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Influence of Na₂O contamination on changing the cristobalite phase into amorphous in mullite ceramics with excess silica

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Authors have been trying to fabricate cristobalite-containing mullite bodies with high strength and toughness by reheating mullite-glass sintered bodies. In this process, a phenomenon that once-crystallized cristobalite layer changed back to amorphous was observed by the microstructure observation of the sample contaminated with Na₂O. In this study, the minimum amount of Na₂O to change the cristobalite phase into amorphous was quantitatively determined by the electron probe microanalysis (EPMA) method. As a result, the amount of Na₂O in the amorphous phase just near the cristobalite-amorphous phase boundary was 1.6–1.9 mass%, which almost corresponded with the minimum amount of Na₂O in the liquid phase coexisting with mullite, estimated from a phase diagram.

Key-words : Mullite-glass ceramics, annealing treatment, Na₂O contamination, Cristobalite, Amorphous phase

1. Introduction

Mullite ceramics is one of the attractive candidates for high-temperature engineering ceramics. In order to densify mullite ceramics under normal pressure, however, high temperature heating over the eutectic temperature (1587 ± 10°C) in the phase diagram1 is necessary, due to its low sinterability accompanied by strong covalent materials. Therefore, even though a sintered body of mullite is prepared from a starting material with stoichiometric composition, a glass phase often occurs during firing, which lowers its high-temperature strength.2 In order to circumvent this problem, we have been trying to prepare cristobalite-containing mullite sintered bodies with high strength and toughness by reheating mullite-glass sintered bodies with excess silica. In the previous works,3,4 we reported the crystallization behavior occurred by reheating mullite-glass sintered bodies, which had been obtained by liquid-phase sintering under normal pressure. The result suggested that 1) the glass phase in the sintered body can be almost completely crystallized even for a specimen with 16.4 mass% excess silica by reheating at 1500°C for 96 h; 2) the crystallization occurs from the surface where elastic strain energy generated by the volume change from the glass phase to cristobalite is small; 3) the crystallization proceeds toward the inner part of the body by the compressive stress induced by the volume change of the surface crystallized phase.

In this reheating process, the specimens were wrapped with Pt foil to avoid the contamination from the electric furnace. When the reheating was performed without wrapping the specimens, the area that once-crystallized layer changed back to amorphous was observed. As the result of the qualitative observation of the surface of the specimen by the secondary ion mass spectroscopy (SIMS), more Na component was detected in the surface layer than the inner part of the sample. This result suggested that the change of the cristobalite phase to amorphous was due to the contamination of Na₂O component. The authors are planning the industrial use of this material in the future, so it is very important to clear its behavior in an alkaline atmosphere.

In this study, various fired bodies of mullite-glass doped with Na₂O were prepared and their crystallization behavior during reheating was investigated. In addition, using these samples as standards, the minimum amount of Na₂O to change the cristobalite phase to amorphous was cleared by the electron probe micro-analysis (EPMA) at the cristobalite-amorphous phase boundary in a surface-contaminated sample by Na₂O component.

2. Experimental

2.1 Preparation of materials

Starting powders were synthesized by the hydrolysis of alkoxides as reported in the previous reports.5,6 Aluminum isopropanoxide and tetramethyl orthosilicate (Al[OCH(CH₃)₃]₃ and Si(OCH₃)₄, Tokyo Chemical Industry Co., Ltd.) were dissolved in isopropyl alcohol with the Al₂O₃ concentration of 60 mass%. The solution was hydrolyzed with a largely excessive amount of 0.05 mol% NH₄OH solution at 60°C. The obtained gel was dried in vacuum to be a powder. The powder was calcined at 1000°C for 1 h, and was wet-milled with ethanol for 96 h with an iron potmills. The contaminated iron was removed with 1 + 1 HCl solution. The milled powder was classified under 2 μm by elutriation in water. The chemical composition of the obtained powder by the gravimetric analysis was Al₂O₃: 58.7% and of SiO₂: 41.3 mass%. The amount of Na₂O analyzed by the flame photo-spectroscopy was lower than its quantitative limit, 0.001 mass%. This sample will be referred as 60A.

The sample 60A was soaked in NaCl aqueous solutions with four different concentrations and dried with a hot plate at 80°C to be Na₂O-added samples. The amount of Na₂O analyzed by the flame photo-spectroscopy was 0.22, 0.38, 0.63 and 0.97 mass%. Hereafter, these samples will be designated as 60A–0.2S, 60A–0.4S, 60A–0.6S, 60A–1S, with increasing Na₂O content, respectively.

