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MECHANISM OF GRAIN BOUNDARY CORROSION OF ALUMINIUM IN HIGH TEMPERATURE WATER

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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 Draley¹⁾ and Altenpohl²⁾, 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 aluminium³⁻⁵⁾. This report summarizes the work and proposes a mechanism of grain boundary corrosion of aluminium.

1) J. E. Draley and W. E. Ruther, *ANL-5430* (1955), *ANL-5658* (1957)

2) D. Altenpohl, *Z. Metallk.*, **48**, 306 (1957)

3) S. Nomura, G. Ito and M. Kawasaki, *Proc. of 2nd Symp. on Progress of Atomic Energy in Japan*, **III** (1958)

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5) S. Kondo and S. Nomura, *unpublished data*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 × 50 mm and 2 mm thick. Each

Table 1 Chemical composition of Al test specimens

No.	Al	Si	Fe	Cu	Mn	Mg	Zn
A	99.149%	0.18%	0.64%	0.02%	0.009%	0.0017%	+
B	99.93	0.024	0.036	0.003	0.0023	0.0011	+
C	99.991	0.005	0.001	0.002	0.0007	0.0012	-

of these specimens was annealed for one hour at 400°C, polished and put into quartz test tubes which contained 150cc 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

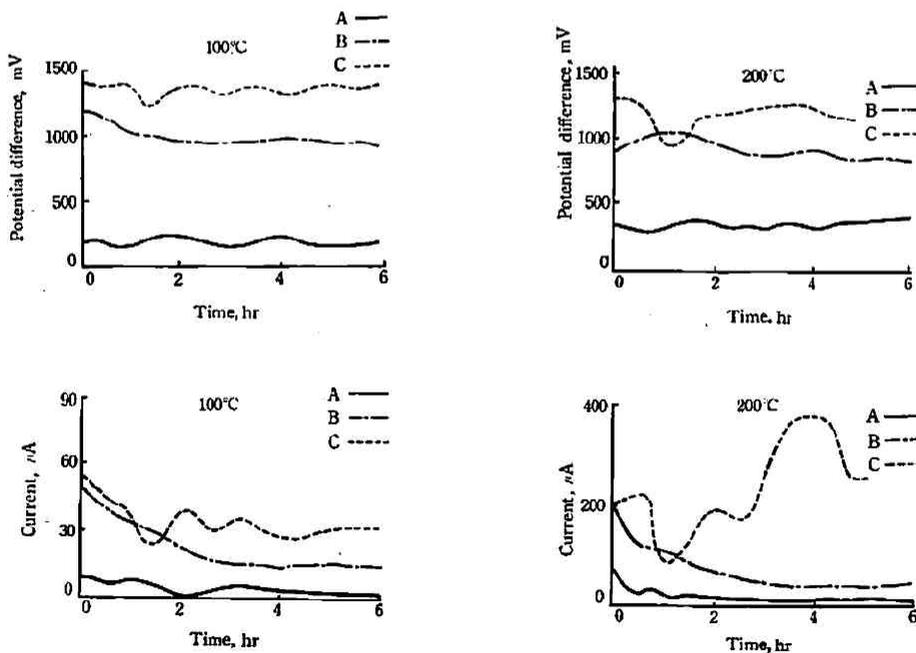


Fig. 1 Changes of voltage and current between Al sample and autoclave body in high temperature pure water

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

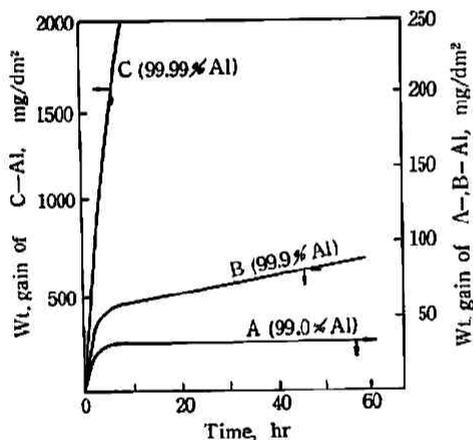


Fig. 2 Weight changes of Al samples in demineralized water at 200°C

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.

