Prestress in alumina-strengthened porcelain as estimated with Raman scattering spectroscopy

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Prestress in alumina-strengthened porcelain, caused by the mismatch in thermal shrinkage between the porcelain matrix and alumina particles during porcelain cooling, is estimated using Raman spectroscopy by monitoring the frequency shift of Raman band at 417 cm⁻¹, which is assigned to the $A_{1g}$ vibrational mode of $\alpha$-alumina. This spectroscopic estimation supports the validity of prestress which is expected to accumulate during porcelain cooling beginning at ~850 °C.

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1. Introduction

Alumina-strengthened porcelains (ASPs) have been produced industrially as commercial tableware for use in schools, airplanes, and nursing homes, among other facilities, because of their high mechanical reliability in comparison with conventional porcelains. The strengthening mechanism of ASPs has not been sufficiently clarified despite extensive and vigorous research ever since Austin et al. launched their research program in 1946. Akatsu et al. recently revealed that the strengthening can be attributed to both suppression of microcracks around relatively large quartz grains and compressive prestress on the porcelain matrix, caused by a mismatch in thermal shrinkage between the matrix and alumina particles during ASP cooling. In the previous study, prestress was quantified with micromechanics calculation, in which the prestress was assumed to accumulate during ASP cooling beginning at ~850 °C. However, no obvious evidence demonstrates that the prestress occurs at ~850 °C during ASP cooling, although the calculated prestress does describe ASP strengthening quite well.

Raman spectroscopy is a useful technique to quantify the strain in a material by monitoring the frequency shift of a certain vibrational mode that is susceptible to change in strain. The Raman-active vibrational modes of $\alpha$-alumina with corundum structure, which belongs to $D_{3d}$ group, are categorized into two modes denoted by the irreducible representations; $A_{1g}$ modes typically at 418 and 645 cm⁻¹ and $E_g$ modes for 378, 432, 451, 578, and 751 cm⁻¹. Kimachi et al. showed that these vibrational modes undergo frequency shift as a function of strain in the material.

In this study, Raman spectroscopy is used to quantify the prestress in ASPs by probing the vibrational bands of alumina. We examined the validity of presence of prestress estimated by micromechanics calculation.

2. Experimental procedure

In the present study, ten types of ASPs fired at 1295 °C were selected based on the previous study. Each was named $AxTy$, where $x$ and $y$ refer to the mass % of alumina ($x = 15$, 30) and 10 times the mass % of talc ($y = 0, 1, 3, 5, 7$), respectively. The talc addition controls the mismatch in the thermal shrinkage between the porcelain matrix and alumina particles. The raw materials and chemical compositions of the ASPs and the ASP specimen manufacture procedure using slip casting are described in detail elsewhere, as are the ASP flexural strengths, densities, and porosities as functions of maximum firing temperature.

Similarly, ASP characterizations using X-ray diffraction and scanning electron microscopy are described in detail elsewhere.

In the Raman measurement, a near-infrared DPSS laser (Cobolt, Rumba 05-01) producing the 1064 nm beam was used as the light source. The 1064 nm excitation was chosen to reduce the luminescence from the APS specimens. The backscattered light was directed into a spectrometer (Teledyne Princeton Instruments, SpectraPro HRS-300) and dispersed onto an InGaAs array detector (Andor, iDus-1.7) to measure the Raman spectra. In Fig. 1(a), the Raman spectra of ASPs consist of the vibrational bands at 379 and 417 cm⁻¹ from $\alpha$-alumina and the band at ~460 cm⁻¹.
cm\(^{-1}\) from quartz in the ASPs\(^{26}\) on the broad luminescence background.\(^{27}\) The \(A_{1g}\) Raman mode of \(\alpha\)-alumina at 417 cm\(^{-1}\) (equivalent to 418 cm\(^{-1}\))\(^{19,20,24}\) was analyzed using curve fitting technique with the Gauss function as shown in Fig. 1(b). To obtain the calibration curve for the tensile stress of \(\alpha\)-alumina versus the frequency shift of the 417 cm\(^{-1}\) mode \((\Delta\omega_{417})\), the Raman measurement was performed for dense alumina polycrystals (AR-4N, ASUZAC Inc., Nagano, Japan) during four-point bending test, as shown in Fig. 1(c). The bending test employed the inner and outer spans of 10 and 30 mm, respectively. Each specimen for the bending test was prepared with dimensions of approximately \(3 \times 4 \times 40\) mm\(^3\). The uniaxial tensile stress \(\sigma_T\) of the bent specimen was derived from the tensile strain \(\varepsilon_T\) according to Hooke’s law \((\sigma_T = E \varepsilon_T)\) with a measured Young’s modulus \(E\) of 390 GPa, where the \(\varepsilon_T\) value was determined by the maximum compressive strain \(\varepsilon_C\) measured with a strain gauge (KFGS-02-120-C1-11 L1M2R, KYOWA Electronic Instruments Co., Ltd., Tokyo, Japan) considering mechanical symmetry \((\varepsilon_T = \varepsilon_C)\).

