Effect of cordierite crystallization on the water absorption and pyroplastic deformation of an alumina-strengthened porcelain that contains fine talc

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The effect of cordierite crystallization on the densification and pyroplastic deformation (PD) of alumina-strengthened porcelain that contains talc is examined herein. During firing at a relatively low temperature below 1200 °C, the addition of fine talc powder with a mean diameter of approximately 7 µm is more effective in promoting the liquid phase sintering of the porcelain through an increase in the amount of the low-viscosity liquid phase due to Mg²⁺ doping than the addition of a coarse talc powder with a mean diameter of approximately 14 µm. Beyond the firing temperature, cordierite crystallization that is accelerated by the fine talc addition suppresses the PD of the porcelain through a decrease in the amount and an increase in the viscosity of the liquid phase due to the transfer of Mg²⁺ from the liquid to the cordierite crystals. As a result, a decrease in the water absorption (<0.5%) and PD index (<1.5 × 10⁻⁵ mm⁻¹) is realized for the porcelain with 32 mass % addition of the fine talc powder over a relatively wide firing temperature range from 1194 to 1336 °C.

Key-words : Porcelain, Talc, Water absorption, Pyroplastic deformation, Fine powder, Cordierite

1. Introduction

Imari porcelain made from Amakusa pottery stone is a typical product with a long history in the Saga and Nagasaki prefectures in Japan.¹) The porcelain is still an important product for the regional manufacturing base and economy.²) It has been widely used as tableware, sanitary ware, insulating materials, and other ceramic items worldwide. The pyroplastic deformation (PD) of the porcelain, which is basically caused by the sintering shrinkage and/or viscous flow of the liquid phase, which is accelerated by applied stresses,³)⁶) is one of the critical problems that must be solved to improve the application of the porcelain because PD reduces the aesthetic and functional properties of the porcelain as an artistic and industrial product, respectively.

Many studies have been performed to decrease the PD by managing the composition of raw materials, such as kaolinite, feldspar, and quartz.⁵)⁹)⁶) According to previous studies, PD is greatly influenced by viscous deformation of the liquid phase in the porcelain during firing, which could be controlled by adjusting the amount and chemical composition of the glass matrix in the porcelain and/or by adding fillers, such as quartz and alumina, to the porcelain. Recently, Sanchez³) and Daniel¹⁰) reported the influence of Ca²⁺ and Mg²⁺ doping on the PD, respectively, and found that alkaline earth ions degraded the resistance to PD through the formation of a glass matrix in the porcelain. Austin et al. demonstrated that the addition of alumina was effective in preventing PD.¹¹) The production of a large amount of a glass matrix, which changes to a low-viscosity liquid phase during firing of the porcelain, promotes densification, but it is not advantageous for the production of a low PD. The addition of fillers to the porcelain helps to suppress the PD, but the prevention of sintering shrinkage by the fillers leads to a low density in the porcelain. These findings indicate that a trade-off in the material design is required to develop a dense porcelain with a small PD. Therefore, the optimization of porcelains is required to produce a high densification with a small PD over a wide firing temperature range.

The addition of talc is one of the attractive methods to obtain a dense porcelain with a small PD because of the presence of cordierite crystals, which appear as a chemical reaction product among the talc, alumina, and liquid phase during firing.¹²)¹³) the cordierite is expected to suppress the PD through increasing the viscosity, which is a...
behavior that occurs with fillers.\textsuperscript{10,14} The cordierite crystallization, in addition, decreases the amount and increases the viscosity of the liquid phase during firing of the porcelain because the concentration of Mg\textsuperscript{2+} in the liquid, which fragments the SiO\textsubscript{4} tetrahedral network structure in the silicate-based liquid\textsuperscript{15} and decreases with the transfer of the ions from the liquid to the cordierite crystals. Contrary to expectations, as demonstrated in our previous study,\textsuperscript{16} cordierite crystallization was not effective in suppressing the PD so that the optimization between the high densification, but a small PD of alumina-strengthened porcelain over a wide firing temperature range was realized with the addition of a small amount of talc. This indicates that the talc addition was more effective at increasing the amount and decreasing the viscosity of the liquid phase during firing of the porcelain due to Mg\textsuperscript{2+} doping than activating the chemical reaction to create cordierite crystals. As a result, the effect of cordierite crystallization on the densification and PD of the porcelain was not observed clearly in our previous study.\textsuperscript{16} However, according to previous study,\textsuperscript{16} there seems to be room for further investigation of cordierite crystallization to optimize both the densification and PD in porcelain. Thus, it is important to activate cordierite crystallization effectively during the porcelain firing process.

