Strengthening in porcelain reinforced with alumina particles

Takashi AKATSU\textsuperscript{1,2,†}, Miho TOMIYASU\textsuperscript{3}, Takahito SHINGAE\textsuperscript{1} and Nobuaki KAMOCHI\textsuperscript{4}

\textsuperscript{1}Ceramic Research Center of Saga University, 2441–1 Oono-otsu, Arita-cho, Nishimatsuura-gun, Saga 844–0013, Japan
\textsuperscript{2}Faculty of Art and Regional Design, Saga University, 1 Honjo-cho, Saga 840–8502, Japan
\textsuperscript{3}Faculty of Science and Engineering, Saga University, 1 Honjo-cho, Saga 840–8502, Japan
\textsuperscript{4}Saga Ceramics Research Laboratory, 3037–7 Kuromuta-hei, Arita-cho, Nishimatsuura-gun, Saga 844–0022, Japan

Alumina has long been known to enhance the strength of porcelain; however, the strengthening mechanism is not sufficiently understood. The strengthening in alumina-strengthened porcelain is examined on the basis of the change in thermal shrinkage of a porcelain matrix upon addition of various amounts of calcined talc. The improvement in flexural strength of the porcelain as a result of the alumina addition is enhanced with increasing difference in the thermal shrinkage between the alumina particle and the matrix. The rate of increase of the flexural strength as a function of the difference in thermal shrinkage is described by the extent to which the compressive prestress on the matrix increases the nominal tensile stress required for the fracture of the porcelain. However, the strengthening due to the internal stress is not sufficient to describe the actual strength of the porcelain. Further strengthening is achieved by the relatively large thermal shrinkage of alumina particles suppressing the formation and extension of microcracks around quartz grains in the glass phase of the porcelain.

Key-words : Porcelain, Alumina, Strength, Stress, Crack

1. Introduction

Porcelain is a typical traditional ceramic widely used in tableware, sanitary ware, insulators, and other ceramic items worldwide. Strengthening is an important issue in improving the reliability of porcelain products. In a 1946 study, Austin et al.\textsuperscript{1)} reported that the addition of alumina particles effectively increased the strength of porcelain. Since then, extensive research related to alumina-strengthened porcelain (ASP) has been conducted.\textsuperscript{2)–13)} Moreover, ASP has been manufactured industrially as commercial tableware used in schools, airplanes, and nursing homes, among other locations.

Despite the mass production of ASP, the mechanism of strengthening in ASP remains unclear, although several hypotheses have been proposed to explain the strengthening. Many researchers support the hypothesis that compressive prestress on the glass phase increases the nominal tensile stress at the fracture of the porcelain,\textsuperscript{14)–18)} because the validity of this hypothesis has been qualitatively confirmed in the strengthening of cristobalite-strengthened porcelain.\textsuperscript{19)} The prestress in cristobalite-strengthened porcelain is caused by large shrinkage of the cristobalite grains as the porcelain cools, where the $\beta$- to $\alpha$-cristobalite phase-transformation occurs. ASP consists of alumina particles and a porcelain matrix; in this case, compressive prestress on the matrix increases the nominal tensile stress at the fracture of the porcelain, which is attributed to the difference in thermal shrinkage behaviors between the alumina particles and matrix during cooling of fired porcelain. An alternative hypothesis is that strengthening occurs via the rigid microstructure formed by entangled needle-like mullite crystals\textsuperscript{20)–22)} in the glass phase of ASP. The refinement of the porcelain microstructure by the dispersion of fine alumina particles can also strengthen porcelains such as ceramic composites reinforced with fine ceramic particles.\textsuperscript{23)} From the viewpoint of composite material design, stress disturbance due to the addition of high elastic modulus alumina particles to the low-elastic-modulus porcelain matrix can also strengthen the porcelain by reducing tensile stress in the matrix at the fracture of ASP. The strength of ASP may increase because of one or several of the aforementioned mechanisms. However, it is unclear which mechanism is most responsible for strengthening. Quantitatively clarifying the contributions of the various mechanisms to the strengthening of porcelain is important because ASP should be designed on the basis of the proper strengthening mechanism to further increase its strength.

