Development of stress on quartz grain in illite ceramics during cooling stage of firing

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If the volume fraction of quartz in traditional ceramics is higher than 10% then the use of Selsing’s formula is questionable. A model of two concentric spheres, in which the inner sphere is a quartz grain and its spherical cladding is glassy phase, is proposed. The development of the stress on the grain surface during cooling stage of the firing and its influence on the microcracking is described. The tensile tangential stress which is developed between the glass transformation temperature and β → α transition of quartz can be a source of the first microcracking. After this transition, the tangential stress becomes compressive. The radial stress on the grain surface, which is compressive before the β → α transition of quartz, turns into tensile after this transition as a steep change of 40–80 MPa (for 10–50% of quartz content). These changes are in a narrow temperature interval around the β → α transition of quartz passing through zero value and no cracks are expected. This is confirmed with acoustic emission (AE) and short recovery of Young’s modulus. When the β → α transition of quartz is finished and the temperature decreases, the creation of the cracks continues. The radial tensile stress on the grain and in its close vicinity reaches 100–180 MPa, consequently, circumferential cracks can be formed. This is indirectly confirmed with a decrease of Young’s modulus and weak AE activity.

Key-words: Quartz in ceramics, Cooling stage of the firing, Radial stress, Crack formation

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different.14)–16) The stress distribution in α-quartz grains embedded into a glassy matrix in fired porcelain was identified by a confocal Raman microscopy, and the existence of the tensile forces in the particles was shown. Tensile stress inside the grain occurs as consequence of thermal expansion differences between the quartz grain and the glass matrix and can reach ~2.3 GPa, which can be sufficient to break the microstructure.17) But cracking inside the quartz grains is much rarer than the cracking in the matrix.13) A very similar relationship between Young’s modulus of ceramic clay and temperature in the cooling stage of the firing shown in Fig. 3 was also obtained by Nigay et al.18)

In order to evaluate the stresses acting upon the glassy matrix, a simple model, in which isotropic elastic sphere is surrounded by an infinite glassy elastic matrix, was also used in several researches.6),7),11),19),20) This model is described by Selsing’s formula for radial stress in the matrix19),21)

\[
\sigma_r = \frac{(\alpha_m - \alpha_g)\Delta T}{1 + \mu_m} \frac{1 - 2\mu_g}{2E_m} \left( \frac{R}{r} \right)^3, \quad r \geq R \tag{1}
\]

where \(\mu_m\) and \(\mu_g\) are Poisson’s ratios of the glassy matrix and quartz grain, \(E_m\) and \(E_g\) are the Young’s moduli, \(\alpha_m\) and \(\alpha_g\) are CLTE of the glassy matrix and quartz grain, \(R\) is radius of the grain and \(\Delta T\) is the temperature interval. According to Selsing’s model, the radial stress is constant inside the grain and decays proportionally to \(1/r^3\) outside the grain (\(r\) is the radial distance from the center of the grain, \(r \geq R\)). This model assumes that the stress fields around the grains do not overlap, which is valid when a volume fraction of the grains in the whole composite is less than 10%13) or 15%.11) Equation (1) shows that the magnitude of the stress on the grain surface, i.e. when \(r = R\), is independent of the grain size. But, as experiments show, the formation of cracks depends on the stress magnitude and grain size.22) A more realistic model, in which the spherical isotropic grains are periodically distributed in an isotropic infinite matrix, is described in.14),15) This model, based on fundamental equations of solid continuum mechanics, takes into account the grain volume fraction and grain radius. Thermal stresses originate during the cooling process due to the difference in thermal expansions of the grains and matrix.

As discussed above, if the volume fraction of the grains is higher than 10%, the use of Selsing’s formula is questionable. In this paper a model of two concentric spheres
is described. This model was used for composites in which spherical particle was embedded in matrix. According to the authors’ knowledge, this model was never applied for traditional ceramics in which the inner sphere is quartz grain and its spherical cladding is made from glassy material.

