Minimization of water absorption and pyroplastic deformation of wollastonite-containing alumina-strengthened porcelain

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\textbf{ABSTRACT}

The densification and pyroplastic deformation of alumina-strengthened porcelain were examined within a range of alumina and wollastonite contents. Both the alumina addition and anorthite crystallization not only prevent the liquid-phase sintering, which plays an important role in the densification of the porcelain during firing, but also suppress the pyroplastic deformation at high firing temperatures. The prevention of densification as well as the suppression of pyroplastic deformation is basically described by the change in the amount of liquid phase at firing. As a result, optimization between small water absorption and small pyroplastic deformation was found out in the relatively wide firing temperature range for porcelain with 30 mass\% alumina addition and <10 mass\% wollastonite addition. This study serves as a guide to achieve minimal water absorption and pyroplastic deformation in alumina-strengthened porcelain fired at temperatures from 1290 to 1380°C.

1. Introduction

Porcelain is commonly used in tableware, sanitary ware, tiles, insulators, and crucibles, and can be strengthened by adding alumina particles for specialized applications (e.g. tableware used in hospitals, nursing homes, and airplanes) [1]. However, alumina-strengthened porcelain (ASP) is prone to pyroplastic deformation (PD) during firing at elevated temperatures, which is caused by inhomogeneous sintering shrinkage and/or viscous flow of the liquid phase [2–4]. This can lead to a large amount of production loss. Although PD is easily suppressed by decreasing the firing temperature, sufficient densification of ASP cannot be achieved at very low firing temperatures. Consequently, the porosity of the ASP is compromised, leading to water absorption (WA) issues. Thus, there is an inevitable trade-off between the suppression of PD and WA in ASP products.

The development of ASP materials that offer minimal PD and WA after firing within a relatively broad temperature range is important for industrial ASP production, as large kilns with a wide temperature distribution are typically used. ASPs with a rigid microstructure consisting of entangled needle-like mullite crystals and a relatively small proportion of low-viscosity liquid phase at firing temperature have previously been reported to offer a good balance between low PD and WA [4]. ASP was optimized by adding talc and petalite, which contributed Mg\textsuperscript{2+} and Li\textsuperscript{+} ions to control the amount and viscosity of the liquid phase, respectively [4]. In the case of doping of Mg\textsuperscript{2+} and Li\textsuperscript{+} ions into ASP, there is a possibility to form crystals with very low thermal expansion/shrinkage, such as cordierite and spodumene, leading to the decrease in the thermal expansion/shrinkage of ASP. The decrease of the thermal expansion/shrinkage of ASP is a disadvantage for the improvement of the strength through the compressive stress in the glaze on ASP [5], which is owing to the mismatch in thermal shrinkage between the glaze and ASP. While there is no possibility to form any crystals with very low thermal expansion/shrinkage in the case of Ca\textsuperscript{2+}-doping, the effect of Ca\textsuperscript{2+}-doping on ASP liquid phase formation has not yet been clarified.

Limestone, calcite, dolomite, and wollastonite are potential Ca\textsuperscript{2+} sources for porcelain optimization [6–8], of which wollastonite is the most attractive due to its low cost, flux formability, low shrinkage, transparency, and white color [8–10]. Wollastonite can be used as a flux agent in porcelain production to lower the firing temperature by ~30°C, maintain high hardness [8,11,12], and improve the luster of the glaze [10]. Wollastonite is also used as a raw material in anorthite-based ceramics, where the volume expansion due to the transformation of wollastonite (2.90 g/cm\textsuperscript{3}) to anorthite (2.76 g/cm\textsuperscript{3}) can counteract sintering shrinkage in the ceramics [13]. Wollastonite addition has been reported to result in an ASP with relatively poor strength [8,14]. However, minimizing the WA and PD of ASP via the addition of wollastonite has not yet been examined in detail.
This study aimed to find out the optimization to minimize WA and PD in ASPs with various levels of added alumina and wollastonite. Specifically, WA and PD of ASP was minimized at the amount of \( \sim 30 \text{ mass}\% \) added alumina.

2. Experimental

2.1. Raw materials

The raw materials used in this study were the same as those used in a previous study by the current authors [4] with the exception of wollastonite. The raw materials included Amakusa clay (Fuchino Ceramic Raw Materials Co., Japan), Masuda feldspar (Nishi-Nihon Kogyo Co., Japan), Motoyama Gairome clay (KCM Co., Japan), alumina (A-34, Japan Light Metal Co., Japan; mean diameter = \( \sim 4 \) \( \mu \)m), and wollastonite powder (Saga Ceramic Materials Co., Japan). The chemical composition of the wollastonite powder is provided in Table 1.

