Corrosion of High Thermal Conductive AlN Ceramics in Aqueous Solutions

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Although there is a strong need to understand the chemical corrosion resistance of aluminum nitride (AlN) ceramics for their applications as structural parts in semiconductor processes, there is insufficient information on chemical corrosion. We examined two kinds of commercial AlN ceramics with high thermal conductivity (170 and 200 W m⁻¹ K⁻¹) in both acid and basic aqueous solutions, such as KOH, NaOH, HNO₃, and H₂SO₄, using different concentrations. Weight changes, phases present, and microstructures on the surfaces before and after testing were evaluated. Basic aqueous solutions corroded AlN ceramics in exactly the same way as acid aqueous solutions. Although secondary phases, such as yttrium aluminate, were mainly dissolved in acid aqueous solutions, AlN itself was corroded in basic aqueous solutions. Furthermore, we observed that the weight loss of AlN ceramics with higher thermal conductivity exceeded that of lower thermal conductivity. It seems that oxygen dissolved in AlN grain influences on corrosion of AlN ceramics.

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1. Introduction
Aluminum nitride (AlN) has excellent intrinsic properties such as high thermal conductivity, high electrical insulation, and high corrosion resistance to halogen and plasma.1-3) These advantages promote the application of AlN ceramics to IC/LSI packages and structural parts for semiconductor process. In such applications, sometimes the AlN ceramics is exposed to aqueous solution. In the previous studies, some researchers have reported that the corrosion behavior of AlN depends on the concentration of the agent and the powder characteristics.4-6) Furthermore, it has also been reported that the strength of AlN ceramics is degraded by hydrothermal corrosion.6) However, the corrosion behavior in aqueous solution of AlN ceramics with high density and high thermal conductivity, which is fabricated using an additive such as Y₂O₃,7) has not been clarified. The purpose of this study is to investigate the corrosion behavior of two kinds of commercialized AlN ceramics with different thermal conductivities in several acid and basic aqueous solutions.

2. Experimental procedure
We used two kinds of high thermal conductivity AlN ceramics in this study. The test pieces were 3 × 4 × 38 mm. The properties of the as-received specimens are listed in Table 1. We used Y₂O₃ as a sintering aid in both specimens, and the difference in firing profiles resulted in the different thermal conductivities of 170 W m⁻¹ K⁻¹ in sample A and 200 W m⁻¹ K⁻¹ in sample B. They have the same secondary phases. The grain size of sample B exceeded that of sample A, and the bending strength of sample A is higher than that of sample B.

Various types of aqueous solutions (KOH (5, 15, 35 mass%), NaOH (35 mass%), H₂SO₄ (5, 15, 35 mass%), and HNO₃ (35 mass%)) were prepared. We set the test pieces in each solution, without stirring, at a temperature of 30°C for 1 to 25 h. After soaking, each test piece was rinsed with water and ethanol, and then dried. Weight loss per unit surface area was calculated from the weight before and after the corrosion test. The weight of the specimen was measured using a balance with readability of 0.01 mg and sensitivity of ± 2 ppm. The surface area for the calculation of weight loss was estimated from the shape of the specimen. The surface of the corroded specimen was observed by means of scanning electron microscopy SEM. To estimate the degradation of the specimens, we measured the bending strength using a three-point bending test before and after the corrosion test. The phases present in the specimen and the lattice constant c of AlN were evaluated by means of XRD using Si powder as a standard material.

3. Results and discussion

3.1 Weight change
Figure 1 illustrates the corrosion test results in H₂SO₄ and HNO₃ aqueous solutions. The specimen weights decreased with an increase in soaking time. The weight loss of sample A was smaller than that of sample B. Higher concentration H₂SO₄ aqueous solutions displayed more corrosive behavior. AlN ceramics were corroded more by H₂SO₄ aqueous

Table 1. Properties of AlN Ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
</tr>
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<tbody>
<tr>
<td>Phase present</td>
<td>AlN</td>
<td>AlN</td>
</tr>
<tr>
<td>Y₃Al₂O₁₂</td>
<td>Y₃Al₂O₉</td>
<td></td>
</tr>
<tr>
<td>Y₃Al₂O₉</td>
<td>Y₃Al₂O₁₂</td>
<td></td>
</tr>
<tr>
<td>Average grain size (μm)</td>
<td>2.7</td>
<td>5.1</td>
</tr>
<tr>
<td>Thermal conductivity (Wm⁻¹K⁻¹)</td>
<td>170</td>
<td>200</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>465</td>
<td>373</td>
</tr>
<tr>
<td>Lattice constant c of AlN (nm)</td>
<td>0.49788</td>
<td>0.49802</td>
</tr>
</tbody>
</table>