The objective of this paper is used the two spheres model for the cooling stage of firing of traditional ceramics in which quartz grains are embedded in glassy phase and also developed the stress on the quartz grain surface. It is known that elastic modulus, Poisson’s ratio and the CLTE of quartz pass through extrema around 573°C. The contribution of this paper is taking these extrema into account:

(1) in the mathematical model,
(2) in calculation the radial stress on the quartz grain,
(3) in determination the relationship between this stress and temperature.

2. Mathematical model

Material consisting of a spherical elastic grain surrounded by elastic cladding can be described as a model with two concentric spheres derived from. The inner sphere (elastic quartz grain) has a radius \( R_1 \), and its material parameters are \( E_g \) (Young’s modulus), \( \mu_g \) (Poisson’s ratio) and \( \alpha_g \) (CLTE). The cladding (elastic glassy matrix) has material constants \( E_m \), \( \mu_m \), and \( \alpha_m \), and its inner radius is \( R_1 \) and outer radius \( R_2 \). The quartz grain is an anisotropic body, but in spite of that, it is considered as isotropic in the model. Therefore, both materials are assumed homogeneous and isotropic and located in homogenous temperature field. It is also assumed that the material parameters are constant in a small temperature region \( \Delta t \).

Let the temperature changes from its initial value \( t_0 \) to \( t \). The radial and azimuthal (tangential) stress in the grain, where \( 0 \leq r \leq R_1 \) (\( r \) is the distance from the center of the grain), is

\[
\sigma_{rg}(r) = \frac{E_g}{1 - 2\mu_g} c_1 - \frac{2E_g}{1 + \mu_g} \int_0^r \int_0^{c_2} \alpha_g r^2 \, dr \, dt
\]

(2)

and the radial component of the displacement vector is

\[
u_{rg}(r) = r c_1 + \frac{1 + \mu_g}{1 - \mu_g} \int_0^r \int_0^{c_2} \alpha_g r^2 \, dr \, dt.
\]

(4)

The integrals in Eqs. (2)–(4) are

\[
\int_0^r \int_0^{c_2} \alpha_g r^2 \, dr \, dt = \alpha_g \Delta t \left( \frac{r^3}{3} \right)
\]

and

\[
\int_0^r \alpha_g \, dr = \alpha_g \Delta t.
\]

For the cladding, where \( R_1 \leq r \leq R_2 \), we have

\[
\sigma_{rm}(r) = \frac{E_m}{1 - 2\mu_m} c_3 - \frac{2E_m}{1 + \mu_m} \int_0^r \int_0^{c_4} \alpha_r r^2 \, dr \, dt
\]

(5)

\[
\sigma_{mr}(r) = \frac{E_m}{1 - 2\mu_m} c_3 + \frac{E_m}{1 + \mu_m} \int_0^r \int_0^{c_4} \alpha_r r^2 \, dr \, dt
\]

(6)

and

\[
u_{rm}(r) = r c_3 + \frac{1 + \mu_m}{1 - \mu_m} \int_0^r \int_0^{c_4} \alpha_r r^2 \, dr \, dt.
\]

(7)

The integrals in Eqs. (5)–(7) are

\[
\int_0^r \int_0^{c_4} \alpha_r r^2 \, dr \, dt = \int_0^r \alpha_r \, dr = \alpha_m \Delta t.
\]

and

\[
\int_0^r \alpha_m \, dr = \alpha_m \Delta t.
\]

The constants \( c_1, c_2, c_3, \) and \( c_4 \) can be calculated from the boundary conditions

\[
u_{rg}(0) = 0, \quad u_{rg}(R_1) = u_{rg}(R_1), \quad \sigma_{rg}(R_1) = \sigma_{rg}(R_1), \quad \sigma_{rm}(R_2) = 0.
\]

