

Influence of Crystallographic Orientation on Corrosion Behavior of 5N Purity Aluminum

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The influence of crystallographic orientation on corrosion behavior of 99.999% (5N) purity aluminum in four concentrations of hydrochloric acid solutions has been investigated using SEM/EBSD technique. Before corrosion test the surface of specimen was analyzed to examine crystallographic orientation distribution, and then the same area was observed by optical microscopy to detect corrosion behavior, such as rate, feature and site. It was shown that the corrosion rate depended strongly on the crystallographic orientation of the planes parallel to the surface. Moreover, the orientation dependence was varied with the concentration of the solution. While {111} plane has corrosion resistance in a low concentration of 2.9 mol/L HCl, the pitting rate on {100} plane was lowest in a high concentration of 11.6 mol/L HCl. Further, the reason of the variation of the orientation dependence is discussed.

Keywords: *Crystallographic orientation, Corrosion, high purity, EBSD analysis, hydrochloric acid.*

1. Introduction

It is well known that aluminum and its alloys owe their good corrosion resistance to the barrier oxide film. However, corrosion sensitivity may rise after a kind of heat treatment, and then, dependence of microstructure on corrosion behavior is interesting to make high performance materials. Generally grain boundaries are relatively weak for corrosion owing to their high free energy. Crystallographic plane with lower surface energy should exhibit higher corrosion resistance. However, Kim et al [1] reported that the improved corrosion resistance arose from the lower dissolution rate of grains with (001) plane parallel to the surface in a high purity aluminum. This fact suggests that corrosion behavior does not always depend on free energy only. On the other hand, grain orientation dependence on corrosion behavior was investigated using different concentrations of hydrochloric acid solutions in consideration of oxide film formation [2].

In the present study, to make clear the relation between crystallographic orientation and corrosion behavior, corrosion tests were performed in 5N purity aluminum analyzed in advance by scanning electron microscopy/ electron back scatter diffraction (SEM/ EBSD) technique. Further, corrosion behaviors in four concentrations of hydrochloric acid solutions were compared to confirm effect of corrosion environment.

2. Experimental Procedure

2.1 Sample

High purity aluminum sheet of 5N was prepared. Chemical composition of the sheet is listed in Table 1. The as-received sheet of 1mm thick had been made by hot rolling, cold rolling and annealing. Grain size of the sheet was ranged from 100 μ m to 200 μ m. Specimens were machined with a 20mm length, a 10mm width and a 1mm thickness. The surface was polished mechanically and electrochemically before microstructural analysis and corrosion test. In order to observe the same field on specimen repeatedly, Vickers hardness indents were imparted on the specimens to be used as fiducial markers.

Table 1 Chemical composition of high purity aluminum used.

5N-Al (ppm)	B	Na	Mg	Si	P	Ti	V
	0.2	0.1	0.6	1.5	0.7	0.4	0.1
	Cr	Mn	Fe	La	Ce	Nd	Al
	0.1	0.3	0.9	0.4	0.8	0.1	Bal.

2.2 Crystallographic orientation analysis

Microstructure and crystallographic orientation were examined on the surface of specimens using the EBSD technique by TSL Orientation Image Microscopy (OIM) system.

2.3 Corrosion test

After the EBSD analysis, simple corrosion tests were performed for the 5N aluminum specimens. The specimens were immersed in 11.6, 5.8, 2.9 and 1.5 mol/L HCl aqueous solutions, and observed by optical microscopy in intervals of time. The 11.6 mol/L HCl aqueous solution, which is called ‘concentrated hydrochloric acid,’ is close to the solubility limit of HCl to water at 1atm in room temperature.

3. Experimental Results and Discussion

3.1 Corrosion behavior in 11.6 mol/L HCl

Figure 1 displays change in the surface feature during corrosion test of 5N Al in 11.6 mol/L HCl. Corroded parts are found after 900s immersion at both of grain interiors and boundaries. As time passed, corrosion was extended not by expansion of each part but by increase in the number of parts.

