Effect of talc addition on pyroplastic deformation of an alumina strengthened porcelain

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The influence of talc addition on the pyroplastic deformation of alumina-strengthened porcelain was investigated in this study. Along with the lower content of feldspar, the addition of talc contributed to the crystallization of the cordierite during the firing process, and the resulting cordierite crystals formed complicated filler structures. The porcelain samples made with the addition of talc showed an unprecedented pyroplastic deformation characteristic with almost no changes in the pyroplastic deformation index value during further firing at over 1000°C after the water absorption reached almost zero. This improvement of pyroplastic deformation was thought to synchronize with the crystallization of cordierite.

Key-words : Pyroplastic deformation, Talc, Cordierite, Porcelain, Filler

In the long history of porcelain manufacturing, controlling the deformation of a porcelain body during its firing process is one of the most important problems due to its tendency to decrease the precise shape reproducibility of the final product after the firing process. During the firing process, shrinkage deformation and pyroplastic deformation are two main factors responsible for the distortion of the final products. Shrinkage deformation occurs in the first stage of firing before the full dense temperature, and pyroplastic deformation is dominant during the final stage of firing.11) Pyroplastic deformation affects the optimum firing temperature range, and is related to many factors such as chemical composition, particle size of raw materials, and firing pattern.

The chemical reactions, phase development, and microstructural evolution of a porcelain body during the firing process have been studied extensively with some researches focused on pyroplastic deformation.2–9) Tuncel et al. have studied the effect of chemical composition on pyroplastic deformation at 1250°C, and demonstrated that the Na2O/K2O ratio had a more prominent effect on pyroplastic deformation compared to changes in the SiO2/Al2O3 ratio.10) Deng et al. reported the effect of the distribution of mullite in the glass matrix on pyroplastic deformation.11) Other studies revealed that the dissolution of quartz in the melt resulted in increasing the viscosity of the liquid phase, thus, reducing the pyroplastic deformation.12–14) These studies mainly focused on the viscosity of the liquid phase or mullite phase formation in the glass matrix. However, there are only few reported studies on the role of filler in the pyroplastic deformation of porcelain. Austin et al. have reported that the addition of alumina, with higher refractoriness than quartz, in vitreous whiteware was effective in decreasing deformation during firing,15) which suggests the characteristic of filler is a sensitive factor on pyroplastic deformation of a porcelain body. On the other hand, Kobayashi studied the crystallization and densification of cordierite ceramics, and reported a high refractoriness cordierite phase was formed from a talc and kaolinite.16)

Thus, we expect the formation of the cordierite phase, as a new filler with talc addition in the porcelain body, to affect pyroplastic deformation in the firing process. In this study, the talc was added to the alumina-strengthened porcelain body to improve the pyroplastic deformation. The prepared porcelain bodies were fired from 1100 to 1400°C, and pyroplastic deformation, water absorption and bulk density were measured. The phase development of the porcelain body was examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

For this study, three kinds of porcelain bodies, namely, new porcelain 1 (NP1), new porcelain 2 (NP2) and traditional porcelain (TP, a commercial Amakusa clay), were prepared. The Amakusa clay is made from Amakusa pottery stone with sericite, kaolinite and quartz. NP1 was prepared from Amakusa clay (36 mass %), Gairei clay (10 mass %), calcined talc (18 mass %), Musada feldspar (6 mass %), and calcined alumina (corundum 30 mass %). As for NP2, bone ash (3 mass % outer percentage) was added to NP1 to confirm the influence of varying liquid phase amounts. The chemical compositions of the three porcelain bodies are shown in Table 1.

The specimens used for all characterization analyses were fabricated into test bars (120 × 20 × 7 mm) by slip casting in plaster molds. The water concentration of the slips was 27 mass %, and the optimal amount of dispersant (type A6012: toagosei co.) was determined to be 0.2 mass % on the basis of the total dry raw materials.

After drying, the specimens were fired in an electric kiln at a firing rate of 200°C/h to 1100–1400°C, and kept at that temperature for 1 h. Thermal history of the samples was measured using a Referthermo (type-M: JFCC), and the measured values were used in this paper as experimental temperatures. The specimens used for measuring the pyroplastic index values (PI) were...
suspended between two refractory supports during the firing process.\(^7\)

The PI of specimens were calculated according to Eq. (1).

$$PI = \frac{sb^2}{l}$$  \hspace{1cm} (1)

where, \(s\): max deformation (mm)

\(b\): sample thickness (mm)

\(l\): distance between supports (100 mm).

A driving force of sintering in porcelain body at elevated temperature is a viscous flow of liquid phase formed from the thermal reaction of raw materials. This viscous flow occurs over all densification period and soaking period after vitrification at elevated temperature. The liquid phase also promotes deformation over all heat-treatment period. In this paper, the deformation before the water absorption reaches zero was defined as shrinkage deformation and the deformation after it was defined as pyroplastic deformation.

