<table>
<thead>
<tr>
<th>Title</th>
<th>Mechanism of grain boundary corrosion of aluminium in high temperature water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Nomura, Sueo</td>
</tr>
<tr>
<td>Citation</td>
<td>The Review of Physical Chemistry of Japan (1960), 30(2): 100-108</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1960-12-30</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/46803">http://hdl.handle.net/2433/46803</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
MECHANISM OF GRAIN BOUNDARY CORROSION OF ALUMINIUM IN HIGH TEMPERATURE WATER

By Sueo Nōmura

(Received November 3, 1960)

Mechanism of grain boundary corrosion of aluminium in high temperature water is studied by metallographic and electrochemical methods.

It was found that grain boundary corrosion of aluminium in high temperature water showing different behavior from so-called "grain boundary corrosion" was governed by (1) grain boundary diffusion of hydrogen atoms, (2) over-voltage of hydrogen produced by the reaction between aluminium and water and (3) the property of surface film on aluminium.

In demineralized water, the rate of corrosion of pure aluminium is determined by the grain boundary diffusion of hydrogen atoms and by the effect of small amounts of cathodic elements on the surface film properties. In dilute acidic solution, grain boundary corrosion of pure aluminium does not occur and this is explained by the low over-voltage of hydrogen in the solution.

Introduction

Absorption cross-section of aluminium for thermal neutron is small; and because of its good physical and chemical characteristics as well as its low cost, aluminium is widely used as an atomic reactor material. However, when it is used in high temperature and high pressure water cooled reactors, the deterioration of its mechanical properties and its high corrosion rate become an important problem. Particularly, the grain boundary corrosion of aluminium in pure water over 100°C becomes greater with increasing aluminium purity which is in contradiction to ordinary concept. Such heavy grain boundary corrosion of pure aluminium is, according to Draley and Altenpohl, due to breakdown of crystal structure when hydrogen atoms produced by the reaction between Al and water diffuse into grain boundary and form gaseous molecules. Therefore, we have carried out various experiments in our research group in order to investigate the causes of grain boundary corrosion of aluminium. This report summarizes the work and proposes a mechanism of grain boundary corrosion of aluminium.

4) M. Kawasaki, S. Nomura and T. Kondo, J. of Japan Inst. of Metal, on printing
5) S. Kondo and S. Nomura, unpublished data
Experimental Procedure

The test specimens used were from three different batches of commercial aluminium containing impurities as given in Table 1. The specimen size was 20 mm x 50 mm and 2 mm thick. Each of these specimens was annealed for one hour at 400°C, polished and put into quartz test tubes which contained 150 cc of demineralized water. Most of the corrosion test were performed in a 18/8 stainless steel autoclave.

Results and Discussion

1 Preliminary experiment By using the three samples of different aluminium purity as given in Table 1, electrochemical measurement in water of 100°C and 200°C, measurement of

![Graphs showing potential difference and current over time for different samples at 100°C and 200°C](image1)

![Graphs showing potential difference and current over time for different samples at 100°C and 200°C](image2)

Fig. 1 Changes of voltage and current between Al sample and autoclave body in high temperature pure water
corrosion kinetics at 200°C, and metallographic observation were made. The method of electrochemical measurement used was as following: the aluminium test pieces were hanged to insulated platinum electrode in the autoclave, and a primary electric cell was made between the test piece and the autoclave through the pure water. The open circuit potential difference described above and the electric current in a closed circuit were alternatively measured. From the results of above experiments as shown in Fig. 1, we can see that sample C (99.99% Al) has the largest potential difference, that is, the lowest potential and thus the strongest motive force for corrosion. The potential difference of sample B (99.9% Al) is closer to C than to A (99.0% Al) at 100°C and 200°C, and the metallographic inspection as shown in Fig. 3 shows the corresponding agreement between grain boundary corrosion and high potential difference for these samples. On the other hand, electric current decreases parabolically with time for A and B, but C shows rapid increase and variations at 200°C, and these coincide well with curves of weight changes (Fig. 2). From Fig. 3 showing surface and cross-section of sample after corrosion at 200°C, we see that B and C suffered grain boundary corrosion while A was uniformly attacked. According to cross-sectional figures in Fig. 3-(b) and Fig. 7, grain boundary corrosion of C is different from so-called “grain boundary corrosion” because we can observe heavy corrosion not only at grain boundary but also uniformly along the surface, and therefore it is assumed that uniform attack of pure aluminium by water is emphasized strongly along the grain boundary. From the above observations and considering the properties of high temperature and high pressure pure water, it seems necessary to consider a different mechanism on grain boundary corrosion of aluminium. Fig. 3-(b) and Fig. 7 also show that the surface film of C has a rough structure unlike A and B which have thin but good cohesive films, but B shows parabolic corrosion decay curve in spite of the slight grain boundary corrosion indicated in Fig. 3-(b).