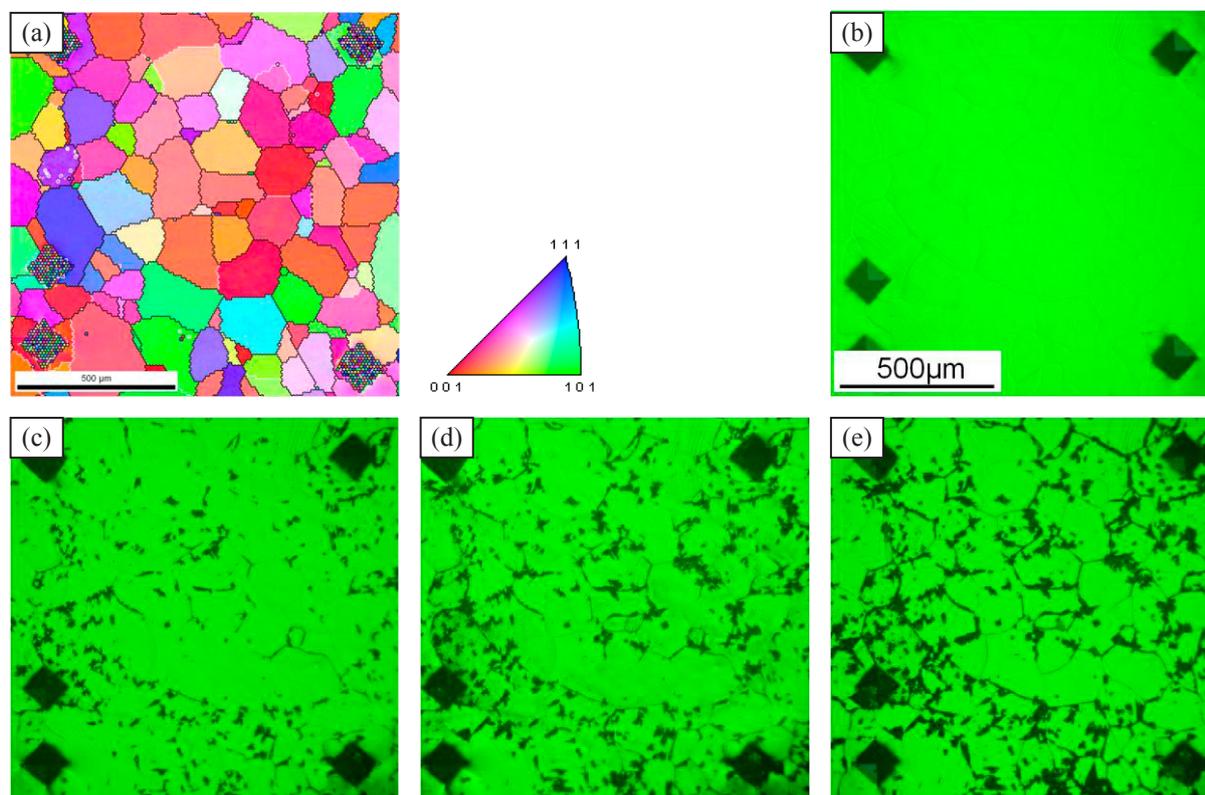


Fig. 1 Crystallographic orientation and corrosion behavior in 11.6 mol/L HCl. (a) Inverse Pole Figure (IPF) Map of the specimen surface before the corrosion test and micrographs showing surfaces at cumulative immersing time of (b) 0s, (c) 900s, (c) 5.4ks and (e) 18ks.

Moreover, grains with little corroded parts can be observed, for example, at lower center of the photo at 18ks (Fig. 1 (e)), which likely suggests orientation dependence of corrosion.

Figure 2 exhibits micrographs of the specimen surfaces at a cumulative immersing time of 18ks in the corrosion test of 11.6 mol/L HCl and corresponding IPF maps before the test. As shown in the upper IPF map (Fig. 2(b)), a grain on the left side had a crystallographic plane close to $\{111\}$, and was corroded preferentially with geometrical pits. In the lower IPF map (Fig. 2(d)) the plane close to $\{110\}$ was damaged also though the extent was not so large as the $\{111\}$ plane. On the other hand, grains having the plane close to $\{100\}$ were scarcely corroded. Further, obvious contrast of the small $\{100\}$ grain to $\{111\}$ appeared in Fig. 2(a). Therefore, corrosion sensitivity in 11.6 mol/L HCl rises in order as $\{100\} < \{110\} < \{111\}$.

