. Nagayama, K. Tamura, This Journal 37 (No. 1), 34 (1968).
6) M. Nagayama, K. Tamura, ibid. 31 (No. 7), 499 (1968).