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2.2 Sintering and reheating of samples
The prepared samples in the previous section were pressed into a rod of $5 \times 5 \times 40 \text{mm}^3$ and isostatically pressed at 98 MPa. They were fired with an electric furnace with MoSi$_2$ heaters. Temperature was raised at 6°C/min to 1600°C, kept for 2 h and cooled in the furnace to room temperature. During firing, the samples were wrapped with Pt foil to prevent the evaporation of Na$_2$O from the samples and the contamination from the furnace.

The obtained fired bodies were reheated at 1500°C, lower than the eutectic temperature. For the reheating, an electric furnace with SiC heaters was used. Temperature was raised at 10°C/min, kept at 1500°C for 8 h and cooled in the furnace. Each specimen was wrapped with Pt foil similar to the firing experiment described in the previous section. The specimen 60A was also reheated for 24 h without wrapping with Pt foil to be “surface-contaminated” specimen 60A.

2.3 Characterization of sintered and reheated specimens
The polished and chemically etched (using 1% HF at 0°C for 24 h) cross section of the surface-contaminated specimen 60A were observed by SEM (JEOL JSM–840).

Powder X-ray diffraction (Phillips, PW–700) of the reheated bodies was measured to check the formation of cristobalite phase in the surface layer of the samples: Cu Kα X-ray was used; the tube voltage and current were 40 kV and 60 mA, respectively.

The distribution of elements on the surface and the inner part of the specimens was measured by SIMS, the secondary ion mass spectroscopy (ATOMIKA, SIMS–4000). The measurement condition was as follows: the primary ion beam, Cs$^+$ gun of 6 keV and 80 nA; scanning area, 20 μm (analysis area, 10 μm); sample tilt angle, 0° (vertical beam incident); charge-up correction, electron beam of 1.2 kV and 2.8 A.

Quantitative analysis of Na element, together with Al and Si, on the surface area of the surface-contaminated specimen 60A was performed by the EPMA, the electron probe microanalysis (JEOL JSM–8900). Measurement condition was as follows: acceleration voltage, 15 kV; sample current, $1 \times 10^{-8}$ A; probe diameter, 10 μm; crystal, TAP. For one point, peak acquisition time was 10 s, and background was measured for 5 s. The measurement was carried out at 20 points randomly on the surface and their average was calculated. In this EPMA analysis, the specimen 60A–0.4S was used as a standard sample, in which Na distribution was found to be homogeneous by SIMS analysis in the previous section, and its concentration was known by the flame spectroscopy. Moreover, Na (together with Al and Si) concentration was quantitatively analyzed also by SIMS for this specimen, and used to ensure the accuracy of the EPMA analysis by the comparison of the results of the two analysis methods.

In order to estimate the amount of Na$_2$O to change the cristobalite into amorphous, it is necessary to obtain the Na$_2$O amount at the phase boundary between the amorphous and the cristobalite phase. Therefore, the cross section of the surface-contaminated and reheated specimen 60A was polished and

![Fig. 1](image)

**Fig. 1.** SEM micrographs of the surface-contaminated specimen 60A: the surface was polished and chemically etched with 1% HF at 0°C for 24 h.
surface analysis was performed by EPMA. Average Na concentration in the analysis area was expressed with a line profile, and finally the Na$_2$O concentration near the phase boundary was obtained using the thickness of the amorphous layer measured from the SEM micrograph. The analysis condition was as follows: acceleration voltage, 15 kV; sample current, $1 \times 10^{-7}$ A; analysis position, $600 \times 600$ points by 0.18 $\mu$m step; beam mode, focused; analysis time, 20 msec for one point. The data for the surface-contaminated and reheated specimen 60A were corrected using similar analysis of the specimens 60A–0.4S (Na$_2$O: 0.38 mass%) and clean 60A (Na$_2$O: < 0.005 mass%) to increase the accuracy of analysis.

3. Results and discussion

3.1 Changing of the cristobalite phase in specimens back to amorphous due to surface contamination during reheating

The SEM micrographs of the polished and chemically etched cross section of the surface-contaminated specimen 60A are shown in Fig. 1. In these photographs, dark-colored layer which corresponds to the crystallized area of the glass phase, and bright colored layer outside the dark layer which was once crystallized and then changed to amorphous are observed. The bright layer was not observed when the sample was wrapped with Pt foil and reheated, so some impurity components in the furnace atmosphere seemed to attach the surface of the sample and diffuse inside.