2.2. Preparation of porcelain green bodies

Seven raw material compositions were used to produce ASPs with different amounts of wollastonite and alumina (Table 2). The seven groups of ASPs are denoted as WxWy, where \( x \) and \( y \) denote the wollastonite and alumina contents, respectively. Namely, these sample groups were W14.3A0, W12.1A15, W10A30, W7.9A45, WOA30, W20A30, and W30A30. The raw materials were mixed with water (28 mass%) and two dispersants, namely a deflocculant (0.2 mass%; Taihei Chemical Industrial Co., Japan) and a sulfonic acid-based dispersant (A-6012, 0.2 mass%; Toa Gosei Co., Japan), via ball milling for 1 h. The slurry was slip cast in a plaster mold to fabricate green bodies (120 \( \times \) 20 \( \times \) 7 mm\(^3\)). The calculated chemical composition of the green bodies in each sample group are listed in Table 3.

Both small WA and small PD is optimized in ASPs with 30 mass% alumina at the MFT of 1290–1300°C. Therefore, the role of wollastonite addition in the optimization of PD and WA was evaluated with a fixed amount of alumina (30 mass%) by comparing sample groups W0A30, W10A30, W20A30, and W30A30.

2.3. Pyroplastic deformation test

PD testing was conducted according to a procedure previously reported by the current authors [4]. The green bodies were dried at room temperature for 2 d. PD testing was conducted in a muffle furnace, where the specimens were suspended on a refractory support with a span of 100 mm and placed in the furnace. Firing was conducted in air at various maximum firing temperatures (MFTs) ranging from 1150 to 1400°C. The furnace was heated to MFT at a rate of 200°C/h, held at MFT for a dwell time of 1 h, and cooled naturally. The maximum deformation around the center of the fired specimens was measured to determine the PD index (PI).

2.4. Characterization

The crystalline structure of the fired ASPs was analyzed using X-ray diffraction (XRD; RINT 2000, Rigaku Co., Japan) at an X-ray wavelength of 0.15418 nm (Cu-Ka) and scanning speed of 2°/min in a scanning angle (28) range of 10° to 80°. Quantitative phase analysis was performed using the Rietveld method, in which XRD spectra were collected from 10° to 90° with a counting time of 5 s per 2 \( \theta = 0.02^\circ \) step. The microstructure of

| Table 2. Raw material composition of porcelain samples (mass %). |
|---------------------------------------------------------------|
| **Amakusa clay** /mass% | **Wollastonite** /mass% | **Motoyama gairome clay** /mass% | **Alumina** /mass% |
| W14.3A0 | 57.1 | 14.3 | 28.6 | 0 |
| W12.1A15 | 48.6 | 12.1 | 24.3 | 15.0 |
| W10A30 | 40.0 | 10.0 | 20.0 | 30.0 |
| W7.9A45 | 31.4 | 7.9 | 15.7 | 45.0 |
| WOA30 | 45.0 | 0 | 25.0 | 30.0 |
| W20A30 | 35.0 | 20.0 | 15.0 | 30.0 |
| W30A30 | 30.0 | 30.0 | 10.0 | 30.0 |

| Table 3. Chemical composition of porcelain samples before firing (mass%). |
|---------------------------------------------------------------|
| **Ig Loss** /mass% | **SiO\(_2\)** /mass% | **Al\(_2\)O\(_3\)** /mass% | **Fe\(_2\)O\(_3\)** /mass% | **TiO\(_2\)** /mass% | **CaO** /mass% | **MgO** /mass% | **Na\(_2\)O** /mass% | **K\(_2\)O** /mass% |
| W14.3A0 | 6.61 | 63.35 | 20.20 | 0.69 | 0.07 | 43.45 | 0.84 | 0.08 | 0.13 |
| W12.1A15 | 5.61 | 53.85 | 32.13 | 0.59 | 0.17 | 5.36 | 0.19 | 0.13 | 1.96 |
| W10A30 | 4.62 | 44.33 | 44.04 | 0.49 | 0.14 | 4.43 | 0.16 | 0.17 | 1.61 |
| W7.9A45 | 3.64 | 34.82 | 55.94 | 0.39 | 0.11 | 3.50 | 0.12 | 0.22 | 1.27 |
| W0A30 | 4.87 | 45.73 | 46.54 | 0.51 | 0.16 | 0.09 | 0.09 | 0.17 | 1.83 |
| W20A30 | 4.38 | 42.93 | 41.55 | 0.47 | 0.13 | 8.76 | 0.23 | 0.17 | 1.40 |
| W30A30 | 4.13 | 41.53 | 39.05 | 0.46 | 0.09 | 13.08 | 0.30 | 0.17 | 1.19 |
the fired ASPs was observed using field emission scanning electron microscopy (FE-SEM) with an energy-dispersive X-ray spectrometry (EDS) system (JSM-7900 F, JEOL Co, Japan). The specimens were polished and etched with a hydrofluoric acid solution prior to FE-SEM and EDS analysis. Bulk density (BD), open porosity and WA of the fired ASPs were evaluated based on Archimedes’ principle according to the standard procedure given in ASTM C373.