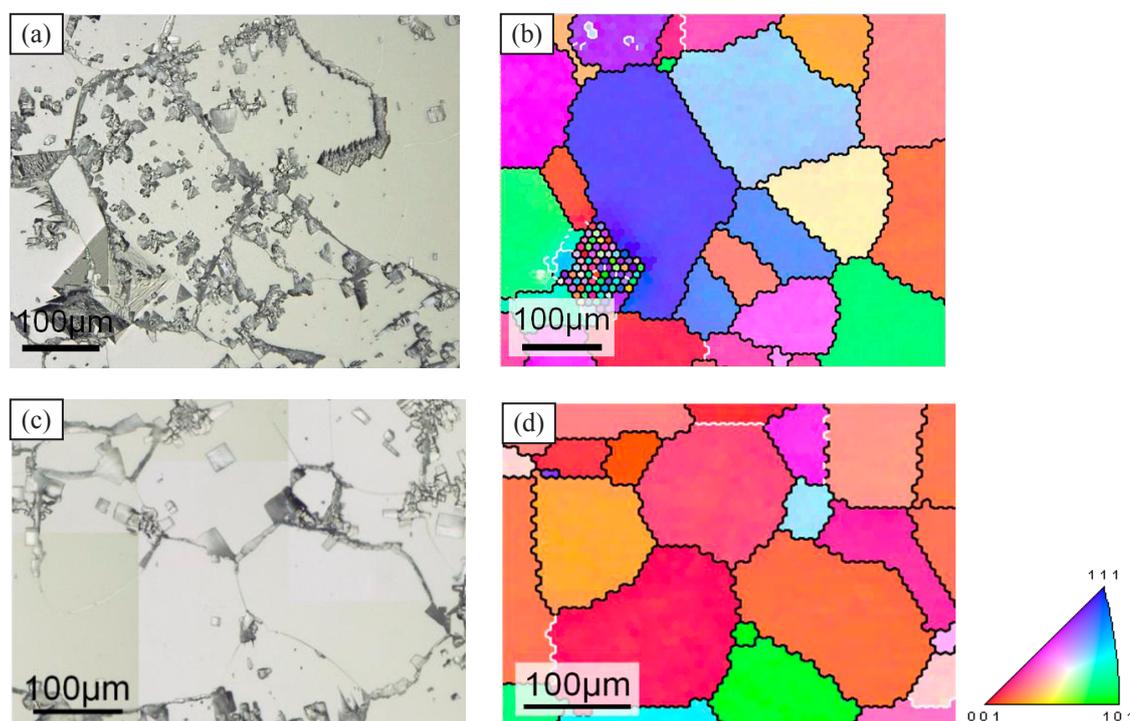


Fig. 2 Optical micrographs of the specimen surfaces at a cumulative immersing time of 18ks in the corrosion test of 11.6 mol/L HCl and corresponding IPF maps before the test. (a) and (c) Optical micrograph, and (b) and (d) IPF map, respectively.

3.2 Corrosion behavior in 5.8 mol/L HCl

Change in the surface feature during corrosion test in 5.8 mol/L HCl was also examined. At a cumulative immersion time of 86.4ks (1 day) grain boundaries were found and at 432ks (5 days) markedly corroded grains were distinguished from the others. As time passed, corrosion was extended to all of boundaries and some small grains were lost by dissolution in HCl solution.

Optical micrographs of the specimen surfaces at 432ks (5 days) in the corrosion test of 5.8 mol/L HCl and corresponding IPF maps before the test are shown in Fig. 3. Steps between neighboring grains are observed as a whole. Near $\{111\}$ grains (Fig. 3(a), (d)) are somewhat high compared with neighbors. Near $\{110\}$ grain in the center (Fig. 3(b), (e)) is slightly lowered to surrounding grains. Then, corrosion rate for near $\{110\}$ grains is probably higher than the others. Clear steps about near $\{100\}$ grains (Fig. 3(c), (f)) cannot be observed. It is, therefore, understood that corrosion sensitivity in 5.8 mol/L HCl is higher in order: $\{110\} > \{100\} > \{111\}$. This result is contrary to that in 11.6 mol/L HCl. Thus, orientation dependence of corrosion behavior is changed with concentration of solution.