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solution than by HNO₃ aqueous solution with the same concentration. Taylor and Lenie³ estimated the corrosion resistance of hot-pressed AlN ceramics in water, concentrated HCl, 1 : 1HCl, concentrated H₂SO₄, 1 : 1H₂SO₄, concentrated HNO₃, 1 : 1HNO₃, concentrated HF and 1 : 1HF. They revealed that 1 : 1 acid solutions corroded AlN ceramics more than concentrated acid solutions. However, Barba et al.⁵ reported that AlN powder is easier to dissolve into acid solution with higher concentrations. However, the concentration has little to do with the corrosion by an acid solution in this study, although corrosion by an acid solution with a higher concentration produced slightly more weight loss of the specimens as shown in Fig. 1(b).

Figure 2 indicates the weight changes of samples A and B in the corrosion test using basic aqueous solutions. Weight losses of samples A and B in basic aqueous solutions increased with an increase in the soaking time and the concentration of solution. In particular, the soaking time dependence of weight loss in basic aqueous solutions was almost linear. Young and Duh⁷ also reported that AlN substrates are corroded more quickly in basic aqueous solutions than acid ones. Furthermore, sample A exhibited higher corrosion resistance than sample B. The tendency for basic aqueous solution to corrode AlN ceramics was the same as that for acid aqueous solution. However, we confirmed a greater weight loss during the corrosion test using basic aqueous solutions. An NaOH aqueous solution corroded the AlN ceramics more than a KOH aqueous solution of the same concentration.

In the previous paper on the corrosion of AlN powder, it was reported that the following reactions occurred between aqueous solution and AlN.⁴)

\[ \text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NH}_3 \text{OH} \]  

\[ \text{NH}_3 \text{OH} \rightarrow \text{NH}_4^+ + \text{OH}^- \]  

\[ \text{Al(OH)}_3 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_4^- \]  

These reactions indicate that more Al(OH)_3 is formed in basic solution than in acid solution because of the amount of OH⁻. Furthermore, it is well known that Al(OH)_3 is dissolved in strong acid and basic solutions.

\[ \text{Al(OH)}_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O} \]  

\[ \text{Al(OH)}_3 + \text{OH}^- \rightarrow \text{AlO}_2^- + 2\text{H}_2\text{O} \]  

As a result, it seems that AlN grains were corroded in basic solution. Moreover, Y₂O₃, which was used as a sintering aid in this study, is stable in basic solution, but is easily dissolved in acid solution.

\[ \text{Y}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow 2\text{YSO}_4^{2-} + \text{SO}_4^{2-} + 3\text{H}_2\text{O} \]  

\[ \text{YSO}_4^{2-} \rightarrow Y^{3+} + \text{SO}_4^{2-} \]  

It was probable that, although Y₂O₃ existed as yttrium aluminates at the grain boundary, the acid solution mainly corroded the grain boundary. In both corrosion tests, in acid and basic solutions, AlN ceramics with higher thermal conductivity was easily corroded. Higher thermal conductivity results from the purification of AlN grains because the dissolution of oxygen, namely Al₂O₃, in AlN results in the replacement of N with O, and the formation of vacancies at Al sites to scatter phonon transfer.¹ Barba⁵ also reported that AlN powder with lower oxygen content is easier to corrode in diluted HCl, which
is the same tendency as our results in spite of differences between the powder and the sintered body in grain size, presence of sintering aid, grain boundary, and so on. The Al–O bond seems to be more stable in an aqueous solution than the Al–N bond, and the vacancies probably become the starting point of corrosion. Although the reason for this has not been clarified yet, the effect of oxygen in AlN on the corrosion in aqueous solution will probably be investigated by means of MO or MD calculation and in situ observation of corrosion behavior on the atomic level.