Porcelain made from Amakusa clay, so called “Imari”, is a typical ceramic product and one of the iconic Japanese traditional ceramics. It represents more than 400 years of the long manufactural history of the Saga and Nagasaki prefectures in Japan.\textsuperscript{24)} Porcelain remains an important product that sustains the regional industry and economy in

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the area.\textsuperscript{25} The aim of the present study is to investigate the strengthening mechanism of ASP made from Amakusa clay. We control the prestress in the porcelain through changes in the thermal shrinkage of the porcelain matrix by varying the amount of talc added from 0 to 0.7 mass \%. The effect of prestress on the strengthening of ASP is examined quantitatively. Moreover, the mechanism of the strengthening in ASP is discussed on the basis of micromechanics and fracture mechanics. The strengthening mechanism revealed in the present study is valid not only for porcelain made from Amakusa clay but also for other conventional porcelains because their oxide compositions and microstructures are similar.\textsuperscript{13,17,18}

2. Experimental procedure

2.1 Preparation of ASP

Commercial-grade raw material powders of Amakusa clay (Fuchino Ceramic Raw Materials Co., Japan), Masuda feldspar (Nishi-Nihon Kogyo Co., Japan), and calcined talc were used in the present study. Alumina powder (A-34, Japan Light Metal Co., Japan) with a mean particle diameter of approximately 4 \( \mu \)m was used to prepare ASP. The chemical compositions of the raw materials are listed in Table 1. In addition, the composition of raw materials in each porcelain is shown in Table 2. The porcelain is denoted as \( A_xT_y \), where \( x \) and \( y \) indicate the amount of alumina and 10 times the amount of talc in mass \%, respectively. For example, A15T5 refers to the porcelain containing 15 mass \% of alumina and 0.5 mass \% of talc. In the present study, the talc addition was limited to 0.7 mass \% to avoid cordierite crystallization. The chemical compositions of the porcelains according to the chemical compositions of the raw materials and the raw material composition of each porcelain are shown in Table 3. Although the ratio of raw materials was varied for each porcelain (Table 2), the amount of (Na\(_2\)O + K\(_2\)O) was constant for porcelain with a certain amount of alumina: 5 mass \% for A0T5, 4.3 mass \% for A15T5 and 3.6 mass \% for A30T5. Notably, the porcelains contained different amount of MgO because of the addition of different talc amounts, which implies that the formation of glass and its mechanical/thermal properties are strongly dependent on the MgO content reported in Table 3.

The specimens used in the present study were prepared as test bars by slip-casting in a plaster mold. The casting slurry was prepared by ball milling the raw material powder mixtures for 10 h at approximately 70 rpm to uniformly disperse the powders in water in the presence of two dispersants (Deflocculant, Taihei Chemical Industrial Co., Japan and A-6012, Toa Gosei Co., Japan), where the water content was set as 28–30 mass \%. As a result of the ball milling, more than 99 \% of the milled powder particles was smaller than 40 \( \mu \)m, as confirmed by particle diameter measurements using laser diffraction (Laser Micron Sizer LMS-2000e, Seishin Enterprize Co., Japan). Each green body was prepared with dimensions of approximately 50 \( \times \) 10 \( \times \) 5 mm\(^3\). The green bodies were fired at different temperatures (\textasciitilde 1230, \textasciitilde 1290, and \textasciitilde 1330 °C) in air at a ramp rate of 100 °C/h and with a dwell time of 1 h. The cooling rate from the maximum firing temperature was not controlled and depended on the natural cooling behavior of the furnace.