For the specification of the contamination source, SIMS analysis with high sensitivity and wide range of qualitative analysis was performed for the surface-contaminated specimen 60A. When a qualitative analysis was performed on the surface of the sample as a preliminary experiment, Na$^+$ ion was detected besides Al$^+$, Si$^+$, O$^-$ ions which are main components constituting the sample. So the signal intensity from the surface part and the inner part of the specimen was obtained for the three components except O$^-$. In this measurement, cluster ions with Cs$^+$ ion, i.e. CsNa$^+$ (MASS = 156), CsAl$^+$ (MASS = 160) and CsSi$^+$ (MASS = 161), were detected in order to suppress the scattering of signal intensity caused by sensitization effect of O$^-$ ion. The results, shown in Fig. 2, indicate that the Na$^+$ concentration in the surface layer is two-digits higher than the inner part, so the contamination element from the furnace atmosphere was found to be Na.

The thickness of the amorphous phase in the sample reheated for 8–96 h in this atmosphere observed by SEM is shown in Fig. 3. The result shows that the amorphous layer (caused by Na contamination) increases with the reheating time; the growth rate of amorphous layer, however, gradually decreases with increasing time. If the growth of the amorphous layer is dominated by the diffusion of Na component from the surface to the inner part of the specimen, the growth rate is considered to follow parabolic law. This experimental result shown in Fig. 3 supports this consideration.

After 96 h heating, the depth reached about 80 $\mu$m. It was already reported that the glassy phase in the 5 $\times$ 5 $\times$ 40 mm$^3$ sample wrapped with Pt foil was almost completely crystallized by heating for 96 h. Therefore, the progressing rate of the amorphous phase was substantially lower than the crystallization of the glassy phase.

3.2 Crystallization behavior of the Na$_2$O-added and reheated samples

Power X-ray diffraction spectra were obtained for the surface of the specimens 60A–0.2S, 60A–0.4S, 60A–0.6S and 60A–1S reheated at 1500°C for 8 h. The results are summarized in Fig. 4. For the specimen 60A–0.2S, which contains 0.22 mass% Na$_2$O, the maximum peak of cristobalite (101) is observed. But the other samples, the peak is not observed. For the ground specimen 60A–0.2S, XRD peak of cristobalite was smaller than that in Fig. 4, so the crystallization occurred from the surface of the specimen, similar to the specimens without Na$_2$O.

In order to check the Na$_2$O distribution in the specimens, the surface and the inner center of the reheated bodies were analyzed by SIMS. For example, Fig. 5 shows the result of the specimen 60A–0.2S. This illustrates that significant difference was not

![Fig. 2. SIMS analysis data for the surface-contaminated specimen 60A: signal intensity data for the surface part (a) and for the inner part of the sample (b).](image)

![Fig. 3. Development of the amorphous phase with reheating time at 1500°C in the specimen 60A without wrapping with Pt foil.](image)
observed for the signal intensity of each ion between the surface and the inside of the sample. Therefore, the Na$_2$O component evaporates very little during firing and reheating, so it homogeneously distributes in the fired bodies.

From these results, it was confirmed that the glass phase in the mullite-glass fired body was crystallized if only 0.22 mass% of Na$_2$O was contained, but not crystallized if more than 0.38 mass% of Na$_2$O was contained.

3.3 Estimation of the Na$_2$O amount which changes the cristobalite phase into amorphous by reheating

For the surface of the surface-contaminated specimen 60A, Na$_2$O concentration was quantitatively analyzed by EPMA and SIMS. The results are summarized in Table 1. The analysis results by both methods are in good agreement each other. In addition, concentrations of Al$_2$O$_3$ and SiO$_2$, which are components of the matrix, are also in agreement with the initially-mixed composition obtained by the gravimetric method. This confirms that Na$_2$O can be analyzed quantitatively with good accuracy by EPMA.

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<th>Na$_2$O</th>
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<tr>
<td>EPMA*1</td>
<td>58.22</td>
<td>41.33</td>
<td>0.452</td>
</tr>
<tr>
<td>SIMS*2</td>
<td>58.79</td>
<td>40.75</td>
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</tr>
<tr>
<td>SIMS*3</td>
<td>58.40</td>
<td>41.60</td>
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</tr>
<tr>
<td>60A*4</td>
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<td>41.28</td>
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*1, *2: Surface part  
*3: Inner part  
*4: Raw material (gravimetric analysis)

The distribution of Na in the surface-contaminated specimen 60A was shown as graphical data of EPMA: this analysis is based on the quantitative area analysis data of 360,000 points from the cross section of this specimen, and similar analysis data of the standard sample and the clean sample, respectively. These results are summarized in Fig. 6. The result of area analysis of the surface-contaminated specimen 60A is shown in Fig. 6 (a), which is graphically correlated using the amount of Na in the specimens clean 60A (b) and 60A–0.4S (c) as standards. Figure 6 (d) illustrates both the result of the area analysis (a) and the in-depth line profile of the average Na concentration from the surface to the inner part of the specimen in the area between two horizontal white lines shown in this Fig.