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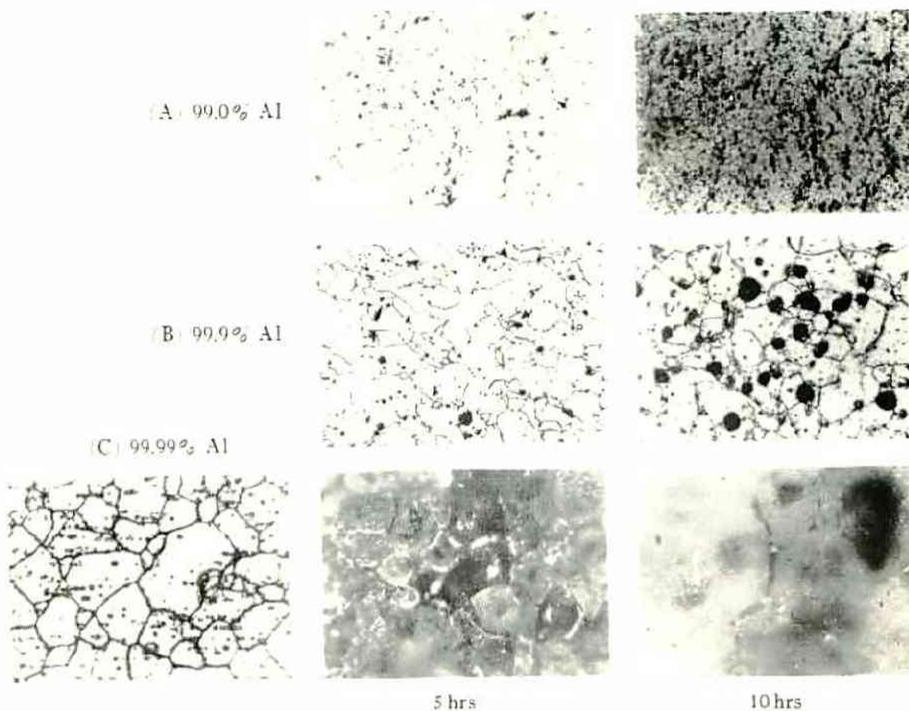


Fig. 3-(a) Metallographic observation of Al samples corroded in demineralized water at 200°C ($\times 300$)

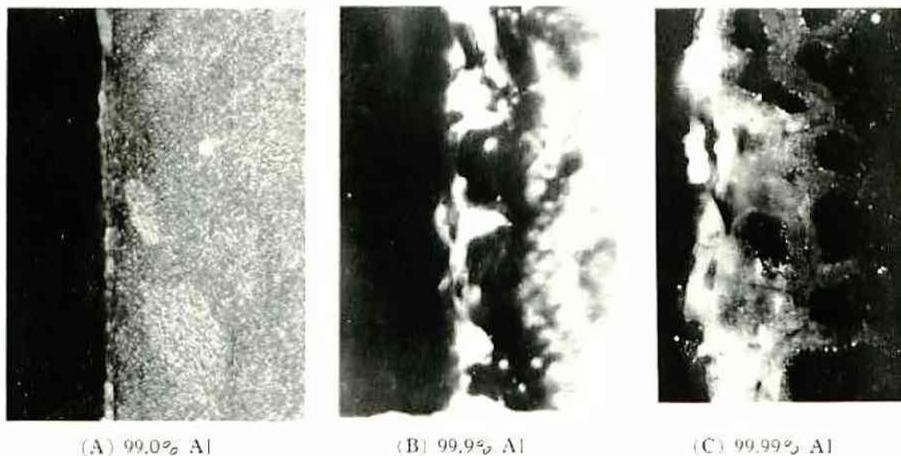


Fig. 3-(b) Cross-sectional views of Al samples after corroded in demineralized water at 200°C for 10 hrs (Polarized light, $\times 250$)

