Preparation of Beta-Alumina Fibers by Sol-Gel Method

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ソル-ゲル法によるベータ・アルミナファイバーの調製

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Na₂O-Al₂O₃ beta-alumina fibers were prepared by sol-gel method. Viscous sols corresponding to Na₂O:11Al₂O₃, Na₂O:8.8Al₂O₃, Na₂O:7.3Al₂O₃ and Na₂O:5.5Al₂O₃ in oxide composition were prepared by heating slurries consisting of Al(NO₃)₃·9H₂O, Al powder, NaNO₃, H₂O and HNO₃ in reflux. Fiber-drawing from the viscous sols yielded gel fibers of about one meter long and 5-250 μm in diameter. Heating of the gel fibers in a covered crucible with Na₂O-Al₂O₃ gel powder at 1100°C for 10 min resulted in ceramic fibers consisting of beta-alumina crystals. Conditions for the occurrence of spinnability in the starting sols and for the precipitation of beta-alumina crystals in gel fibers have been discussed.

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1. Introduction

Beta-alumina ceramics, known as ionic conductor, are utilized as solid electrolyte for solid state cells and chemical sensors. It is expected that beta-alumina fibers would be utilized for producing flexible ion-conducting cloths or bundles which are heat-resistant. The large surfaces of fibers might be favorable when used as sensors. The conventional fabrication procedures can not be easily applied to preparation of this material in the form of thin coating films or fibers, because very high temperatures reaching 1600°C are required for the synthesis. In this study, the sol-gel processing, which makes the synthesis of ceramics at relatively low temperatures possible, has been applied for making beta-alumina fibers.

2. Experimental procedures

2.1 Preparation of beta-alumina sols

Table 1 shows characteristics of sols used in this study. Al(NO₃)₃·9H₂O, NaNO₃ and Al (metallic powder) were used as starting materials. The total amount of Al as main component was fixed so that 4.0 mole of Al might be found in the sol at the final stage. In addition to sols corresponding to this composition, sols corresponding to compositions Na₂O·8.8Al₂O₃, Na₂O·7.3Al₂O₃, and Na₂O·5.5Al₂O₃ in mol were prepared. The sols

<table>
<thead>
<tr>
<th>Sol</th>
<th>Mixing ratio (mol/l) in starting materials</th>
<th>Na₂O/Al₂O₃ ratio in the sol</th>
<th>Appearance</th>
<th>Content of NO₃⁻ (mol/l)</th>
<th>Viscosity at 25°C (mPa.s)</th>
<th>Initial pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5 2.5 0.56 1:11</td>
<td>Clear**</td>
<td>1.1 2.4 3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1'</td>
<td>1.5 2.5 0.45 1:8.8</td>
<td>Clear**</td>
<td>0.9 2.4 3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1 3 0.36 1:11</td>
<td>Opaque</td>
<td>0.7 16 4.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2'</td>
<td>1 3 0.45 1:8.8</td>
<td>Opaque</td>
<td>0.6 18 4.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1 3 0.56 1:11</td>
<td>Clear</td>
<td>0.9 2.3 3.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1 3 0.45 1:8.8</td>
<td>Clear</td>
<td>1.0 2.4 3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1 3 0.54 1:7.3</td>
<td>Clear</td>
<td>1.0 2.5 3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1 3 0.72 1:5.5</td>
<td>Clear</td>
<td>0.9 2.3 3.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1, 1', 2 and 2' dissolved with pure water by heating in reflux.
3, 4, 5 and 6 dissolved with about 1 mol/l HNO₃ solution by heating in reflux.
* Measured using an Ostwald viscosimeter.
** Sols 1 and 1' are slightly less clear than sols 3, 4, 5 and 6,
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Prepared by placing Al(NO$_3$)$_3$•9H$_2$O, NaNO$_3$ and Al powder in a separable flask with water or about 1 mol/l HNO$_3$ solution and heating at about 100°C in reflux for 18 h were filtered with an aspirator.

3. Results

3.1 Characteristics of sols

The sols are clear when they contain 0.9–1.0 mol/l NO$_3$ ions after preparation (Nos. 1, 1', 3, 4, 5 and 6 in Table 1), while the sol is opaque when most NO$_3$– ions are gone during preparation (Nos. 2 and 2'). Table 1 also shows that the clear sols have similar viscosities and pH values, which are lower than those of opaque sols.
3.2 Fiber drawing

Figure 1 shows a photograph of gel fibers drawn from viscous clear sols of the composition Na₂O•7.3 Al₂O₃. Clear sols of other compositions can be also drawn into the gel fibers of about one meter long and 5-250 μm in diameter. It has been found that clear sols obtained with about 1 mol/l HNO₃ solution (Nos. 3, 4, 5 and 6 in Table 1) showed better spinnability than clear sols obtained with water (Nos. 1 and 1' in Table 1).

3.3 DTA and TG

Figure 2 shows DTA and TG curves for gel fibers of the calculated composition Na₂O•5.5 Al₂O₃ (No. 6 in Table 1). Similar curves are obtained with gel fibers of the other compositions (Nos. 3, 4 and 5 in Table 1). As seen from Fig. 2, about 60% of the weight loss takes place up to 500°C.