Therefore, two factors governing the grain boundary corrosion of aluminium in high temperature pure water are proposed as follows:

1. Characteristics or protectiveness of surface film on Al.
Mechanism of Grain Boundary Corrosion of Aluminium in High Temperature Water

Fig. 3-(a) Metallographic observation of Al samples corroded in demineralized water at 200°C (×300).

Fig. 3-(b) Cross-sectional views of Al samples after corroded in demineralized water at 200°C for 10 hrs (Polarized light, ×250).
Fig. 4 Effect of atmospheric gas on corrosion of 99.99% Al in demineralized water at 150°C for 20 hrs (×250)

(A) 99.0% Al

(C) 99.99% Al fine grain

(B) 99.9% Al

(C') 99.99% Al coarse grain

Fig. 5 Effect of hydrogen atmosphere on grain boundary corrosion of Al samples corroded in demineralized water at 200°C for 10 hrs (H₂: 5 atm) (×150)
Mechanism of Grain Boundary Corrosion of Aluminium in High Temperature Water

![Surface view, ordinary light (x100)](image)

![Cross-sectional view, polarized light (x100)](image)

Fig. 7 Grain boundary corrosion of 99.99% Al samples which have both fine and coarse grained structure corroded by demineralized water at 100°C
S. Nomura

**Fig. 6** Effect of pH in solution of grain boundary corrosion of 99.99% Al corroded at 200°C for 10 hrs (×160)

**Fig. 8** Effect of cold rolling on grain boundary corrosion of 99.99% Al in demineralized water at 170°C for 20 hrs (cross-sectional view, ×100)

<table>
<thead>
<tr>
<th>Atmospheric gas</th>
<th>Added pressure atm</th>
<th>Weight gain mg/dm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1</td>
<td>126</td>
</tr>
<tr>
<td>O₂</td>
<td>1</td>
<td>112</td>
</tr>
<tr>
<td>H₂</td>
<td>1</td>
<td>126</td>
</tr>
<tr>
<td>Ar</td>
<td>5</td>
<td>76</td>
</tr>
<tr>
<td>O₂</td>
<td>5</td>
<td>26</td>
</tr>
<tr>
<td>H₂</td>
<td>5</td>
<td>150</td>
</tr>
<tr>
<td>Ar</td>
<td>15</td>
<td>121</td>
</tr>
<tr>
<td>O₂</td>
<td>15</td>
<td>140</td>
</tr>
<tr>
<td>H₂</td>
<td>15</td>
<td>119</td>
</tr>
</tbody>
</table>

Table 2 Effect of atmospheric gas and its pressure on corrosion of 99.99% Al in demineralized water at 150°C for 20 hrs

*face to p. 103*
Mechanism of Grain Boundary Corrosion of Aluminium in High Temperature Water

(2) Easiness of penetration of H$_2$O or OH ion into grain boundaries with resulting grain boundary corrosion.

Because pure aluminium has more defects or vacancies at the grain boundaries, the hydrogen atoms produced by reaction between aluminium and H$_2$O or OH ion are absorbed and diffused easily into the grain boundaries where these combine into H$_2$ gas thus destroying the crystal structure. The breakdown of the crystal structure then controls the penetration rate of H$_2$O or OH ion into grain boundaries. The latter factor (2) will then be controlled, in the case of Al with 1% maximum impurity, by (i) diffusion of hydrogen atoms into grain boundary and (ii) hydrogen over-voltage.

For the purpose of ascertaining the above three factors such as (1), (2)-(i) and (2)-(ii), the following experiments were carried out.