2.2 Flexural strength test

Three-point bending tests were carried out according to standard JCRS203 to\textsuperscript{26} at room temperature in air with a testing machine (AUTOGRAPH AG-X 10kN, Shimadzu Co., Japan) to evaluate the flexural strength of the porcelain samples. Specimens with approximate dimensions of 40 \( \times \) 8 \( \times \) 4 mm\(^3\) for the flexural test were not machined after the green bodies were fired. The span \( L \) of the bending was 30 mm, and the loading rate was 5 mm/min. To avoid the fracture induced by concentrated stresses at loading points, a rubber plate with a thickness of approximately 3 mm was inserted between the loading point and the specimen. The flexural strength \( \sigma \) of the specimen was calculated using the following equation:\textsuperscript{27}

\[
\sigma = \frac{3PL}{2bh^2}
\]  

\( L \) is the distance between the supports, \( P \) the applied load, \( b \) the specimen width, and \( h \) the specimen thickness.
where $P$ is the maximum load at fracture and $b$ and $h$ are the width and thickness of the specimen, respectively. Flexural strength measurements were performed on more than 20 specimens for each porcelain. Analysis on the basis of the Weibull statistics with shape parameter $m$ and scale parameter $\xi$ was carried out for the strength $\sigma$

$$\ln \ln \left(\frac{1}{1 - F}\right) = m \ln \sigma - m \ln \xi$$

where $F$ is the cumulative distribution function (failure probability) estimated using the Johnson’s rank method on the basis of a multimodal Weibull distribution, where the data of $\sigma$ were distinguished depending on the location (edge or surface) of the fracture origin. The value of $m$ was uniquely derived from the slope of the linear relationship between the left-hand term of Eq. (2), i.e., $\ln \ln (1 - F)$, and $\ln \sigma$. In the present study, only a few specimens were fractured from a defect at the edge. Thus, the $m$-value was determined only for the strength of the specimens fractured from a defect on the surface.

### 2.3 Characterization

X-ray diffraction (XRD) analysis was conducted using an X-ray diffractometer (RINT2100, Rigaku Corp., Japan) equipped with an X-ray radiation generator (Cu-Kα, $\lambda = 0.15418$ nm); samples were scanned over the angle range $5^\circ \leq 2\theta \leq 80^\circ$. As shown in Fig. 1, which shows the XRD profile of ASP fired at $\sim 1290^\circ$C: (a) 0.7 mass % talc addition (AxT7 series, $x = 0, 15, 30$) and (b) 30 mass % alumina addition (A30T0 series, $y = 1, 3, 5, 7$), all obvious XRD peaks without a diffraction halo around $2\theta = 23^\circ$ were assigned to $\alpha$-quartz, $\alpha$-alumina, or mullite; no peaks attributable to cordierite were observed in the XRD pattern of any of the porcelain samples.

The bulk, apparent, and true densities were evaluated on the basis of Archimedes’ principle. The average volume fraction of pores in the porcelain fired at $\sim 1290^\circ$C was 11 % for A0T0, 7 % for A15T0, and 5 % for A30T0; these results were confirmed through comparisons between the bulk and true densities. Relatively good densification was achieved with the addition of feldspar, because potassium ions in the feldspar promote the formation of a liquid phase during firing. Relatively large porosity observed for A0T0 is attributed to the modest bloating of bubbles in the viscous phase, even in the sample fired at $\sim 1290^\circ$C.

The thermal expansion and shrinkage of A0T0 as a porcelain matrix were measured using a dilatometer (Thermo Plus2, Rigaku Co., Japan) in air with heating and cooling rates of $10^\circ$/min. The thermal expansion and shrinkage

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<th>Table 3. Oxide composition of each porcelain</th>
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<td>Ig. Loss</td>
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</tr>
<tr>
<td>A0T0</td>
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<td>A0T1</td>
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<td>A0T3</td>
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![Fig. 1. XRD profiles of ASP fired at $\sim 1290^\circ$C: (a) 0.7 mass % talc addition (AxT7 series, $x = 0, 15, 30$) and (b) 30 mass % alumina addition (A30T0 series, $y = 1, 3, 5, 7$).](image-url)
of alumina particles were estimated from those of dense alumina polycrystals measured with the dilatometer under the same conditions as those previously mentioned.

The microstructure of the porcelain was observed by scanning electron microscopy (SEM, JSM-7900F, JEOL Corp., Japan).