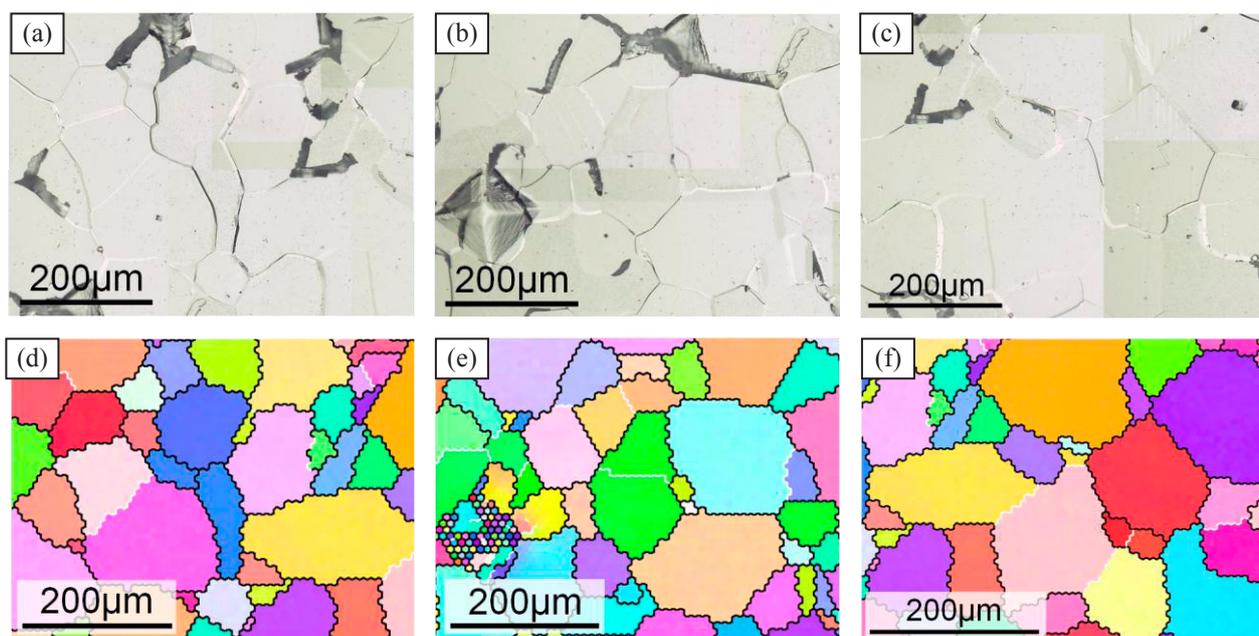
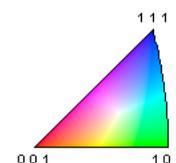


Fig. 3 Optical micrographs of the specimen surfaces at a cumulative immersing time of 432ks (5days) in the corrosion test of 5.8 mol/L HCl and corresponding IPF maps before the test. (a), (b) and (c) Optical micrograph, and (d), (e) and (f) IPF map, respectively.



3.3 Corrosion behavior in 2.9 mol/L HCl

Surface feature during corrosion test in 2.9 mol/L HCl was also observed. After 86.4ks (1 day) immersion, intergranular corrosion was found and at 432ks (5 days) marked grain boundaries appeared. The marked grain boundaries did not mean extension of intergranular corrosion. They appeared to be small steps generated at the boundaries by different corrosion rates of grain. At 1.04Ms (12days) corrosion pits were found.

Figure 4 shows surface feature after a immersion of 864ks (10 days) in 2.9 mol/L HCl and corresponding IPF map. A distinct low hill made of near $\{111\}$ and near $\{100\}$ grains is confirmed in the center. The two grains have higher corrosion resistance that near $\{110\}$ one. Moreover, it should be noted that the grain boundary between $\{111\}$ and $\{110\}$ is not found clearly. This demonstrated a small difference in corrosion rate between the two grains.

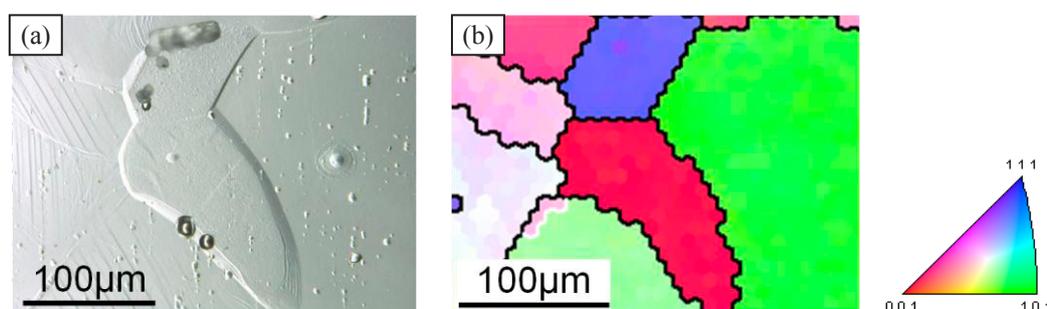


Fig. 4 Optical micrograph of the specimen surface at a cumulative immersing time of 864ks (10days) in the corrosion test of 2.9 mol/L HCl and corresponding IPF maps before the test. (a) Optical micrograph and IPF map.