2 Effect of gas atmosphere If the grain boundary corrosion is influenced largely by diffusion of hydrogen atom into grain boundary, we can anticipate increased grain boundary corrosion due to increased hydrogen absorption in aluminium by enhancing the diffusion of hydrogen into boundary by employing hydrogen gas atmosphere. On the other hand, if we use oxygen atmosphere, hydrogen atom produced by the reaction between aluminium and H$_2$O or OH ion will combine immediately with oxygen at the film surface and form H$_2$O or OH ion. Thus, it is expected that grain boundary diffusion of hydrogen atom will be prevented under oxygen atmosphere.

We carried out corrosion experiments of pure aluminium in demineralized water under H$_2$, O$_2$, and Ar atmospheres and in vacuum at 100°C, and obtained the results as shown in Fig. 4. From this we can see that deep hydrogen penetration has taken place under hydrogen atmosphere and no grain boundary attack under oxygen atmosphere. The grain boundary attack was also observed in argon gas atmosphere and vacuum. The amount of corrosion of pure aluminium under hydrogen atmosphere is larger than that in oxygen atmosphere at 1 atm due to increased grain boundary corrosion. However, when hydrogen pressure is increased further, total amount of corrosion decreases due to the reducing action of H$_2$ gas though grain boundary penetration increases. In contrast to this, when oxygen pressure is increased, total amount of corrosion by oxidation becomes larger than that of hydrogen although no grain boundary corrosion has taken place. Table 2 confirms this fact.

The above mentioned phenomena can be explained well when we consider that the grain boundary diffusion of hydrogen is the main factor controlling boundary corrosion of pure aluminium, and we can not explain satisfactorily the action of oxygen by Carlsern's argument which attributes the cause of grain boundary corrosion to local concentration of OH ions near the grain boundary.

In order to examine further the effect of hydrogen, an experiment was performed under hydrogen atmosphere for the three kinds of samples A, B and C and results are shown in Fig. 5. As can be seen from the figure, grain boundary attack occurs for sample A in which no grain boundary corrosion took place in ordinary atmosphere as seen in Fig. 3. For sample C', we

observe many blisters on all surface which can be considered to be due to the penetration of
many hydrogen atoms into the grains. These facts also suggest that grain boundary diffusion
or penetration of hydrogen atom is considered to be the most effective factor among the three
factors described above.

3 Effect of hydrogen ion concentration By adjusting the pH of the solution with
sulphuric acid and alkali, we investigated the influence of hydrogen ion concentration on corrosion
of sample C at 200°C. The result showed the minimum corrosion at pH 3, and grain boundary
corrosion did not occur in this solution as can be seen in Fig. 6. The decrease of total
corrosion is due to decrease of OH ions because of the acidity of the solution with pH 3, but
the largest reason for the disappearing of grain boundary corrosion is considered to be due to the
remarkable decrease of hydrogen over-voltage caused by increase of hydrogen ions. Low hydrogen
over-voltage makes the combination of the hydrogen atoms to gaseous molecules easier at the
film surface so that absorption and grain boundary diffusion of hydrogen atoms decrease in acidic
solution. The surface film formed in the solution of pH 3 is very thin, but is very uniform,
and shows high electric resistance per unit thickness although total resistance is small as will
be described in “6”.

4 Effect of crystal grain size Preparing test specimens of different crystal grain
size (area ratio is about 1 : 10) by using aluminium of purity 99.99%, we compared the grain bound-
dary corrosion, and obtained the results shown in Fig. 7. Each grain boundary shows about equal
corrosion width and penetration depth. Therefore, total corrosion is smaller for the coarse grained
specimen than for the fine grained one which of course has larger grain boundary areas. This
result is entirely opposite to the results obtained for aluminium alloys such as Fe, Ni and Si
alloys10, and we can explain the reason by considering that the diffusion and penetration of
hydrogen atom into grain boundaries govern the grain boundary corrosion of pure aluminium
and are taking place uniformly.

5 Effect of cold rolling We investigated the effect of cold rolling of pure aluminium
on grain boundary corrosion by breaking up the grain boundary structure. The result shows
that the grain boundary corrosion decreases as the boundary structure of aluminium surface was
broken by increased cold rolling (Fig. 8). However, due to many stresses and defects remaining
on or near the surface, hydrogen atom diffusion and hydrogen gas formation become active near
the surface: thus they make the surface film spall off easily, and corrosion increases occasionally
as shown in Table 3.