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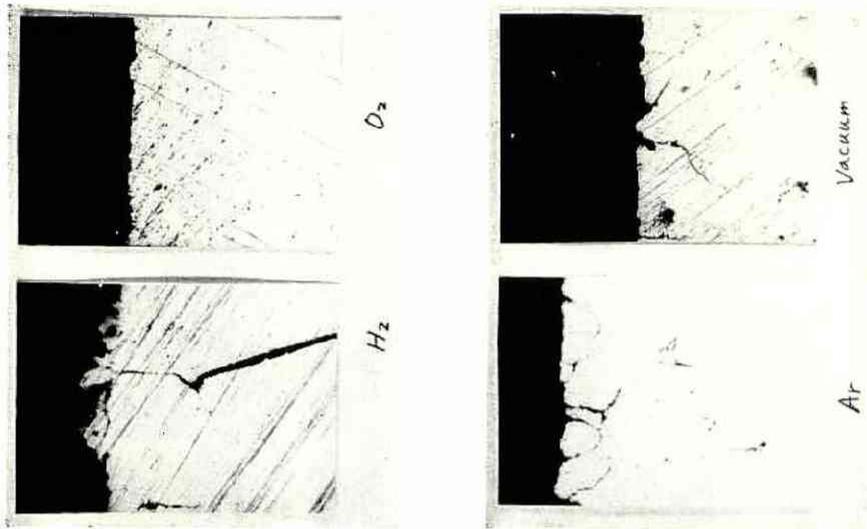


Fig. 4 Effect of atmospheric gas on corrosion of 99.99% Al in demineralized water at 150°C for 20 hrs ($\times 250$)

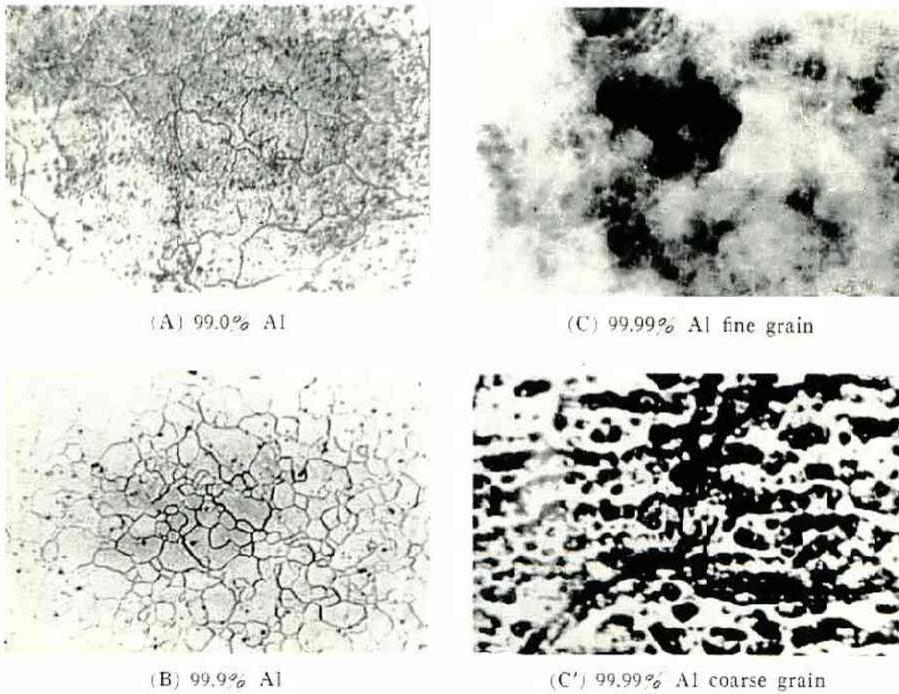


Fig. 5 Effect of hydrogen atmosphere on grain boundary corrosion of Al samples corroded in demineralized water at 200°C for 10 hrs (H_2 : 5 atm) ($\times 150$)