### 3. Results and discussion

Figure 2(a) shows \(\Delta\omega_{417}\) as a function of \(\varepsilon_T\). The \(A_{1g}\) mode at 417 cm\(^{-1}\) showed the frequency shift of ca. 0.2 cm\(^{-1}\) with increasing tensile strain of the bending alumina specimen. This magnitude of the frequency shift is consistent with that observed in the four-point bending test of polycrystalline alumina by Pezzotti and Zhu.\(^{28}\) When the tensile stress, \(\sigma_T\) (MPa), calculated from the \(\varepsilon_T\) value is plotted against the \(\Delta\omega_{417}\) in Fig. 2(b), the empirical calibration curve for \(\sigma_T\) vs. \(\Delta\omega_{417}\) can be obtained as,

\[
\sigma_T = -1.082 \times 10^3 \Delta\omega_{417}
\]  

Using Eq. (1), we firstly estimate the tensile stress \(\sigma_T\) of alumina particles in ASPs. However, \(\sigma_T\) is quite different from \(\sigma_B\) because \(\sigma_T\) is three-dimensionally isotropic,\(^{16}\) while \(\sigma_B\) is uniaxial. To find a correspondence between \(\sigma_T\) and \(\sigma_B\), the effect of the stress and strain on the \(A_{1g}\) vibrational mode of \(\alpha\)-alumina should be examined. The strain-induced frequency shifts of alumina phonons, including the \(A_{1g}\) mode, were formulated previously.\(^{20,28}\) The Raman tensor \(R\) for the \(A_{1g}\) mode of alumina with \(D_{3d}\) symmetry is expressed by

\[
R = \begin{bmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b
\end{bmatrix}
\]  

where \(a\) and \(b\) are constants. In the first approximation where the deformation of vibrational potential is linear in
strain, the frequency shift of this totally symmetric $A_{1g}$ mode occurs not due to shear but due to normal stresses and strains.\(^{24),25}\) Then, $\Delta \omega_{417}$ is expressed as

$$
\Delta \omega_{417} = c_0 (E_{xx} + E_{yy} + E_{zz}) + c_1 E_{zz}
$$

(3)

where $c_0$ and $c_1$ are constants, and $E_{xx}$, $E_{yy}$ and $E_{zz}$ are strains defined by the crystal coordinate system $(x, y, z)$ of $\sigma$-alumina. For the polycrystal, the tensile strains are averaged over all orientations. We thus obtain

$$
\Delta \omega_{417} = (2c_0 + c_1) \times \frac{E_{XX} + E_{YY} + E_{ZZ}}{3}
$$

(4)

where $(X, Y, Z)$ is laboratory coordinate system and $\sigma_T$ is the isotropic tensile stress. According to the relationship between the octahedral normal stress $\sigma_{oct}$ and the principal stresses $\sigma_i$ ($i = 1, 2, 3$) as $\sigma_{oct} = (\sigma_1 + \sigma_2 + \sigma_3)/3$, $\sigma_T$ is correlated with $\sigma_{T}$ if we choose $X$ axis in Eq. (4) as the direction of uniaxial stress $\sigma_{R}$ in the bending test,

$$
\sigma_{T} = \frac{\sigma_{XX}}{3} = \frac{\sigma_{R}}{3}
$$

(5)

Table 1 shows the $\Delta \omega_{417}$ value of ASPs whose prestress is controlled by adding a small amount of talc.\(^{14}\) The tensile stress $\sigma_T$ of alumina particles in each of the ASPs can be estimated according to Eqs. (1) and (5) using the $\Delta \omega_{417}$ value in Table 1.