3.2 Phases present and microstructure

There was almost no change in XRD patterns of the specimens between before and after the corrosion tests, except that the peak intensity of yttrium aluminate increased after corrosion in the bases. Figures 3 and 4 illustrate SEM photographs of the specimen surfaces after the corrosion test. The surface appearance was clearly different between the acid and basic aqueous solutions. We observed that the corrosion of AlN ceramics by 5 mass% H_2SO_4 aqueous solution yielded mainly intergranular corrosion, which indicates that Y and Al seem to be easily dissolved in acid aqueous solution. However, in corrosion by basic aqueous solution, the corroded surface of AlN ceramics was extremely rough. The observation of surfaces with shorter soaking times revealed that the corrosion of AlN ceramics in a basic aqueous solution mainly occurred from AlN grains. This result seems to be consistent with the higher peak intensity of yttrium aluminate in AlN ceramics corroded by basic aqueous solution as compared to that before corrosion.

Furthermore, we observed that AlN has surfaces which are both easy and difficult to be corroded. This phenomenon has been reported for the wurtzite or zinblende type crystal, such as ZnO, ZnS, CdS, CdSe, and CdTe. The reason is that the corrosion behavior of piezoelectric crystals is affected by the positive and negative surface charges that result from polarization due to strain for the relaxation of the surface structure. Because the crystal structure of AlN is also wurtzite type, two types of surfaces were observed in corrosion testing.

3.3 Bending strength

The results of bending strength after soaking in various solutions are illustrated in Table 2. In acid solutions, there was little change in bending strength, and it was not affected by type or concentration of solution because the weight loss

Fig. 3. SEM photographs of the corroded surfaces of sample A. (a) 5 mass% H_2SO_4 for 1 h soaking. (b) 5 mass% H_2SO_4 for 25 h soaking. (c) 5 mass% KOH for 5 min soaking. (d) 5 mass% KOH for 1 h soaking.

Fig. 4. SEM photographs of the corroded surfaces of sample B. (a) 5 mass% H_2SO_4 for 1 h soaking. (b) 5 mass% H_2SO_4 for 25 h soaking. (c) 5 mass% KOH for 5 min soaking. (d) 5 mass% KOH for 1 h soaking.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Weight loss [g/m²]</td>
<td>Bending strength [MPa]</td>
</tr>
<tr>
<td>5mass% H_2SO_4aq</td>
<td>0.50</td>
<td>467</td>
</tr>
<tr>
<td>15mass% H_2SO_4aq</td>
<td>0.47</td>
<td>442</td>
</tr>
<tr>
<td>35mass% H_2SO_4aq</td>
<td>0.54</td>
<td>468</td>
</tr>
<tr>
<td>5mass% HNO_3aq</td>
<td>0.40</td>
<td>449</td>
</tr>
<tr>
<td>5mass% KOHaq</td>
<td>41.44</td>
<td>370</td>
</tr>
<tr>
<td>15mass% KOHaq</td>
<td>72.66</td>
<td>341</td>
</tr>
<tr>
<td>35mass% KOHaq</td>
<td>101.25</td>
<td>336</td>
</tr>
<tr>
<td>5mass% NaOHaq</td>
<td>81.84</td>
<td>347</td>
</tr>
</tbody>
</table>
was small. In basic solutions, the bending strength was degraded with increased concentration of bases, namely, increased weight loss. Tamai et al.\textsuperscript{6)\textsuperscript{}} investigated the hydrothermal corrosion and strength degradation of AlN ceramics. In their study, the weight gain in AlN ceramics after corrosion occurred because of the formation of boehmite, and they concluded that the corrosion kinetics of AlN with water was diffusion-controlled through the boehmite layer. They also revealed that water of high temperature and water vapor resulted in strength degradation. Although it is difficult to directly compare their results and our results, this degradation probably resulted from an increase in flaw size by the preferential attack of water or agents in the intergranular phase.\textsuperscript{10)\textsuperscript{}}

4. Conclusion

We examined two kinds of commercial AlN ceramics with high thermal conductivity (170 and 200 W m\textsuperscript{-1} K\textsuperscript{-1}) in acid and basic aqueous solutions, such as KOH, NaOH, HNO\textsubscript{3}, and H\textsubscript{2}SO\textsubscript{4}, with different concentrations. We illustrated that basic aqueous solutions corroded AlN ceramics in exactly the same way as acid aqueous solutions. Although secondary phases, such as yttrium aluminates, were mainly dissolved in acid aqueous solutions, AlN itself was intensely corroded in basic aqueous solutions. Furthermore, we observed that the weight loss of AlN ceramics with higher thermal conductivity was larger than that with lower thermal conductivity. It seems that oxygen content dissolved into the AlN grain influences the corrosion of AlN ceramics.

References