<table>
<thead>
<tr>
<th>Reduction ratio (cold rolling)</th>
<th>0</th>
<th>10%</th>
<th>35.5%</th>
<th>85%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. gain, mg/dm²</td>
<td>969</td>
<td>1241</td>
<td>1156</td>
<td>810</td>
</tr>
<tr>
<td>Fallen corr. product, mg/dm²</td>
<td>0</td>
<td>15</td>
<td>165</td>
<td>288</td>
</tr>
<tr>
<td>Total wt. increase, mg/dm²</td>
<td>969</td>
<td>1256</td>
<td>1321</td>
<td>1098</td>
</tr>
</tbody>
</table>
Mechanism of Grain Boundary Corrosion of Aluminium in High Temperature Water

6 Effects of properties of surface film and alloying elements

Since hydrogen ions, which are formed by reaction between aluminium and water, and hydrogen atoms formed by discharge of these ions diffuse through surface film of aluminium, the structure and nature of surface film is considered to have inevitably marked effect on progression of grain boundary corrosion. In fact, as described in "1", the sample B at 200°C shows grain boundary corrosion, but the amount of corrosion decreased with time. This indicates that the protective property of surface film has large effects on corrosion, although we cannot neglect impurity atoms in the grain boundaries which resist the diffusion of hydrogen atoms into grain boundary. We also pointed out from Fig. 1 that sample A always shows uniform corrosion and higher potential than B and C samples having grain boundary corrosion. Thus in order to ascertain the results of "1", we measured electric conductivity of water and electric potentials of samples after corrosion at 200°C for 3 hours. The potentials were measured at 25°C in N/100 NaOH solution. The reason for using dilute NaOH solution is as follows. (a) In the case of pure water, electric resistance is so high that potential measurement in pure water can easily give rise to errors. (b) Pure water is heavily polluted by the salt bridge. (c) Corrosion behavior of aluminium in pure water is similar to that in dilute alkali solutions. Table 4-(b) gives results of conductivity measurement of water after corrosion test. The measurements were made by using conductivity cell having both platinum black electrodes and also similar cell having platinum black electrode on one side and corroded specimen being used as the other electrode. The word "Film factor" which is the ratio of the two measurements as shown in Table 4-(b) is believed to give a scale for electric resistivity of surface film on aluminium.

Table 4-(a) Natural electrode potentials of Al samples corroded in demineralized water at 200°C for 3 hrs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volt vs. S. C. E.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in N/100 NaOH</td>
</tr>
<tr>
<td>A (99.0% Al)</td>
<td>-1.45</td>
</tr>
<tr>
<td>B (99.9% Al)</td>
<td>-1.49</td>
</tr>
<tr>
<td>C (99.99% Al)</td>
<td>-1.51</td>
</tr>
<tr>
<td>C* (ν)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4-(b) Specific electric resistance of water after corrosion test measured by Pt-Pt electrode cell and Pt-corroded Al electrode cell

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific resistance</th>
<th>Film factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt-Pt electrodes</td>
<td>Pt-Al electrodes</td>
</tr>
<tr>
<td>A (99.0% Al)</td>
<td>56.5 kΩ·cm</td>
<td>41.0 kΩ·cm</td>
</tr>
<tr>
<td>B (99.9% Al)</td>
<td>76.0</td>
<td>48.0</td>
</tr>
<tr>
<td>C (99.99% Al)</td>
<td>95.0</td>
<td>34.0</td>
</tr>
<tr>
<td>C* (ν)</td>
<td>42.0</td>
<td>29.0</td>
</tr>
</tbody>
</table>