3. Results and discussion

3.1 Effect of firing temperature on the densification and flexural strength of ASP

Figure 2 shows the bulk, apparent, and true densities and the three-point bending strength of ASP without talc addition (A0xT0 series, x = 0, 15, 30) as a function of firing temperature. The bulk and apparent densities of the porcelain, which increase with increasing alumina content, also increase as the firing temperature is increased to ~1250 °C for A0T0 and A15T0, and to ~1300 °C for A30T0. These results indicate that the addition of alumina prevents sintering of the porcelain. At higher firing temperatures, the densities decrease with increasing temperature because of the bloating of bubbles in the viscous phase of the porcelain.30 The difference between the bulk and apparent densities of the porcelain fired at 1230–1330 °C is very small, as shown in Fig. 2. This similarity suggests that the volume of open pores in the porcelain is very small. Experimentally, the water absorption of all of the porcelain prepared in the present study was measured to be less than 0.5 %. The true density of the porcelain, which increases with increasing alumina addition, is almost constant or slightly decreases with increasing firing temperature. The slight decrease in the true density is attributed to the higher firing temperature modestly promoting the formation of the glass phase (viscous phase at elevated temperatures). The flexural strength of the porcelain, which increases with the increasing alumina content, changes as a function of firing temperature corresponding to the change in bulk and apparent densities (Fig. 2). This observation clearly indicates that densification strongly affects the flexural strength of the porcelain. As previously mentioned above, the bloating of bubbles observed for the porcelain fired at temperatures greater than 1300 °C drastically reduces the density of the porcelain. Therefore, to sufficiently densify ASP and avoid an undesirable decrease in the strength of the ASP because of the bloating, a series of porcelains with different talc amounts, which were prepared for the flexural strength tests, were fired at ~1290 °C.

3.2 Change in the thermal shrinkage of the porcelain matrix due to talc addition

Figure 3 shows the linear thermal expansion and shrinkage of porcelain without alumina addition (A0T0 series) as a function of temperature. Broken lines in the diagram indicate the linear thermal expansion and shrinkage of alumina for reference. The thermal expansion and shrinkage of the porcelain increase with increasing talc addition from 0 to 0.1 mass % because Mg2+ ions disrupt the SiO4-tetrahedra network structure of the glass phase in the porcelain.31 On the contrary, an increase in talc addi-
tion from 0.1 to 0.7 mass% decreases the thermal expansion and shrinkage. This behavior is attributed to an increase in the amount of glass phase formed through the dissolution of quartz into the liquid phase at elevated temperatures by Mg\(^{2+}\)-ion doping through talc addition.\(^{31}\) As a result of the increase in the amount of glass phase, the true density of the porcelain decreases with increasing talc addition, as shown in Fig. 4. In addition, as shown in Fig. 5, the XRD peak intensity ratio between \(\alpha\)-quartz (100) and \(\alpha\)-alumina (113) slightly decreases with increasing talc addition, which clearly indicates the dissolution of quartz into the liquid phase at elevated temperatures promoted by Mg\(^{2+}\)-ion doping through talc addition; this behavior is attributed to alumina particles stably existing in the porcelain containing relatively small amounts of alkali and alkaline-earth ions (see Table 3) even at elevated temperatures.\(^{33,34}\) The densification of the porcelain with the glass phase is enhanced at elevated temperatures because of liquid phase sintering, which increases the gap between the expansion and shrinkage curves with increasing talc addition (see Fig. 3); thus, sintering shrinkage occurs even in the case of the firing of the porcelain already fired at a temperature greater than 1200 °C. The gradient of both the thermal expansion and shrinkage curves steeply increases at 550–600 °C (Fig. 3), which is attributable to a substantial increase of the Si–O–Si angle of \(\alpha\)-quartz\(^{32,33}\) and to the volume expansion due to the phase transformation from \(\alpha\)- to \(\beta\)-quartz\(^{32,33}\). The small thermal expansion of the porcelain at temperatures greater than 600 °C is attributable to the deformation of \(\beta\)-quartz, which absorbs the further increase of the Si–O–Si bond angle and the rotation of SiO\(_4\) tetrahedra.\(^{32,33}\) In addition, a step is typically observed in each shrinkage curve at \(\sim 700 \) °C. This step in the shrinkage curves appears to coincide with collective crack openings around quartz grains in the porcelain. The cracking around quartz grains at \(\sim 700 \) °C\(^{34}\) is described in detail in section 3.4.