The first boundary condition is fulfilled if \( c_2 = 0 \). Then we obtain from Eqs. (2) and (3)

\[
\sigma_{rg}(r) = \frac{E_g}{1 - 2\mu_g} c_1 - \frac{2E_g \alpha_g \Delta t}{3(1 - \mu_g)}.
\]

(9)

The radial stress and tangential stress in the grain are constant and homogeneously distributed in the grain. From the second boundary condition it follows that

\[
\frac{E_m}{1 - 2\mu_m} c_3 = \frac{E_m}{1 - 2\mu_m} c_4 - \frac{2E_m \alpha_m \Delta t}{3(1 - \mu_m)}.
\]

(10)

From the third boundary condition we have

\[
\frac{E_m}{1 - 2\mu_m} c_3 = \frac{E_m}{1 - 2\mu_m} c_4 - \frac{2E_m \alpha_m \Delta t}{3(1 - \mu_m)}.
\]

(11)

and from the fourth boundary condition we obtain

\[
\frac{E_m}{1 - 2\mu_m} c_3 = \frac{E_m}{1 - 2\mu_m} c_4 - \frac{2E_m \alpha_m \Delta t}{3(1 - \mu_m)}.
\]

(12)

where \( v = R_1^3 / R_2^3 \) is a volume part of the grain in the combined sphere. If the radius of the cladding, \( R_2 \) is considered to be constant, the grain radius \( R_1 \) depends on the volume fraction of the grain \( v \) in the model as

\[
R_1 = R_2 \sqrt{v}.
\]

For convenience, we introduce abbreviated terms

\[
A_g = \frac{\alpha_g \Delta t}{3}, \quad B_g = \frac{E_g}{1 - 2\mu_g}, \quad D_g = \frac{2E_g}{1 - \mu_g}, \quad F_g = \frac{1 + \mu_g}{1 - \mu_g},
\]

\[
A_m = \frac{\alpha_m \Delta t}{3}, \quad B_m = \frac{E_m}{1 - 2\mu_m}, \quad D_m = \frac{2E_m}{1 - \mu_m}, \quad G_m = \frac{2E_m}{1 + \mu_m}.
\]
Solving the system of Eqs. (10)–(12), we obtain the constants $c_1$, $c_3$, and $c_4$

$$c_1 = \frac{D_m A_m (1 - v) (G_m + B_m) + v G_m A_g (D_g + F_g B_m) + A_g B_m (D_g - G_m F_g)}{B_g (B_m + v G_m) + B_m G_m (1 - v)},$$

(13)

$$c_3 = \frac{D_m A_m (1 - v) (G_m + B_g) + v G_m A_g (D_g + B_g F_g)}{B_g (B_m + v G_m) + B_m G_m (1 - v)},$$

(14)

$$c_4 = \frac{D_m A_m (1 - v) (B_m - B_g) + B_m A_g (F_g B_g - D_g)}{B_g (B_m + v G_m) + B_m G_m (1 - v)} R_1^3.$$  

(15)

After substituting the constant $c_1$ into Eq. (9), the radial and tangential stress in the grain can be determined. The radial and tangential stress in the cladding can be determined from Eqs. (5) and (6) after substituting the constants $c_3$ and $c_4$ into it.

3. Determination of the stress in the grain and cladding

Illite-based ceramics can contain a significant amount of the glassy phase after firing at temperatures higher than $1000^\circ C$. For example, ceramics fired from illitic clay supplied from the mine in Füzér (North-Eastern Hungary) contains 79% of the glassy phase, 11% of quartz, 6% of feldspar, and 4% of mullite after firing at $1100^\circ C$. Development of the mechanical stress on a quartz grain is can be summarized as follows (see Table 1).