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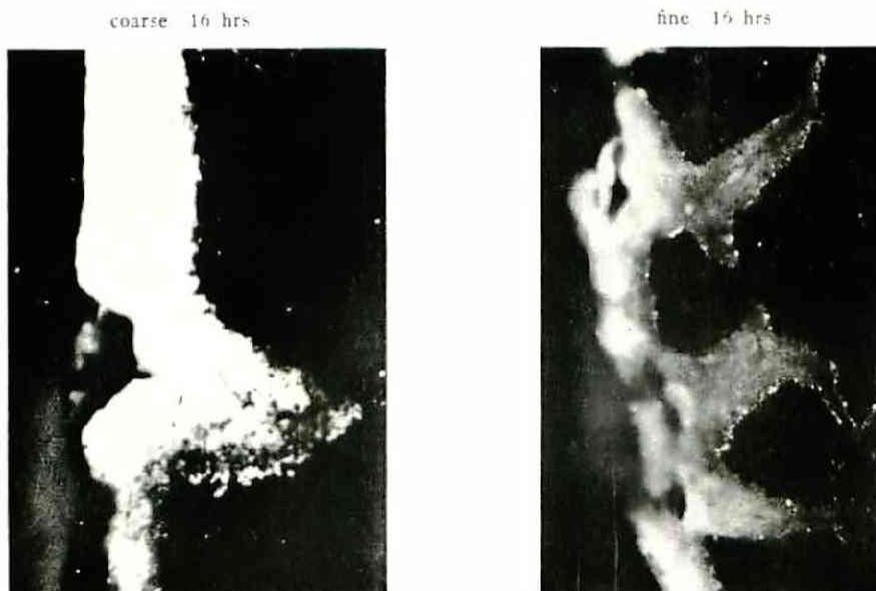
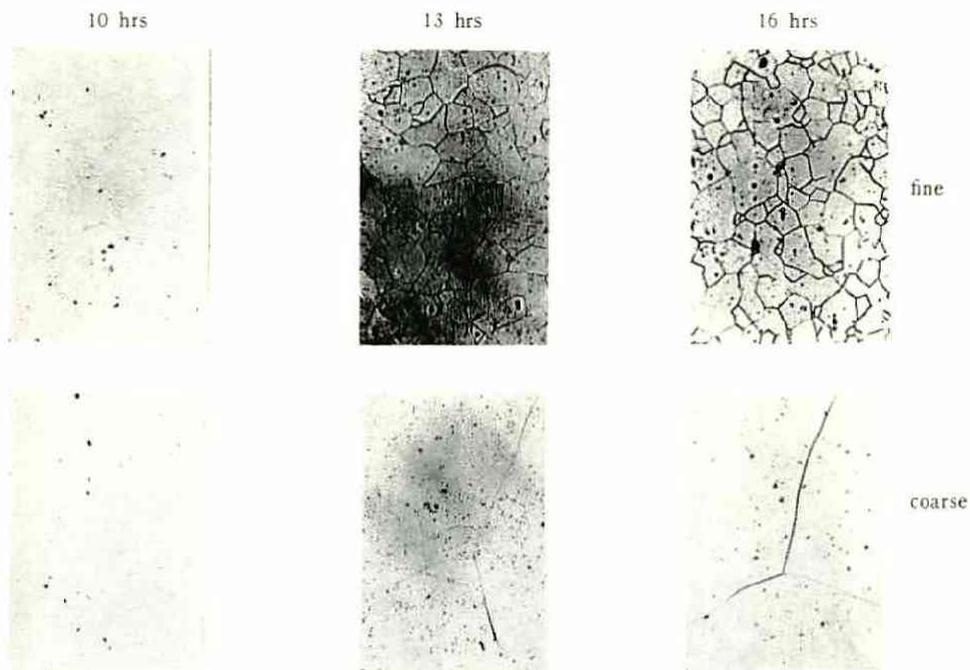


Fig. 7 Grain boundary corrosion of 99.99% Al samples which have both fine and coarse grained structure corroded by demineralized water at 100°C

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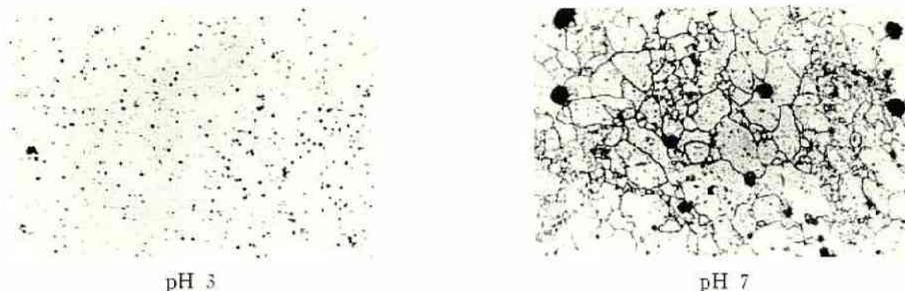


Fig. 6 Effect of pH in solution of grain boundary corrosion of 99.99% Al corroded at 20°C for 10 hrs ($\times 160$)