3.4 Corrosion behavior in 1.5 mol/L HCl

Surface feature during corrosion test in 1.5 mol/L HCl was also examined. Changing tendency was similar to that in 2.9 mol/L HCl. Figure 5 shows surface feature after a immersion of 518ks (6 days) in 1.5 mol/L HCl and corresponding IPF map. Very small steps are generated at the boundaries by different corrosion rates of grain as well as in 2.9 mol/L HCl. As the time passed to 10.8ks (3 days) number of corrosion pits increased. In addition, the higher grains with near $\{100\}$ revealed that near $\{100\}$ grain has a smaller corrosion rate.

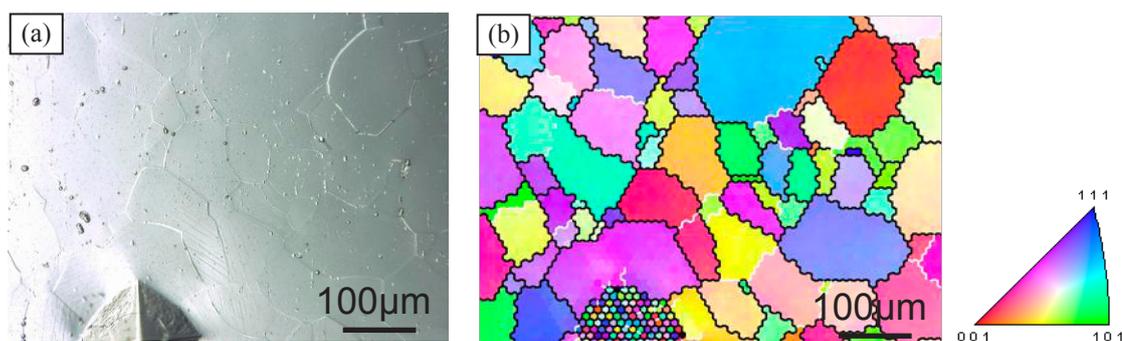


Fig. 5 Optical micrograph of the specimen surface at a cumulative immersing time of 518ks (6days) in the corrosion test of 1.5 mol/L HCl and corresponding IPF maps before the test. (a) Optical micrograph and IPF map.

3.5 Corrosion behaviors in different concentration of HCl

Corrosion behaviors in different concentration of HCl are summarized in Table 2.

Table 2 Corrosion behaviors in different concentration of HCl.

HCl aq. solution	Corrosion sensitivity			Local corrosion
	Low		High	
11.6 mol/L	$\{100\}$	\longleftrightarrow	$\{111\}$ $\{110\}$	Pits
5.8 mol/L	$\{111\}$	$\{100\}$	$\{110\}$	Intergranular
2.9 mol/L	$\{111\}$	$\{100\}$	$\{110\}$	Pitting (little)
1.5 mol/L	$\{111\}$	$\{100\}$	$\{110\}$	Pitting (much)

4. Summary

In the present study, to make clear the relation between crystallographic orientation and corrosion behavior, corrosion tests were performed in 5N purity aluminum analyzed in advance by SEM/ EBSD technique. Further, corrosion behaviors in four concentrations of hydrochloric acid solutions were compared to confirm effect of corrosion environment. It was shown that the corrosion rate depended strongly on the crystallographic orientation of the planes parallel to the surface. Moreover, the orientation dependence was varied with the concentration of the solution. While $\{111\}$ plane has corrosion resistance in a low concentration of 2.9 mol/L HCl, the pitting rate on $\{100\}$ plane was lowest in a high concentration of 11.6 mol/L HCl.

References

- [1] S.H. Kim, U. Erb, K.T. Aust and G. Palumbo: Mater. Sci. Forum Vol. 408-412 (2002), pp. 1043-1048.
- [2] J.J. Gray, B.S. El Dasher and C.A. Orme: Surface Science 600 (2006), 2488-2494.