In this study, the crystallization of cordierite is accelerated during the firing of the alumina-strengthened porcelain made from Amakusa clay by using a fine talc powder with a mean diameter of approximately 7\textmu m. The effect of the fine talc addition on the densification and PD of the porcelain is examined by comparing the bulk density (BD), water absorption (WA) and PD index (PI) for the porcelain with fine and coarse (a mean diameter of approximately 14\textmu m) talc powder. In addition, the crystalline phase evolution and microstructural development in the porcelain are investigated with X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental procedures

2.1 Raw materials

The commercial-grade powder comprising the raw materials used in this study were basically the same as those used in our previous study,\textsuperscript{16} i.e., Amakusa clay (Fuchino Ceramic Raw Materials Co., Japan), Masuda feldspar (Nishi-Nihon Kogyo Co., Japan), Motoyama gairome clay (KCM Co., Japan), and calcinated talc and alumina (A-34, Japan Light Metal Co., Japan) with a mean diameter of approximately 4\textmu m. The chemical compositions of the raw materials are listed in Table 1 from Ref. 16. To make fine talc powder, the calcined talc powder was milled in water with alumina balls for 10 h. The mean diameter of the fine talc powder was confirmed to be approximately 7\textmu m, as measured by laser diffraction (Laser Micron Sizer LMS-2000e, Seishin Enterprize Co., Japan). As described in the following section, the slurry to make the porcelain green body for this study was prepared by ball milling the powder comprising the raw materials in water for 1 h. To check the particle size of the calcined talc in the powder that were milled, the mean diameter of the calcined talc milled in water with the balls for 1 h was also measured with laser diffraction and was confirmed to be approximately 14\textmu m.

2.2 Preparation of the porcelain green bodies

The specimens used in this study were fabricated into test bars by slip casting in a plaster mold. Two kinds of processes were adopted to make the slurry for the casting. One was the ball milling of all the powder raw materials in water with a dispersant (A-6012, Toa Gosei Co. Ltd., Japan) for 1 h. Another process was the ball milling of the powder without the calcined talc in water with the same dispersant for 45 min followed by an additional 15 min of ball milling after the addition of the fine talc powder. The water concentration in all the slurries was set to 28 mass %.

The green body was prepared with dimensions of 120 × 20 × 7 mm\textsuperscript{3}.

The raw material composition for each porcelain is listed in Table 1. Seven different types of green bodies were fabricated and noted as xTC or xTF, where x refers to the amount of talc addition, which ranged from 18 to 37 mass %. The last character “C” in the porcelain name indicates that the porcelain comprised the relatively coarse talc powder made by the first ball-milling process described above. The character “F” indicates the porcelain comprised the fine talc particles made by the second ball-milling process described above. For example, 37TF indicates porcelain containing 37 mass % of the fine talc powder.