### 3.3 Flexural strength of ASP with talc addition

Figure 6 shows the three-point bending strength of porcelain as a function of the amount of talc added. In the case of porcelain without alumina (A0T\(_y\) series), the flexural strength slightly increases with increasing talc content to 0.1 mass%, followed by a gradual decrease of the strength as the talc content is increased from 0.1 to 0.7 mass%. The slight increase in the strength of the porcelain is attributable to the densification enhancement by the Mg\(^{2+}\)-doped low-viscosity liquid in the porcelain fired at elevated temperatures. The gradual decrease in the strength of the porcelain is due to the increase in the amount of low-strength glass phase.

In the case of ASP (A15T\(_y\) and A30T\(_y\) series), the flexural strength decreases when the talc content is increased to 0.1 mass%, followed by an increase in the flexural strength as the talc content is increased from 0.1 to 0.3 mass%. The further addition of talc to 0.7 mass% slightly decreases the flexural strength of A15T\(_y\) but does not substantially affect that of A30T\(_y\). The dependence of the flexural strength of ASP on the amount of added talc is discussed in the following section on the basis of the quantitative consideration of the prestress and the change in crack size.

Figure 7 shows the Weibull plot of the flexural strength for each of the investigated porcelains. High reliability
with an \(m\)-value greater than 35 is observed, especially in the data showing relatively high strength (170–175 MPa on average for A30T5 and A30T7, which is \(\approx 1.9\) times greater than the strength of conventional porcelain).

3.4 Strengthening in ASP with talc addition

3.4.1 Effect of prestress on the strengthening in ASP

A difference is observed in thermal shrinkage between alumina particles and the porcelain matrix, as shown in Fig. 3, which likely leads to the compressive prestress on the matrix, as described in section 1. The prestress occurs as the porcelain is cooled from a certain temperature at which the prestress cannot be relaxed by the viscous deformation of a glass phase in the porcelain. However, identifying the temperature at which the prestress begins to occur is difficult even though identifying this temperature is important for quantifying the prestress. In the present study, the temperature is estimated to be 850 °C for the quantification of the prestress because slight inflections of the thermal expansion and shrinkage curves are observed at \(\approx 850°\)C (Fig. 3), which may correspond to the glass-transition point. The increase in the three-point bending strength of porcelain due to alumina addition, \(\Delta \sigma\), which can be derived as the difference in strength between A0T and A15T or A30T, is plotted as a function of the difference in thermal shrinkage from 850 to 35 °C between an alumina particle and the porcelain matrix, \(\Delta \varepsilon\), which is an index of the prestress, as shown in Fig. 8. The \(\Delta \sigma\) value increases with increasing \(\Delta \varepsilon\) for both A15T and A30T, although the \(\Delta \sigma\) values for A30T are larger than those for A15T. The increase in the rate of \(\Delta \sigma\) as a function of \(\Delta \varepsilon\) increases with increasing alumina addition. To describe the dependence of \(\Delta \sigma\) on \(\Delta \varepsilon\) quantitatively, we estimated the internal stress in ASP according to Eshelby’s inclusion problem with the Mori–Tanaka method, where the geometry of alumina particles is assumed to be spherical for simplicity, as

\[
\sigma_m = \frac{1}{1 - f_p} \left( I - f_p B \right) \sigma_0 + f_p B Q \Delta \varepsilon \tag{3}
\]

\[
\sigma_p = B \sigma_0 - \left( 1 - f_p \right) B Q \Delta \varepsilon \tag{4}
\]

with

\[
B = \left[ I + \left( 1 - f_p \right) Q (C_p^{-1} - C_m^{-1}) \right]^{-1} \tag{5}
\]

\[
Q = C_m (I - S_p) \tag{6}
\]

\[
S_p = -1 + 5 \mu_m \left( \frac{\delta_{ij} \delta_{kl}}{15(1 - V_m)} + \frac{4 - 5 \mu_m}{15(1 - V_m)} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \right) \tag{7}
\]