Water absorption and bulk density of the fired samples were measured with a test method based on ASTM C373. To visualize the microstructure in the fired samples, the specimens were ground and polished to a 1 μm finish with diamond pastes and imaged by SEM (JSM-6700FSS: JEOL Ltd.). The crystalline phases of the fired samples were analyzed by XRD (XpertPRO; PANalytical Ltd.).

Table 2 presents the measured water absorption and bulk density values of the fired specimen. The water absorption of TP was less than 0.3% after firing at 1291–1325°C, and the bulk density reached a maximum (2.35 g/cm\(^3\)) at 1291°C. At 1369°C, the bulk density decreased rapidly while the water absorption increased due to bloating of the porcelain body. Hence, the optimum firing temperature range for TP was determined to be 1290 to 1325°C. NP1 showed less than 0.3% water absorption and a maximum bulk density was seen (2.56 g/cm\(^3\)) at 1228°C. At 1369°C firing temperature, the water absorption was maintained at the minimum value with a gradual decrease in the bulk density. However, unlike TP, a sudden drop in the bulk density was not observed for this sample. The water absorption of NP2 reached below 0.3% at 1182°C, which was 50°C lower than that of NP1 by the effect of addition of 3 mass % bone ash. Bloating in the body was observed at 1325°C.

The calculated PI values of the fired samples are given in Table 3. The PI values of TP showed typical pyroplastic deformation characteristics that increase with the firing temperature. Kobayashi et al.\(^8\) reported that the bloating at elevated temperature was restricted by controlling the ratio of the feldspar and kaolin content in the range of 1:1 to 1:1.5, independent of the alumina content, but did not mention about the pyroplastic deformation of alumina strengthened porcelain. In contrast, the PI values of NP1 remained constant (1.48–1.59 × 10^{-6} mm^{-1}) at 1236–1321°C. As shown in Table 2, the water absorption of NP1 at 1228–1369°C was almost zero. This is a unique and novel pyroplastic deformation characteristic when compared to that of a commercial porcelain (TP) at a wide range of firing temperatures. The results of the firing deformation tests for NP1 and TP are shown in Fig. 1. The maximum deformation of NP1 fired at 1236°C was 3.5 mm; most of this deformation was caused by shrinkage deformation, since the maximum bulk density of NP1 was reached at 1228°C. As shown in Fig. 1 (NP1), the shape of NP1 fired at 1236–1321°C was similar, indicating that the pyroplastic deformation of NP1 did not progress at these temperatures. Therefore, porcelain products made from NP1 material under the same molding conditions have uniform shape without careful control of the firing temperature within 1236–1321°C. The degree of deformation of TP increased with the firing temperature [Fig. 1(TP)], indicating the necessity of a fine control of firing temperatures to achieve a high precision porcelain product. The PI values of NP2 were almost constant (1.99–2.07 × 10^{-6} mm^{-1}) at 1236 and 1292°C. Upon further firing at 1321°C, the PI value slightly increased to 2.49 × 10^{-6} mm^{-1}, which was lower than that of the TP sample despite the occurrence of bloating in the body. Such results indicate that the NP1 and NP2 series have a high resistance to pyroplastic deformation during excess firing.

Figures 2 and 3 show the XRD patterns of the fired samples of TP and NP1 at 1130–1369°C. In the TP sample, mullite can be observed throughout the sample, and its diffraction intensity increased with increasing firing temperature, while the diffraction intensity of quartz decreased slightly with increasing firing temperatures attributed to the dissolution of quartz in the glass matrix. In the NP1 sample fired at 1130°C, quartz, corundum, mullite, and glass were observed. Cordierite (2MgO·2Al\(_2\)O\(_3\)·3SiO\(_2\)) was formed at 1182°C and the peaks intensity of cordierite was not observed at 1369°C.

Table 2. Characterization results of the samples after firing

<table>
<thead>
<tr>
<th>Firing temperature</th>
<th>water absorption/%</th>
<th>bulk density/g/cm(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NP1</td>
<td>NP2</td>
</tr>
<tr>
<td>1088°C</td>
<td>—</td>
<td>8.30</td>
</tr>
<tr>
<td>1130°C</td>
<td>7.28</td>
<td>0.60</td>
</tr>
<tr>
<td>1182°C</td>
<td>1.68</td>
<td>0.15</td>
</tr>
<tr>
<td>1228°C</td>
<td>0.22</td>
<td>0.13</td>
</tr>
<tr>
<td>1291°C</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>1325°C</td>
<td>0.15</td>
<td>2.47</td>
</tr>
<tr>
<td>1369°C</td>
<td>—</td>
<td>8.94</td>
</tr>
</tbody>
</table>