The chemical composition of each porcelain is listed in Table 2, which was calculated based on the chemical composition of the raw materials and the raw material composition of the porcelain. The ratio of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} varied from 1.14 to 1.57, which is relatively low compared with that of the previous study.\textsuperscript{15} The low SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio promoted the crystallization of the mullite during porcelain firing process. Since the ratio of Na\textsubscript{2}O/K\textsubscript{2}O greatly influences the amount of a glass matrix, the value of Na\textsubscript{2}O/ K\textsubscript{2}O was almost constant at approximately 0.18 in this study. That is, the fluxing agent was stable in this study and had little influence on the glass matrix formation.
to the precise control of the talc addition, the MgO amount varied significantly, inferring that the amount of the glass matrix and cordierite would differ from those in the fired porcelain in the research by Magagnin et al.\(^\text{10}\) As a result, such a design would influence the PD.

### 2.3 Characterization

XRD was conducted by using an X-ray diffractometer equipped with an X-ray radiation generator (Cu-K\(\alpha\), \(\lambda = 0.15418\) nm) and a scanning angle (2\(\theta\)) range of 5°–80° was used (RINT2100, Rigaku Corp., Japan). To evaluate the amount of cordierite crystals in the fired porcelain through a ratio of the XRD peak intensities, the intensity of the peak at approximately 2\(\theta = 10.46°\) that was assigned to the cordierite (110) planes was compared with that for a peak at approximately 2\(\theta = 47.35°\) that was assigned to the silicon (220) planes. The XRD was conducted on the fired porcelain powder with a quantity of 0.95 g mixed with standard silicon powder with a quantity of 0.25 g. The microstructure of the porcelain was observed by using field-emission SEM equipped with an energy-dispersive X-ray spectrometry system (JSM-6700FSS, JEOL Corp., Japan). The BD and WA of the fired porcelain materials were evaluated based on the Archimedes’ principle according to ASTM C373. The details of the characterization are described in Ref. 16).

### 2.4 Test for PD

Two ends of the green bodies were suspended on an alumina support with a span of 100 mm. The tests for PD were performed in a muffle furnace in air at maximum firing temperatures (MFTs) ranging from 1150 to 1400 °C for 1 h. The PI was calculated with the following equation:\(^{17,18}\)

\[
\text{PI} = \frac{sb^2}{\ell},
\]

where \(s\) is the maximum deformation (mm), \(b\) is the thickness of the specimen (mm), and \(\ell\) is the distance between the two supports (mm). The details of the test are described in Ref. 16).

### 3. Results and discussion

#### 3.1 Effect of the fine talc addition to the alumina-strengthened porcelain on the densification

Using a fine powder in slurries for casting usually tends to result in low packing density of the resulting green bodies because of a decrease in the water pressure of the Darcy flow on the cakes caused by clogging of the gaps between the particles with the fine powder. Thus, the packing density of all of the green bodies was checked before firing. As a result, it decreased from 1.96 to 1.86 g/cm\(^3\) with an increase in the fine talc amount from 18 to 37 mass%. However, it was confirmed that the packing densities were sufficiently high to densify the green body by firing at approximately 1300 °C.

**Figures 1 and 2** show the BD and WA, respectively, of the alumina-strengthened porcelain as a function of the MFT. The BD increased and the WA decreased significantly with an increase in the MFT up to approximately 1200 °C (1250 °C for 32TC only), where the porcelain reached its maximum densification herein. The increase in the BD and decrease in the WA were due to an acceleration in the liquid phase sintering through an increase in the amount of a low-viscosity liquid phase as the MFT increased (see a halo pattern at approximately 2\(\theta = 23.0\)–24.0° in **Fig. 3**). In this MFT range, where cordierite crystallization cannot be obviously observed (see **Fig. 3**), the porcelain with the addition of fine talc powder showed a higher BD and lower WA than those of the porcelain with a coarse talc powder because the activated chemical reaction

| Chemical compositions of the porcelain samples before firing |
|-----------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|                | Ig. Loss | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | TiO\(_2\) | CaO | MgO | Na\(_2\)O | K\(_2\)O |
| 18TC\&F         | 2.89    | 47.04   | 41.38   | 0.33   | 0.07   | 0.16 | 5.77  | 0.35  | 1.99  |
| 22TC\&F         | 2.82    | 47.86   | 39.48   | 0.32   | 0.07   | 0.18 | 7.04  | 0.34  | 1.90  |
| 32TC\&F         | 2.62    | 49.76   | 34.85   | 0.30   | 0.06   | 0.22 | 10.22 | 0.30  | 1.66  |
| 37TF            | 2.53    | 50.79   | 32.45   | 0.29   | 0.06   | 0.25 | 11.81 | 0.28  | 1.54  |