Fig. 7. Weibull plots for the three-point bending strength of porcelain fired at \(\approx 1290°\)C as a function of talc amount: (a) alumina 0 mass %, (b) alumina 15 mass %, (c) alumina 30 mass %. Circles are strengths for the fracture from a defect on the surface and triangles are those from a defect at the edge.

Fig. 8. Increase in the three-point bending strength of porcelain due to alumina addition, \(\Delta \sigma\), as a function of the difference in the thermal shrinkage from 850 to 35 °C between an alumina particle and the porcelain matrix, \(\Delta \varepsilon\). Black plotted points and the broken line indicate \(\Delta \sigma\) measured for porcelain with 15 mass % alumina. The red points and line indicate \(\Delta \sigma\) measured for porcelain with 30 mass % alumina. Black and red solid lines are \(\sigma_p\) estimated for porcelain with 15 and 30 mass %, respectively, according to Eshelby’s theory.
Table 4. Elastic properties of alumina particles and porcelain matrix used for the calculation of prestress

<table>
<thead>
<tr>
<th>Material</th>
<th>E/GPa</th>
<th>v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina particle</td>
<td>390</td>
<td>0.25</td>
</tr>
<tr>
<td>Porcelain matrix</td>
<td>120</td>
<td>0.22</td>
</tr>
</tbody>
</table>

where $\sigma_m$ and $\sigma_p$ are the average stress in the porcelain matrix and alumina particles, respectively, $\sigma_0$ is the nominally applied stress of the porcelain, $f_p$ is the volume fraction of the alumina particles, $I$ the unit tensor, $C_m$ and $C_p$ are the elastic stiffness tensor of the matrix and the particles, respectively, $S_p$ is the Eshelby tensor for a spherical inclusion calculated with the summation convention, and $\nu_m$ is the Poisson’s ratio of the matrix. Parameter $\delta_{ij}$ is Kronecker’s delta. The first terms on the right side of Eqs. (3) and (4) represent the internal stress disturbance due to the difference in elastic modulus between the matrix and the particles; the second terms express the prestress (stress disturbance due to $\Delta \varepsilon$, i.e., the difference in inelastic strain between the porcelain matrix and alumina particles). If the matrix and particles are assumed to have isotropic elastic properties, then the elastic stiffness constant $C$ is given as a function of Young’s modulus $E$ and Poisson’s ratio $\nu$ as:

$$C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \tag{8}$$

$$\lambda = \frac{E\nu}{(1 + \nu)(1 - 2\nu)} \tag{9}$$

$$\mu = \frac{E}{2(1 + \nu)} \tag{10}$$

The C-tensor is calculated with the summation convention. The difference between $\sigma_0$ and $\sigma_m$ certainly corresponds to prestress $\sigma_{PS}$ with the stress disturbance due to the elastic inhomogeneity on the matrix. Solid lines (black for A15Ty and red for A30Ty) in Fig. 8 are $\sigma_{PS}$ estimated on the basis of Eshelby’s theory\(^{35-37}\) when $E$ and $\nu$ listed in Table 4 are adopted for the calculation, where the average flexural strengths of each porcelain (A15Ty and A30Ty, see Fig. 6) are input as $\sigma_0$. The increase rate of $\Delta \sigma$ as a function of $\Delta \varepsilon$ and its change in response to change in the amount of alumina are well described by $\sigma_{PS}$ for both A15Ty and A30Ty (Fig. 8), indicating that the prestress definitely affects the strength of the porcelain to some extent. However, the difference between $\Delta \sigma$ (plotted points) and $\sigma_{PS}$ (solid lines) $\Delta \sigma$ values is large especially for A30Ty (Fig. 8).