* It is corroded in N/1000 H₂SO₄ solution at 200°C for 3 hrs
Now, Hunter and Fowle\(^7,8\) found that the oxide film of aluminium in air had double layer structure, and Dillon and Trounser\(^9,10\) also confirmed that the surface film formed in high temperature water had similar double layer structure. Both of the above investigators, then, found that the corrosion resistant properties of aluminium and electric resistance of surface film depend mainly on protective inner layer of surface film. Furthermore, Hunter and Fowle found that similar surface film having double layer structure would be formed by anodic oxidation of aluminium in suitable aqueous solution, and voltage necessary to make anodized film would depend almost entirely on thin protective inner film. From such structural similarity between anodized film and ordinary oxidized film, the author investigated properties of film by comparing electrochemical characteristics of films formed by anodic oxidation of aluminium and its alloy in Na\(_2\)B\(_4\)O\(_7\) solution. The specimens used here were aluminium of 99.99% purity, and two alloyed aluminium having 0.5% and 1.0% Ni respectively. The anodic oxidation curves of these samples with constant current in Na\(_2\)B\(_4\)O\(_7\) solution are shown in Fig. 9. As can be seen from the figure, pure aluminium shows gradual potential rise, while Al–Ni alloys show rapid potential increase and clear critical point. This seems to indicate high electric resistance or high protective property of the films on Al–Ni alloys' surface. We then measured natural decay of potential of film formed anodically in the same solution after the current was cut off. The results are given in Fig. 10 in which the potential at the critical point of the curve is ordinary called "Flade potential"\(^11\). Because we can clearly see the critical point for Al–Ni alloys, it is assumed that Al–Ni alloys and especially Al–1.0%Ni alloy have high stability of surface films. In addition to above mentioned improvement of protectiveness of the film, the alloying of Ni, Fe and etc. to Al prevents diffusion of hydrogen atoms into the grain boundaries at which these alloying

\(^7\) M. S. Hunter and P. Fowle, J. Electrochm. Soc., 101, 481 (1954)
\(^8\) M. S. Hunter and P. Fowle, ibid., 103, 482 (1956)
\(^9\) R. L. Dillon and V. H. Trounser, HW-53389 (1956)
\(^10\) V. H. Trounser, HW-53389 (1956)
\(^11\) F. Flade, Z. phys. Chem., 76, 513 (1911)
elements are concentrated, and also decreases hydrogen over-voltage. Therefore, grain boundary corrosion becomes more difficult with alloying of such elements, and obviously 1.0% Ni alloy is more resistant for corrosion in high temperature water than 0.5% Ni alloy, and uniform corrosion proceeds even at 200°C. Since hydrogen over-voltage of metal in pure water under high temperature and high pressure is difficult to measure, we measured cathodic polarization of pure Al.

![Graph](image1)

Fig. 10 Potential decay curves of Al samples anodized in 1N-Na$_2$B$_4$O$_7$ solution by 1mA/cm at 30°C for 3hrs

1% Ni alloy and 1% Fe alloy at 25°C in N/100 H$_2$SO$_4$ solution as a reference. These results are shown in Fig. 11. Though it is dangerous to extrapolate this result to the case of high temperature water, 1% Ni alloy is seemed to have and does have superior corrosion resistance to

![Graph](image2)

Fig. 11 Cathodic polarization curves of 99.99% Al, 1.0% Ni alloy and 1.0% Fe alloy in N/100 H$_2$SO$_4$ solution at room temperature
S. Nomura

1% Fe alloy. On the other hand, 1% Fe alloy does not show grain boundary corrosion in high temperature water although it shows approximately the same hydrogen over-voltage as pure aluminium has (Fig. 11). This seems to be due to good protective property of surface film and high resisting power for grain boundary diffusion of hydrogen atoms by boundary concentrated Fe atoms.

Conclusion

Summarizing the foregoing results, the following three items may be considered as the controlling factors of grain boundary corrosion of aluminium in high temperature water: (a) grain boundary diffusion and penetration of hydrogen atoms, (b) hydrogen over-voltage and (c) protective property of surface film.

Although two or three of these factors act on the metal simultaneously in many cases, grain boundary corrosion of aluminium in high temperature pure water is considered to be primarily controlled by grain boundary diffusion of hydrogen atoms. When changes in corrosive environment and/or metal composition occur, the other two factors may control grain boundary corrosion. For example, as the hydrogen ion concentration increases, influence of hydrogen over-voltage becomes larger and also when a small amount of alloying element like Fe, Ni etc. is added to pure aluminium, the protectiveness of the surface film seems to affect the grain boundary corrosion of aluminium rather than the diffusion of hydrogen atom into the grain boundary.

Acknowledgement

The author would like to express his sincere thanks to Dr. M. Kawasaki who kindly directed this research and to Mr. and Mrs. Kondo who assisted the experiments and discussed the results.

Japan Atomic Energy Research Institute
Ibaraki Pref., Japan