We next use the $\sigma_T$ to calculate the misfit strain $\Delta \varepsilon$ between the porcelain matrix and alumina particles. According to micromechanics,\(^{16)-18}\) if the geometry of the alumina particles is assumed to be spherical, and the matrix and particles are assumed to have isotropic elastic properties, then the misfit strain $\Delta \varepsilon$ can be derived from the estimated $\sigma_T$ value as

$$
\Delta \varepsilon = - \frac{\sigma_T}{(1 - f_p)BQ}
$$

(6)

with

$$
B = [I + (1 - f_p)Q(C_p^{-1} - C_m^{-1})]^{-1}
$$

(7)

$$
Q = C_m(I - S_p)
$$

(8)

$$
S_p = -1 + 5v_m \delta_i \delta_{kl}
$$

$$
+ \frac{4 - 5v_m}{15(1 - v_m)} (\delta_i \delta_{jl} + \delta_j \delta_{ik})
$$

(9)

Table 1. Frequency shift $\Delta \omega_{417}$ [cm$^{-1}$] for ASPs of various compositions,\(^{14}\) where $x$ and $y$ refer to the mass % of alumina and ten times the mass % of talc, respectively.

| x   | y   | 0   | 1   | 3   | 5   | 7   |
|-----|-----|-----|-----|-----|-----|-----|
| 15  | -0.55 | -0.61 | -0.66 | -0.64 | -0.64 |
| 30  | -0.42 | -0.41 | -0.48 | -0.51 | -0.56 |

\[\text{Table 1}\]

Fig. 3. (a) Misfit strain $\Delta \varepsilon$ between the porcelain matrix and alumina particles as a function of the tensile stress $\sigma_T$ of alumina particles; (b) compressive stress $\sigma_C$ of porcelain matrix as a function of misfit strain $\Delta \varepsilon$.

\[\text{Fig. 3}\]

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

(10)

$$
\lambda = \frac{E}{(1 + v)(1 - 2v)}
$$

(11)

$$
\mu = \frac{E}{2(1 + v)}
$$

(12)

where $f$ is the volume fraction, $I$ is the unit tensor, $C$ is the elastic stiffness tensor, $S_p$ is the Eschelby tensor for a spherical inclusion calculated with the summation convention, $E$ is the Young’s modulus, and $v$ is the Poisson’s ratio.\(^{14}\) The subscripts m and p of the parameters indicate the porcelain matrix and alumina particles, respectively. Parameter $\delta$ is Kronecker’s delta. Figure 3(a) plotted $\Delta \varepsilon$ derived from Eq. (6) against $\sigma_T$, adopting $E$ and $v$ values of 120 GPa and 0.22 for the porcelain matrix and 390 GPa and 0.25 for the alumina particles, respectively. When the $\Delta \varepsilon$ is obtained from $\sigma_T$, the compressive stress $\sigma_C$ of the matrix is finally calculated using $\Delta \varepsilon$ [see Fig. 3(b)];

$$
\sigma_C = f_p BQ \Delta \varepsilon
$$

(13)

Thus, using Eqs. (1), (5), (6) and (13), we can estimate the $\Delta \varepsilon$ from $\Delta \omega_{417}$ and then calculate $\sigma_C$. On the other hand, using Eq. (13), $\sigma_C$ can also be evaluated by estimating $\Delta \varepsilon$ from the experimentally obtained thermal shrinkage mismatch between the porcelain matrix and alumina particles.\(^{14}\) Figure 4 compares these two $\sigma_C$ values in which prestress is assumed to accumulate during ASP cooling beginning at 1000, 950, and 850°C. Good agreement between these two estimates quantitatively supports
the validity of the assumption of prestress occurrence during ASP cooling beginning at \(\approx 850^\circ\text{C}\).

4. Conclusions

The compressive prestress \(\sigma_C\) of the ASP porcelain matrix, caused by \(\Delta \varepsilon\), was estimated using Raman spectroscopy by monitoring \(\Delta \omega_{\text{Raman}}\). The estimated \(\sigma_C\) coincides well with the simulated value, in which prestress was assumed to accumulate during ASP cooling beginning at \(\approx 850^\circ\text{C}\). This agreement quantitatively supports the validity of the prestress occurrence during ASP cooling.

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