![Graph 1](image1.png)

**Fig. 1.** BD of the porcelain as a function of the MFT.

![Graph 2](image2.png)

**Fig. 2.** WA of the porcelain as a function of the MFT.
between the liquid phase and the fine talc powder accelerated the liquid phase sintering through an increase in the amount and a decrease in the viscosity of the liquid phase due to enhanced Mg$^{2+}$ doping by the fine talc powder.

Above the MFT range, the BD gradually decreased with increasing MFT up to approximately 1330 °C. The crystallization of the cordierite progressed during firing above 1200 °C (see Fig. 3); this phenomenon suppressed the densification of the porcelain because it decreased the amount and increased the viscosity of the liquid phase by diluting the Mg$^{2+}$ in the liquid phase. The suppression of the densification was also caused by the prevention of the sintering shrinkage due to the formation of rigid microstructures made by entangled needle-like mullite crystals (see Fig. 4).

Above the MFT of approximately 1330 °C, the BD decreased drastically with an increase in the MFT owing to the enlargement of bubbles that were in the liquid phase during the porcelain firing process (see Fig. 5). The WA, however, remained below 0.5% in this MFT range, except for sample 37TF, because closed pores are mainly formed in the porcelain even at the high firing temperature owing to the formation of the liquid phase with relatively low viscosity. A rigid microstructure consisting of entangled needle-like mullite crystals developed in the glass matrix of the fired porcelain (see Fig. 4) and prevented the significant enlargement of the bubbles at elevated temperatures. The viscosity of the liquid phase in sample 37TF during firing seemed to be relatively high due to the low concentration of alkaline and alkaline earth ions (K$^+$ and Mg$^{2+}$, mainly) in the liquid, which was caused by the significant cordierite crystallization and small amount of feldspar addition due to the large amount talc addition at a certain raw materials balance (see Table 1); thus, the fine crystalline microstructure in sample 37TF could not suppress the extreme expansion of the bubbles in the highly viscous liquid above 1330 °C.

The BD decreased with an increase in the amount of fine talc addition, as shown in Fig. 1. The BD decreased due to the suppression of the liquid phase sintering that was caused by a decrease in the amount and increase in the viscosity of the liquid phase during the porcelain firing process through the small amount of feldspar that was added due to the large amount talc that was added under a certain raw materials balance (see Table 1). The size of the pores in the porcelain fired above approximately 1200 °C was, however, smaller than approximately 30 μm except for sample 37TF, which was fired at above 1330 °C; this occurred because the WA of the porcelain was smaller than 0.5% although the sintering of the porcelain was suppressed, as mentioned above.

### 3.2 Effect of the fine talc addition to the alumina-strengthened porcelain on the PD

Figure 6 shows the PI of the alumina-strengthened porcelain as a function of the MFT. The PI increased steeply.
with an increase in the MFT up to approximately 1200 °C for sample xTF and up to approximately 1250 °C for sample xTC. The increase in the PI was due to the sintering shrinkage that was accelerated by an increase in the MFT through an increase in the amount of the low-viscosity liquid phase. Fine talc particles activated the chemical reaction between the talc and the liquid phase to promote the liquid phase sintering; thus, the steep increase in the PI of the xTF porcelain appeared approximately 50 °C lower than that of the xTC porcelain.

Above the MFT range, the PI had a plateau up to an MFT of approximately 1330 °C (see Fig. 7). As mentioned in the previous section, the sintering of the porcelain was suppressed in this MFT range due to cordierite crystallization. This is the reason for the PI plateau in this MFT range.