Table 3. PI values of NP1, NP2 and TP

<table>
<thead>
<tr>
<th>Firing temperature</th>
<th>PI/×10^{-6}/mm</th>
</tr>
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| NP1                | NP2            | TP
| 1236°C             | 1.48           | 2.07           | 2.13   |
| 1292°C             | 1.48           | 2.07           | 2.69   |
| 1321°C             | 1.59           | 2.49           | 4.23   |
ite increased with increasing firing temperature. On the other hand, the peak intensity of quartz and corundum decreased with increasing firing temperature. The decreasing peak intensity of quartz reveals that a dissolution rate of the quartz is higher in NP1 than in TP, which is attributed to the added talc accelerating the dissolution of quartz. This result indicates that cordierite is formed by the crystallization from liquid phase through the dissolution of quartz, alumina and decomposed talc. This result indicates that cordierite is formed through the interaction of quartz dissolution, corundum and talc relics. Cordierite, mullite, corundum, quartz and glass were confirmed in the NP1 sample at 1369°C. The NP2 sample, which fabricated by adding 3 mass% bone ash to NP1, resulted in about a 50°C lower firing temperature shift of phase evolution compared to NP1 (Fig. 4).

Fig. 2. XRD patterns of TP samples fired at various temperatures.

Fig. 3. XRD patterns of the NP1 samples fired at various temperatures.

Fig. 4. XRD patterns of the NP2 samples fired at various temperatures.

Fig. 5. SEM secondary electron image of the TP fired at 1291°C with etching in 4.5% HF solution for 60 s. (Q: Quartz, M+G: mullite in the glass matrix)

The microstructure of the TP sample fired at 1291°C is shown in Fig. 5. This sample contains quartz grains (2–20 μm in diameter) surrounded with the glass rim, fine needle-like mullite, and closed pores (1–10 μm in diameter) distributed in the glass matrix. It can be noted that most of the quartz grains are distributed separately from each other, which enables mobility of the quartz grains in the presence of an excess glass, ultimately leading to pyroplastic deformation during the firing process. Hence, the shape of a traditional porcelain product is easily deformed.

Figures 6(a) and 6(b) show the microstructure of NP2 fired at 1182°C, and 1088°C, respectively. In Fig. 6(a), hexagonal-shaped cordierite crystals (2–10 μm long and 1–3 μm wide) filled the space between the original filler particles (quartz and corundum), and almost all the cordierite crystals were connected with each other to form the complicated network structure. NP2 fired at 1088°C showed 8.30% water absorption (Table 2). In Fig. 6(b), the network structure in NP2 fired at 1088°C was similar to the NP2 sample fired at 1182°C, but the glass matrix did not occupy the network structure gaps as seen in Fig. 6(a). This indicates that the complicated network structure was formed before the growth of sufficient amount of glass matrix. The surface of NP2 fired at 1291°C, which temperature was just below point the body deformed by bloating, showed a shiny state similar to self-glazing. This observation is an indication of excess glass pushed out through the network structure by bloating of the inner pores, and is evidence that the network structures in the NP2 are hard to move, even though excess glass. The microstructure of NP1 samples fired at 1130–1325°C also showed similar structures to NP2 samples fired at about 50°C lower temperature. However, the drastic
An increase in pore size observed in NP2 fired at 1325°C was not observed in the NP1 sample fired at 1369°C.

As shown in Figs. 3 and 4, the cordierite phase increased with increasing firing temperature, but the original quartz and corundum grains decreased with increasing firing temperature. During the firing process, a new complicated network of cordierite crystallized and developed in place of the original fillers (quartz and corundum). This phenomenon caused an unprecedented pyroplastic deformation characteristic seen in NP1 and NP2. Comparing the pyroplastic deformations of NP1 and NP2, the addition of bone ash favored a lower formation temperature of the liquid phase and faster dissolution of the original filler (quartz and corundum) in the liquid phase (Fig. 4). As a result, the densification (Table 2) and cordierite formation (Fig. 4) were promoted at lower temperature. However, the increase in the amount of glass matrix resulted in drastic bloating at firing temperatures over 1300°C.

In summary, the NP1 and NP2 series showed an unprecedented pyroplastic deformation characteristic with almost no changes in the PI value during further firing at over 100°C after the water absorption reached almost zero.

Further study on the effect of the crystal size and the amount of cordierite, quartz, corundum, mullite, and the glass matrix in the fired body during the pyroplastic deformation is in progress.

References

Fig. 6. SEM compositional image in BSE of the (a) NP2 fired at 1182°C (b) NP2 sample fired at 1088°C without etching. (C: Cordierite, OF: Original filler/Quartz, Corundum)