3.4.2 Strengthening mechanism in ASP to compensate for the difference between $\Delta \sigma$ and $\sigma_{PS}$

As shown in Fig. 5, the XRD peak intensity ratio between mullite (110) and $\alpha$-alumina (113) in the patterns of both A15Ty and A30Ty, which corresponds to the amount of mullite crystals in the ASP, is approximately constant irrespective of talc addition although the strength of ASP varies as a function of the amount of talc added (Fig. 6). Moreover, the ratio for A15Ty is approximately two times greater than that for A30Ty, which means that mullite crystallization is not accelerated by the addition of alumina. These results indicate that mullite crystallization is only a minor factor influencing the strengthening of the ASP.

![Fig. 9. Texture of (a) A0T0, (b) A15T0, and (c) A30T0 fired at ~1290 °C and etched with thin hydrogen fluoride acid, as observed by SEM. Dark grains (“Q” in the figure, for example) are quartz crystals; the bright matrix is the glass phase, which includes alumina particles with a diameter of a few microns and very fine needle-like mullite crystals.](image)
observed. Therefore, the strengthening in ASP is not achieved through refinement of the microstructure, at least in the present study.

As mentioned in the previous section, the first term on the right side of Eq. (3) represents the internal stress disturbance due to the difference in elastic modulus between the porcelain matrix and the alumina particles. Thus, the addition of alumina with relatively high elastic modulus may strengthen the porcelain by reducing tensile stress in the matrix at the fracture of the porcelain. The disturbance is, however, only approximately 5 and 10 % of the average strength for A15T0 and A30T0, respectively, in this material system. Therefore, the magnitude of the stress disturbance is not sufficiently large to account for the difference between $\Delta \sigma$ and $\sigma_{PS}$.

Ohya et al.34 have reported that cracking of a glass phase around quartz grains in porcelain occurs at temperatures above the glass-transition temperature (just below the softening temperature of the glass) with acoustic emission during cooling of the porcelain after firing at 1200 °C. The cracking occurred because of a large thermal expansion mismatch due to the almost-zero thermal expansion of quartz at temperatures greater than the $\beta$- to $\alpha$-quartz phase-transition temperature (573 °C) and the lack of stress relaxation of the glass phase. Ohya et al.34 also reported observing numerous peripheral cracks around the large quartz grains at the phase-transition temperature during cooling of the porcelain because of the large contraction of the quartz grains as a result of the phase transformation.2,14,15,38 The step in the shrinkage curves, as shown in Fig. 3, corresponds to the collective opening of the former cracks simultaneously because the step appears at a temperature greater than the phase-transition temperature.

To examine the correlation between the cracking and the strength of porcelain, we estimated the crack size of the porcelain with the strength of porcelain $\sigma_f$ fractured from a surface half-penny crack with a radius of $r$ using the following equation:39

$$\sigma_f = \frac{0.943}{\sqrt{2\pi r}} K_{IC}$$  \hspace{1cm} (11)

where $K_{IC}$ is the critical stress intensity factor (i.e., the so-called fracture toughness). On the basis of the reported fracture toughness of a porcelain insulator (1.15 MPa$\sqrt{m}$),40 that of porcelain appears to be 1–2 MPa$\sqrt{m}$. If the fracture toughness of porcelain is assumed to be 1.5 MPa$\sqrt{m}$, for example, the estimated flexural strength of 92.8 MPa for the porcelain, which is the average strength of A0T0, indicates the presence of a surface half-penny crack with a radius of 37 $\mu$m, as estimated using Eq. (11). The crack depth is about 10 $\mu$m larger than the maximum diameter of quartz grains (~30 $\mu$m, see Fig. 9). In addition, two kinds of the aforementioned cracks are actually observed around quartz grains, as shown in Fig. 10. Consequently, the cracking around large quartz grains appears to control the strength of porcelain. Moreover, given the geometry of the cracks, the strength of porcelain strongly appears to depend on the former cracking with a length of about 10 $\mu$m at a temperature greater than the phase-transition temperature.