Small peaks which are possibly due to decomposition of nitrate and crystallization of gamma-alumina are found around 530°C and 850°C. A large endothermic peak due to dehydration and a small exothermic peak due to crystallization of beta-alumina are found at 250°C and 1020°C, respectively. The temperatures of the former three peaks are almost independent of the composition. On the other hand, the peak temperature due to the precipitation of beta-alumina increases with increasing Al₂O₃/Na₂O ratio in the gel as shown in Fig. 3. The fibers of the calculated composition Na₂O•11 Al₂O₃ does not show a peak due to the crystallization of beta-alumina in the DTA curve.

3.4 Crystallization and beta-alumina formation in gel fibers

Figure 4 shows X-ray diffraction patterns of gel fibers of the composition Na₂O•7.3 Al₂O₃ heated at a rate of 5°C/min to given temperatures and kept there for 20 min. At 1000°C, a considerable amount of beta-alumina crystals and a small amount of iota-alumina crystals are precipitated. At 1100°C, the peak intensities of beta-alumina crystals become larger although a small amount of alpha-alumina crystals is precipitated. At 1200°C, most of beta-alumina crystals are converted to alpha-alumina crystals.

It is found that the peak intensities of alpha-alumina increase with decreasing fiber diameter, indicating that Na₂O is lost from the surface of fibers by vaporization and the effect is more serious in thinner fibers. To avoid this problem, the fibers of about 10 μm in diameter are heated with Na₂O-Al₂O₃ gel of high Na₂O content in a covered crucible at a rate of 5°Cmin⁻¹ to 1100°C and keeping there for 10 min. As a result, the fibers consisting solely of beta-alumina crystals are formed.

Figure 5(a) shows a SEM micrograph of the fibers. It can be seen that a fiber has a round cross-section and flat surface. The fiber consists of fine crystals of 0.2-0.3 μm in diameter as seen from Fig. 5(b).

3.5 Chemical analysis of fibers

Figure 6 shows the results of chemical analysis of the gel fibers fired at various temperatures up to
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1200°C for 20 min. As shown in this figure, the Al₂O₃/Na₂O ratio of fired fibers increases with increasing heating temperature above 1000°C, indicating that Na₂O is lost by vaporization.

3.6 Electrical conductivity of fired fibers

Preliminary measurements were made by A.C. method with LCR meter on the electrical conductivity of a fiber of 70 µm in diameter, which has the calculated oxide composition Na₂O·5.5Al₂O₃ and was fired at 1100°C for 10 min. A conductivity value of 3.2×10⁻⁶ S·cm⁻¹ at 1 kHz has been obtained at 20°C. It is believed that this conductivity corresponds to the ionic conduction by Na⁺ ions. Detailed investigations on the electrical conductivities will be presented later.

4. Discussion

4.1 Formation of sol

All sols prepared in the present study show good spinnability when they become sufficiently viscous as a result of hydrolysis and polymerization. Good spinnability would be ascribed to the homogeneity of sols in addition to the presence of long-shaped, one-dimensional particles in sols.

In this study, it has been confirmed that the spinnability of the viscous sol is better with sols of increased transparency. An increase in the transparency may be ascribed to the improvement of digestion of Al powder by adding HNO₃ in the process of sol preparation, leading to an increase in spinnability. This is suggested by Everitt for the spinnability of sol consisting mainly of water-soluble aluminum monoacetate, which is affected by the digestion of Al powder in acetic acid.⁷ It is easily assumed that formation of residues or precipitates in sol would make drawing of continuous gel fibers difficult.

It is known that Al₂O₃ component can have the structure composed of continuous aluminous complexes.⁸ The structure is constructed by deprotonation from H₂O coordinating to Al⁺⁺ and oxolation (formation of Al:\(\text{O}^{2-}\)Al bridge) and oxolation (formation of Al:\(\text{O}^{2-}\)Al bridge) processes. It is expected that in the present Na₂O-Al₂O₃ sols, long-shaped, one-dimensional aluminous complexes would be formed, and this would make the beta-alumina sols spinnable alike in the alumina sols where long-shaped, one-dimensional particles were confirmed in the previous study.⁹

4.2 Crystallization of beta-alumina in gel fibers

Metastable iota-alumina crystals are precipitated in the gel fibers at 1000°C, as shown in Fig.4. This agrees with the result of Perrotta and Young, Jr.¹⁰ They found that m-alumina crys-
tals, which are structurally similar to iota-alumina crystals, were formed when Na₂O-Al₂O₃ gels were heated at low temperatures. Hodge et al. reported in the study on beta-alumina gel powders that the formation of m-alumina was an evidence for the homogeneous mixing of Na and Al components in the atomic scale. It is assumed that Na and Al components are mixed at the atomic scale in the gel fibers prepared in this study and that iota-alumina crystals including Na₂O are metastably precipitated in the gel fibers before the precipitation of stable beta-alumina crystals.

5. Summary
In order to produce ion conducting beta-alumina fibers by sol-gel method, the sols of Na₂O-Al₂O₃ system were prepared by heating the slurries consisting of Al(NO₃)₃·9H₂O, Al powder, NaNO₃, H₂O and HNO₃ in reflux. Long gel fibers of 5-250 μm in diameter were drawn from the spinnable viscous sols. When the gel fibers were heated in an open crucible, the amount of Na₂O vaporization from fibers increased as the fiber diameter decreased. When the gel fibers derived from the sol corresponding to calculated oxide composition Na₂O·7.3Al₂O₃ were heated at 1100°C for 10 min with powder of high Na₂O content in covered crucible, ceramic fibers consisting solely of fine beta-alumina crystals were produced.

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References
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