3. Results and discussion

3.1. Role of alumina to minimize the WA and PD of ASP with wollastonite

The BD of the ASPs with varying alumina contents were evaluated as a function of MFT (Figure 1). Porcelain with the alumina addition of 0, 15, and 30 mass% exhibited a slight increase in BD with increasing MFT up to ~1230°C, ~1255°C, and ~1300°C, respectively, at which BD is maximized while WA decreases by less than 0.5% (Figure 2). Beyond that temperature, the BD suddenly dropped with increasing MFT. The initial increase in BD was attributed to densification due to sintering of the liquid phase, while the sudden decrease was caused by the growth of bubbles in the liquid phase at elevated temperatures, so-called “bloating” [4]. The theoretical density of alumina is 3.98 g/cm³, which is larger than that of porcelain matrix of about 2.5–2.6 g/cm³, thus the BD of the ASPs increases with the increased alumina addition. W7.9A45 exhibited the highest BD in this group of ASPs, but the BD is not as high as that expected from 45 mass% alumina addition. Unlike the porcelain that contains less than 30 mass% alumina, there is no decrease in the BD of W7.9A45 at high MFTs because of bloating. These are attributed to the small amount of liquid phase in W7.9A45 at firing (see Amorphous in Table 4) where the mass percentages of each phase derived from the XRD pattern analyzed with the Rietveld method are listed) due to the relatively small amount of wollastonite addition (see wollastonite in (Table 2) and SiO₂ in Table 3, which contributes to the liquid-phase formation at elevated temperatures. Thus, W7.9A45 was not sufficiently densified due to the lack of a liquid phase at the firing. Consequently, the WA of W7.9A45 was reduced to approximately 5% with the increase of MFT, which was much higher than those of the other three porcelains (Figure 2). The XRD patterns of W14.3A0, W12.1A15 and W10A30 exhibited a halo pattern at 2θ values of 23° to 24° (Figure 3), which was assigned to a glass phase in porcelain (Table 4). This indicated that W14.3A0, W12.1A15 and W10A30 contained a much larger amount of liquid phase than W7.9A45. Thus, the WA of W14.3A0, W12.1A15, and W10A30 increased significantly at high MFTs (Figure 2) as a result of bloating.

PI values of ASPs with varying alumina content were evaluated as a function of MFT (Figure 4). A PI below 1.5 × 10⁻⁶ mm⁻¹ was achieved at an MFT of ~1240°C for W14.3A0, ~1290°C for W12.1A15, ~1330°C for W10A30, and ~1380°C for W7.9A45. The small PI values at relatively high MFTs except for those of W7.9A45 were attributed to the rigid microstructure constructed with entangled needlelike Mullite crystals in a liquid

![Figure 1. Bulk density (BD) of porcelain as a function of maximum firing temperature (MFT).](image1)

![Figure 2. Water absorption (WA) of porcelain as a function of maximum firing temperature (MFT).](image2)

![Figure 3. Rietveld analysis result of porcelain with different alumina addition (mass%).](image3)

| Table 4. Rietveld analysis result of porcelain with different alumina addition (mass%). |
|-----------------------------------------------|
| Quartz /mass % | a-Alumina /mass % | Mullite /mass % | Anorthite /mass % | Amorphous /mass % |
|-----------------|-------------------|----------------|------------------|-------------------|
| W12.1A15        | 7.7               | 13.7           | 10.4             | 17.1              |
| W10A30          | 8.4               | 28.7           | 12.6             | 16.9              |
| W7.9A45         | 5.0               | 44.5           | 10.8             | 27.1              |

![Figure 4. PI values of ASPs with varying alumina content as a function of MFT.](image4)
Figure 3. XRD profiles of porcelain samples fired at 1290°C.

Figure 4. Pyroplastic deformation index (PI) of porcelain as a function of maximum firing temperature (MFT).

optimization between small WA and small PI was achieved in W14.3A0 in the MFTs range from 1190 to 1240°C, in W12.1A15 in the MFT range from 1240 to 1290°C, and in W10A30 in the MFT range from 1290 to 1330°C. W10A30 is the most attractive one among the ASPs in terms of mechanical strength, because the strength of ASP increases with increasing alumina amount [1,15]. In the following section, WA and PI are further examined in ASP with an alumina addition of 30 mass% with varying the amount of wollastonite addition to expand the MFT range for the optimization.