In Fig. 6 (d), the detail of Na distribution in the surface-contaminated and reheated specimen 60A is clearly presented. Overall, the concentration is decreasing from the surface to the inner part owing to the diffusion of Na component, but its profile curve is definitely discontinuous at the boundary between the amorphous layer and the inner part. This means that the diffusion coefficient of Na component is different between the two parts; it is reasonable that the diffusion coefficient in the inner part, crystalline cristobalite phase, is smaller than that in the outer amorphous layer.

The position of the boundary between the amorphous layer and the cristobalite phase is estimated as 20–22 μm from the surface using the lower-left photograph in Fig. 1. So Na$_2$O concentration at the front of the amorphous phase is read to be about 0.30–0.35 mass% from Fig. 6 (d). This result substantially agrees with the experimental result shown in Fig. 4: cristobalite doesn’t occur for the samples which contain Na$_2$O more than 0.38 mass%.

The obtained concentration of Na$_2$O at the boundary, however, is too small to explain the change of the cristobalite phase into amorphous, which means the partially melting and solidification of the specimen, referring to an Al$_2$O$_3$–SiO$_2$–Na$_2$O phase dia-

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**Table 1.** Quantitative Surface Analysis of the Surface-contaminated Specimen 60A

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This discrepancy can be explained by assuming the localization of Na\textsuperscript{2+} in the specimen. Because the ion radius of Na\textsuperscript{+}, 0.116 nm,\textsuperscript{7} is considerably larger than that of Al\textsuperscript{3+}, 0.068 nm or Si\textsuperscript{4+}, 0.054 nm, the solid solution of Na\textsuperscript{2+} into the mullite crystal in this system is inferred to be trace or quite small.\textsuperscript{9} Assuming that the glass phase in the mullite-glass fired body in this study is almost composed of SiO\textsubscript{2} only and all of Al\textsubscript{2}O\textsubscript{3} component in the sample is contained in the mullite crystal, the excess SiO\textsubscript{2} amount is calculated to be 18.0 mass%. Consequently, if the minimum amount of Na\textsuperscript{2+} to change the cristobalite phase to amorphous, which is estimated to be 0.30–0.35 mass% from above consideration, is distributed only in the excess SiO\textsubscript{2}, the Na\textsuperscript{2+} concentration in the glass phase at the interface is correspond to be 1.6–1.9 mass%. Meanwhile, the minimum Na\textsuperscript{2+} concentration in the liquid phase which coexists with mullite is read to be about 2 mass% at 1500°C from an Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}–Na\textsuperscript{2+} phase diagram;\textsuperscript{7} this agrees with above discussion.

From above-mentioned consideration, it is concluded that the cristobalite phase in the mullite-cristobalite fired body changes to amorphous by containing Na\textsuperscript{2+} more than about 2 mass% in the grain boundary phase. Similarly, when the glass phase coexisting with mullite grains in the fired body contains this amount of Na\textsuperscript{2+}, the crystallization to cristobalite does not occur by the reheating condition in this study.

4. Summary

The effect of Na\textsuperscript{2+} which changes the cristobalite phase into amorphous in mullite-cristobalite fired bodies was investigated. The results are summarized as follows.

(1) For the specimen 60A–0.2S, i.e. SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} fired body (Al\textsubscript{2}O\textsubscript{3}: 60 mass%) containing 0.22 mass% of Na\textsuperscript{2+}, the glass phase at grain boundary was crystallized into cristobalite by reheating at 1500°C for 8 h.

(2) In the surface-contaminated specimen 60A, i.e. the specimen 60A reheated at 1500°C for 24 h without wrapping with Pt foil, the concentration of the contaminating Na\textsuperscript{2+} at the boundary between the area in which once-crystallized cristobalite was changed into amorphous and the neighboring area in which the cristobalite remained unchanged was found to be 0.30–0.35 mass% by EPMA quantitative analysis.

(3) Assuming that the contaminating Na\textsuperscript{2+} component is localized at the grain boundary in the specimen, the concentration of Na\textsuperscript{2+} in the glass phase was 1.6–1.9 mass%. By use of this value, the change of the cristobalite phase into amorphous by reheating was explained reasonably referring to an Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}–Na\textsuperscript{2+} phase diagram.

Acknowledgments Authors are grateful to Mr. Hideo Kanda

![Fig. 6. EPMA results of Na component for the cross sections of the surface-contaminated specimen 60A (a), the clean specimen 60A (b) and the specimen 60A–0.4S (c). The line profile of average Na concentration between two horizontal white lines overlapped with the result (a) is shown in (d).]
and Mr. Seiki Honda of Seiko I Techno Research Co., Ltd. Japan for the instruction and the cooperation for SIMS analysis.

References