The linear thermal expansion and shrinkage behaviors of ASP shown in Fig. 11 indicate that the step of the shrinkage curve cannot be clearly observed for ASP [see Fig. 11(b)] or, even though the step is observed, the temperature at which the step appears tends to decrease with increasing alumina content [Fig. 11(a)]. As mentioned above, the step corresponds to the collective opening of microcracks in a glass phase around quartz grains as a result of the large thermal expansion mismatch due to the almost-zero thermal expansion of quartz above the phase-transition temperature and the lack of stress relaxation of the glass phase. The disappearance of the step
suggests that the addition of alumina particles, which have a relatively large thermal expansion coefficient, to porcelain suppresses the cracking by reducing the thermal expansion mismatch between the glass phase and other materials in ASP. As a result of the reduction of the thermal expansion mismatch, a large temperature difference would be required to generate sufficiently high tensile stress for cracking to occur during cooling of the ASP. Consequently, the temperature where the step appears tends to decrease with increasing alumina content, as shown in Fig. 11(a). The reduction of the thermal expansion mismatch also results in less accumulation of elastic strain energy, which inhibits crack extension in the glass phase.

When the prestress discussed in section 3.4.2 is considered for porcelain with a surface half-penny crack under the condition that the addition of alumina particles does not affect the fracture toughness $K_{ic}$, Eq. (11) is rewritten as

$$\sigma'_f = \frac{0.943}{\sqrt{2\pi r}} K_{ic} - \sigma_{PS}$$

(12)

where $\sigma'_f$ is modified flexural strength with prestress $\sigma_{PS}$. $\sigma_{PS}$ is positive for tension and negative for compression. The aforementioned crack suppression should be reflected in the first term of the right side of Eq. (12) as a decrease in $r$,

$$\sigma''_f = \frac{0.943}{\sqrt{2\pi(r - \Delta r)}} K_{ic} - \sigma_{PS}$$

(12')

where $\sigma''_f$ is modified flexural strength with $\Delta r$, and $\Delta r$ is the decrease of $r$. The first term of the right side of Eq. (12') simply expresses the contribution of crack suppression to the strengthening of ASP; the second term represents the contribution of prestress. If $\Delta r$ is assumed to be $\sim 3.0 \mu m$ for A15T5y and $\sim 10.5 \mu m$ for A30T7y, $\sigma''_f - \sigma_f$ derived from Eqs. (11) and (12') well coincides with $\Delta\sigma$ (plotted points and dashed lines in Fig. 8). The $\Delta\sigma$-value of about $10 \mu m$ for A30T7y suggests radial cracking around large quartz grains is almost completely suppressed by the 30 mass % alumina particles. The suppression of cracking as a result of the addition of alumina particles leads to high reliability, with an $m$-value greater than 35 typically observed, especially for the relatively high strength of ASP, which is 170–175 MPa on average for A30T5 and A30T7.

Consequently, the addition of particles that undergo large thermal expansion and shrinkage, such as alumina particles, is confirmed to effectively increase the strength of porcelain by increasing compressive prestress in the porcelain matrix and suppressing cracking around quartz grains in the glass phase.

4. Conclusions

We examined the strengthening in ASP through changes in the thermal shrinkage of the porcelain matrix by varying the content of calcined talc additive from 0 to 0.7 mass %. The increase in the flexural strength of ASP due to the alumina addition, $\Delta\sigma$, increased with increasing difference in thermal shrinkage between an alumina particle and the porcelain matrix, $\Delta e$. The rate of increase of $\Delta\sigma$ as a function of $\Delta\varepsilon$ is described by the prestress $\sigma_{PS}$ estimated according to Eshelby’s inclusion problem. Moreover, further strengthening is apparently achieved through relatively large thermal shrinkage of alumina particles suppressing the formation of microcracks around quartz grains in the glass phase of ASP. As a result of the crack suppression due to the addition of alumina particles, a high reliability of strength is typically observed for the relatively high strength of A30T5 and A30T7.

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