3.2. Effect of wollastonite in alumina-strengthened porcelain

Optimization between small WA (<0.5%) and small PI (1.5 × 10⁻⁶ mm⁻¹) was achieved in a MFT range from 1290 to 1330°C for wollastonite-containing ASP with an added alumina content of 30 mass%. This optimization was attributed to the control of the amorphous phase. To further expand this MFT range, the effect of wollastonite addition on the densification and PD of ASPs with 30 mass% alumina was examined. Therefore, the BD and WA of W0A30, W10A30, W20A30, and W30A30 were evaluated as functions of MFT (Figures 6, 7). An increase in the amount of added wollastonite above 10 mass% led to a decrease in BD and an increase in WA, which was attributed to the suppression of liquid-phase sintering owing to the enhanced anorthite crystallization with the consumption of the liquid phase. According to the XRD peak intensity of anorthite and alumina, the peak intensity ratio of anorthite to alumina as a function of the amount of wollastonite addition was plotted in (Figure 8). The XRD peak intensity ratio \( I_{\text{anorthite}}/I_{\text{alumina}} \) should be an index to express the degree of anorthite crystallization, because \( I_{\text{anorthite}} \) increases with the promotion of anorthite crystallization while \( I_{\text{alumina}} \) decreases due to the consumption of alumina for the anorthite crystallization. The peak ratio increases with increasing wollastonite addition, indicating the anorthite crystallization is enhanced by the wollastonite addition. Further, the temperature at which the bloating occurred in the liquid phase was higher with a lower wollastonite content (Figures 6 and 7). Consequently, W0A30 was sufficiently densified at an MFT above 1290°C, where the corresponding WA was less than 0.5% (Figures 6 and 7). Pores in W0A30 fired at 1290°C were not able to be observed obviously as shown in (Figure 9), although there is no big difference in WA between W0A30 and W10A30 fired at 1290°C. In addition, the open porosity of W0A30 and W10A30 fired at 1290°C was measured to be 1.6 and 0.5%, respectively. This indicates W0A30 fired at 1290°C must contain pores as much as W10A30 fired at 1290°C does. Pores in W0A30 fired at 1290°C were hardly observed because the pores were too small to be observed clearly at the same magnification of SEM.
observation as other porcelains (Figure 9). W0A30 fired at >1290°C exhibited smaller PI than that of W10A30 fired at the same temperature (Figure 10). Consequently, small WA (<0.5%) and small PI (<1.5 × 10⁻⁶ mm⁻¹) can be achieved in W0A30 and W10A30 at MFTs ranging from 1290 to 1380°C and 1290 to 1330°C, respectively.

The BDs of W20A30 and W30A30 increased with the increase of MFT above 1330°C (Figure 6), because of the enhancement of liquid-phase sintering. However, there is a significant difference in the amount of liquid phase between W20A30 and W30A30 fired at above 1330°C (a halo at 2θ values of 23° to 24° in Figure 11(a, b)). The amount of liquid phase in W20A30 is so large that WA decreased, and PI increased drastically at MFT above 1330°C (Figures 7 and 10). On the other hand, the WA and PI of W30A30 kept high and low, respectively, regardless of MFT, because the amount of liquid phase was relatively small in W30A30 even fired above 1330°C. In the case of W30A30, anorthite crystallization...
was enhanced so that a relatively large amount of alumina was consumed, which was confirmed by both the peak intensity ratio (Figure 8) and the decrease in the intensity of the XRD peaks assigned to alumina (Figure 11). Crystallization also consumed CaO and SiO$_2$ at a same time, which led to the decrease in the number of chemical species required for the formation of the liquid phase in W30A30 at elevated temperatures.

4. Conclusion

The densification and PD of ASPs were examined within a range of alumina and wollastonite contents. Both the alumina addition and anorthite crystallization not only prevent the liquid-phase sintering, which plays an important role in the densification of the porcelain during firing, but also the suppression of PD at high MFTs. The prevention of densification as well as the suppression of PD is basically described by the change in the amount of liquid phase at firing. As
a result, the optimization between WA (<0.5%) and PI (<1.5 × 10^{-6} mm^{-1}) was found out in the relatively wide MFT range for porcelain with the addition of 30 mass% alumina and the addition of <10 mass% wollastonite. Consequently, WA and PD can be minimized in ASPs fired between 1290 and 1380°C.

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