The small PI for the 32TF sample was due to the cordierite crystallization being accelerated by using the fine talc powder at a relatively low MFT range below 1250 °C, which was confirmed in XRD patterns for the porcelain (see Fig. 7). Regarding the effect of the cordierite crystallization on the production of a small PI, there are two factors to consider, as mentioned above. One is the rigid microstructure constructed by the fine cordierite crystals,
which suppressed the PD of the porcelain. Another is the decrease in the amount and increase in the viscosity of the liquid phase during porcelain firing process through the dilution of the Mg\(^{2+}\) in the liquid. Agglomerated cordierite crystals, which grew from the edges of the coarse talc particles,\(^{20}\) can be observed in sample 32TC, while fine cordierite crystals seem to be distributed uniformly in sample 32TF (see Fig. 8). This indicates that the former factor did not seem to be effective in constructing a rigid microstructure (see Fig. 8), and the microstructure was basically the same as that reported in Ref. 16), in which entangled needle-like mullite crystals constructed a rigid microstructure. The latter factor that involves the amount and viscosity of the liquid was confirmed by an observation of the glass that was exuded on a specimen fired above 1330 °C, where the amount of the glass on sample 32TF was much smaller than that on sample 32TC. There was almost no difference in the PI between samples 32TF and 37TF (see Fig. 6), which basically contained a small amount of feldspar as a raw material. The effect of cordierite crystallization to prevent PD seemed to be saturated at approximately 32 mass% addition of fine talc powder to the porcelain because of the small amount of the liquid phase.

Especially for the xTF porcelain, the PI increased significantly with increasing MFT above 1330 °C. The increase in the PI was attributed to the enlargement of the bubbles in the liquid phase of the porcelain during firing, as mentioned in the previous section.

As a result, the optimization to obtain a small WA (\(<0.5\%\)) and small PI (\(<1.5 \times 10^{-6} \text{mm}^{-1}\)) was realized for the 32TF porcelain over a relatively wide MFT range from 1194 to 1336 °C. In our previous study,\(^{16}\) the optimization was realized for the porcelain with 2 mass% coarse talc addition, where the cordierite crystallization did not obviously affect the densification and PD of the porcelain, over a relatively high MFT range from 1240 to 1384 °C. This clearly indicates that the MFT range for the optimization decreased approximately 50 °C due to the addition of fine talc powder to the porcelain through the activation of the chemical reaction to form a low-viscosity liquid phase over a relatively low MFT range below approximately 1250 °C (see Fig. 7). In a relatively high MFT range above 1200 °C, the chemical reaction to form cordierite crystals was activated by the fine talc addition. The activated cordierite crystallization decreased the amount and increased the viscosity of the liquid phase during firing. As a result of the enlargement of the bubbles in a highly viscous liquid with a rigid microstructure, the increased limit for the MFT for the optimization decreased to approximately 1330 °C.

4. Conclusions

The effect of cordierite crystallization on the densification and PD of alumina-strengthened porcelain is examined herein. In a relatively low MFT range below 1200 °C, the liquid phase sintering of the porcelain is further promoted by the addition of fine talc powder through an increase in the amount of a low-viscosity liquid phase during firing due to Mg\(^{2+}\) doping. Beyond the MFT, cordierite crystallization that was accelerated by the fine talc addition suppresses the PD through a decrease in the amount and an increase in the viscosity of the liquid phase due to the dilution of Mg\(^{2+}\) in the liquid. A rigid microstructure to prevent PD is constructed by entangled needle-like mullite crystals. As a result, the optimization to obtain a small WA (\(<0.5\%\)) and small PI (\(<1.5 \times 10^{-6} \text{mm}^{-1}\)) is realized for the 32TF porcelain over a relatively wide MFT range from 1194 to 1336 °C.

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