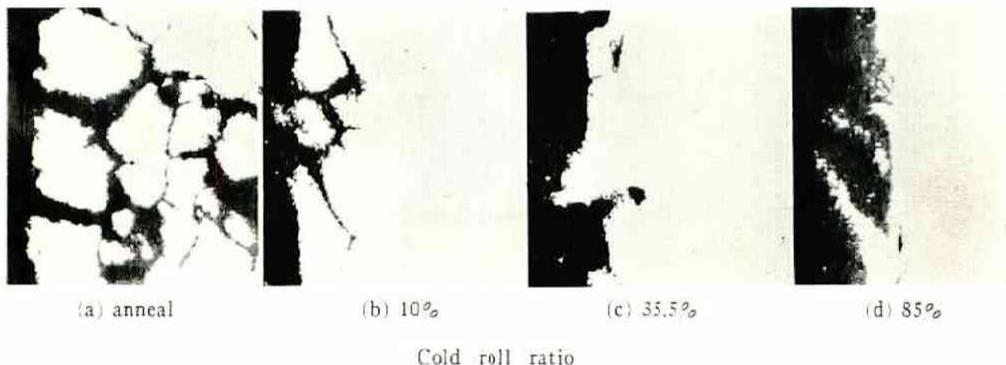


Fig. 8 Effect of cold rolling on grain boundary corrosion of 99.99% Al in demineralized water at 170°C for 20 hrs (cross-sectional view, $\times 100$)

Gas		Weight gain mg/dm ²
Atmospheric gas	Added pressure atm	
Ar	1	126
O ₂	1	112
H ₂	1	126
Ar	5	76
O ₂	5	26
H ₂	5	150
Ar	15	121
O ₂	15	140
H ₂	15	119

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

- (2) Easiness of penetration of H_2O 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_2O 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_2O 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_2O or OH ion will combine immediately with oxygen at the film surface and form H_2O 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 $100^\circ C$, 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 Carlsen's argument⁶⁾ 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

6) K. M. Carlsen, *J. Electrochem. Soc.*, **104**, 147 (1957)

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 results 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 boundary 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 alloys¹⁾, 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 3 Corrosion of cold rolled 99.99% Al in demineralized water at 170°C for 20 hrs

Reduction ratio (cold rolling)	0	10%	35.5%	85%
Wt. gain, mg/dm ²	969	1241	1156	810
Fallen corr. product, mg/dm ²	0	15	165	288
Total wt. increase, mg/dm ²	969	1256	1321	1098

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 can not 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 following. (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 con-

Sample	Volt vs. S. C. E.	
	in $\frac{N}{100}$ NaOH	in $\frac{N}{1000}$ H ₂ SO ₄
A (99.0% Al)	-1.45	—
B (99.9% Al)	-1.49	—
C (99.99% Al)	-1.51	—
C* (")	—	-0.672

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

Sample	Specific resistance		Film factor
	Pt-Pt electrodes	Pt-Al electrodes	
A (99.0% Al)	56.5 k Ω -cm	41.0 k Ω -cm	0.725
B (99.9% Al)	76.0	48.0	0.632
C (99.99% Al)	95.0	34.0	0.357
C* (")	42.0	29.0	0.691

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

* It is corroded in $N/1000$ H₂SO₄ solution at 200°C for 3 hrs

ductivity 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.

Now, Hunter and Fowle^{7,8)} found that the oxide film of aluminium in air had double layer structure, and Dillon and Troutner^{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 $\text{Na}_2\text{B}_4\text{O}_7$ 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 $\text{Na}_2\text{B}_4\text{O}_7$ solution are shown in Fig. 9. As can be seen from the

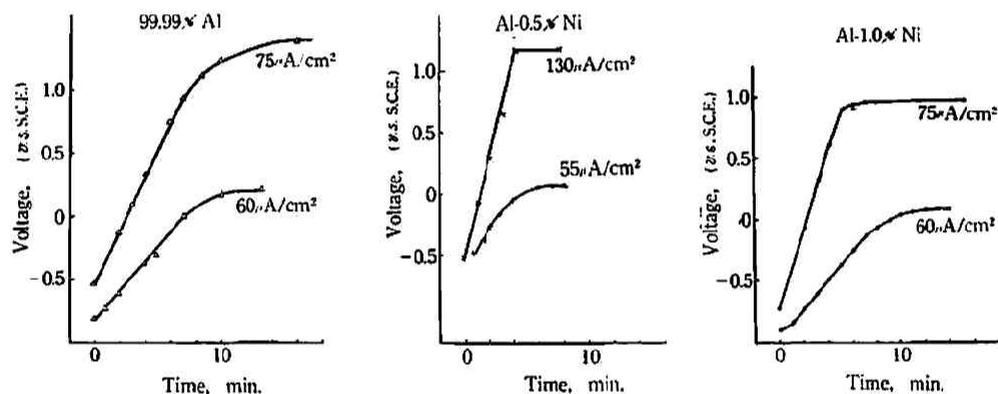


Fig. 9 Anodic oxidation curves Al, Al-0.5%Ni and Al-1.0%Ni alloys in 1N- $\text{Na}_2\text{B}_4\text{O}_7$ solution at room temperature

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. Electrochem. Soc.*, **101**, 481 (1954)

8) M. S. Hunter and P. Fowle, *ibid.*, **103**, 482 (1956)

9) R. L. Dillon and V. H. Troutner, *HW-51849* (1956)

10) V. H. Troutner, *HW-53389* (1956)

11) F. Flade, *Z. phys. Chem.*, **76**, 513 (1911)

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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,

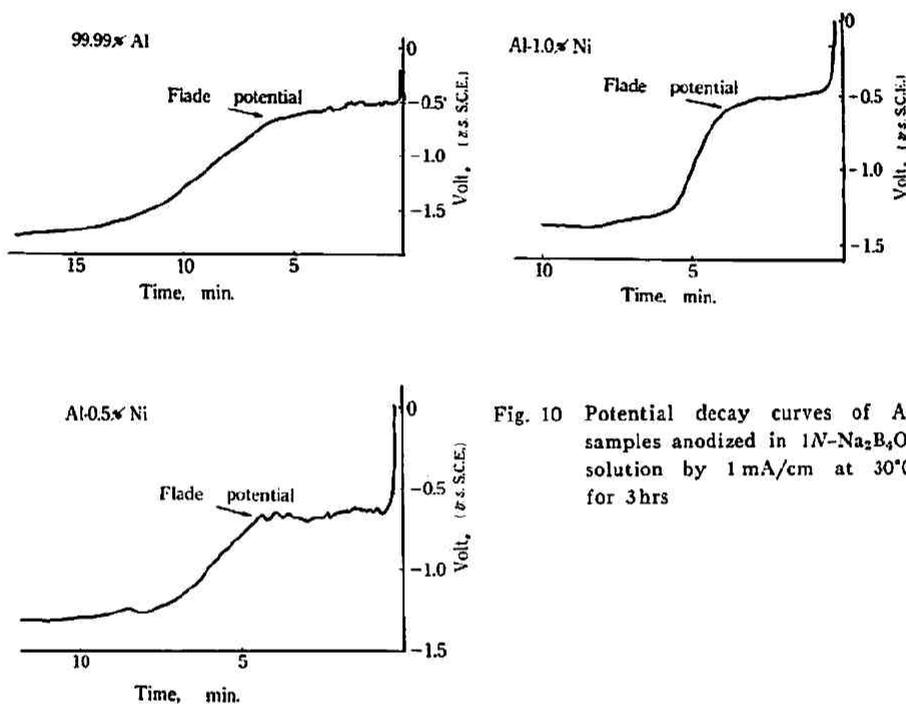


Fig. 10 Potential decay curves of Al samples anodized in 1N-Na₂B₄O₇ solution by 1 mA/cm at 30°C for 3 hrs

1% Ni alloy and 1% Fe alloy at 25°C in N/100 H₂SO₄ 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

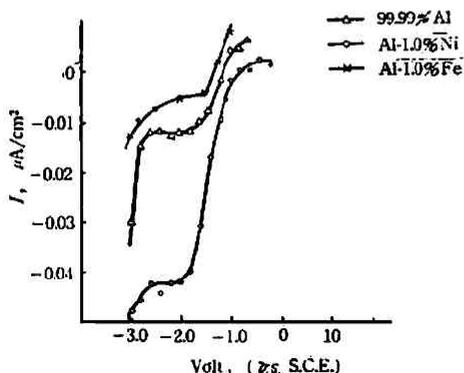


Fig. 11 Cathodic polarization curves of 99.99% Al, 1.0% Ni alloy and 1.0% Fe alloy in N/100 H₂SO₄ solution at room temperature

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.

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