The transformation temperature $T_g$ of the glassy phase in this material is $\sim 750^\circ C$. When the material is cooled from the top firing temperature, the glassy phase becomes almost solid at $T_g$. Below this temperature, the signals of the AE appear, and Young’s modulus begins to decrease slowly, and the thermodilatometric curve changes its slope slightly. The temperature $T_g$ is the natural starting temperature below which the stress is created in the grain and surrounding glassy phase. Since the elastic modulus, Poisson’s ratio, and CLTE of the quartz grain and glassy phase are temperature dependent (Figs. 4–6), the recurrent formula

$$S_{i+1} = S_i + f(E_{g,i+1}, E_{m,i+1}, \alpha_{g,i+1}, \alpha_{m,i+1}, \mu_{g,i+1}, \mu_{m,i+1})$$

(16)

was used for calculating the quantity $S$ which can be the “constant” $c_1$ or $c_3$ or $c_4$ as well as radial or tangential stress. The quantity $S_i$ belongs to the temperature $t_i$ and the quantities with the subscript $i + 1$ belongs to temperature $t_{i+1} = t_i + \Delta t$. The function $f$ is a right side of Eqs. (5) or (6) or (9) or (13) or (14) or (15) in which a small $\Delta t$ is used (e.g. $5^\circ C$).

The temperature dependence of Young’s modulus $E_m(t)$ of the potash glassy matrix was calculated according to Primenko and Galantyv.

$$E_m(t) = 58 - 0.0095 t$$

(17)

where $E_m = \text{GPa}$ and $t = ^\circ C$. The Poisson’s ratio $\mu_m = 0.2253$ and CLTE $\alpha_m = 1.2 \times 10^{-5} \text{K}^{-1}$ was considered constant between 750 and $20^\circ C$. Temperature dependencies of these quantities are pictured in Figs. 4–6 as gray lines.

3.1 Radial and tangential stress on the quartz grain

The radial and tangential stress in the cladding (glassy matrix) was determined from Eqs. (5) and (6) after substituting the constants $c_3$ and $c_4$ into them. After calculations of these stresses for $r = R_1$, the radial and tangential stress on the grain surface was obtained (Figs. 7 and 8).

While the viscosity of the glassy phase was low above its transformation temperature, the mechanical stress generated due to different CLTE of grain and glass was relaxed, and the radial stress did not affect the grain. When the viscosity reached sufficient high value (below the transformation temperature), the compressive radial stress (having a negative value in Fig. 7) affected the grain. This also simply follows from an inspection of Fig. 2 or Fig. 6 in which the glassy phase contracts and the quartz particles expands between 750 and $600^\circ C$, which leads to the compressive radial stress on the grain. Young’s modulus and Poisson’s ratio of quartz and glass are approximately constant between 750 and $600^\circ C$, thus they do not change the radial stress. In the same time, the tensile tangential

| Temperature | Event and state of material |
|-------------|-----------------------------|
| $900^\circ C$ | Low viscosity glassy phase is present. No stress on the quartz grain. No cracking. |
| $750^\circ C$ | Glass transformation temperature. The glassy phase becomes rigid. Compressive radial stress and tensile radial stress develops. The first cracking starts. Young’s modulus reaches its maximum value. |
| $750^\circ C \rightarrow 573^\circ C$ | Compressive radial and tensile tangential stress increases, both depending on the quartz amount, and reaches the maximum value at $\sim 600^\circ C$: 80 MPa for radial stress and 10% of quartz; 80 MPa for tangential stress and 50% of quartz. The cracking continues. Young’s modulus slightly decreases. |
| $573^\circ C$ | $\beta \rightarrow \alpha$ quartz transition. Steep jump of the stresses: 120 MPa for radial stress and 10% of quartz; 110 MPa for tangential stress and 50% of quartz. The radial stress alters from compressive to tensile and the tangential stress alters from tensile to compressive. No cracking appears. Short recovery of Young’s modulus takes place. |
| $570^\circ C \rightarrow 20^\circ C$ | Tensile radial and compressive tangential stress increases and reaches the maximum value at $\sim 130^\circ C$: 180 MPa for radial stress and 10% of quartz; 235 MPa for tangential stress and 50% of quartz. The cracking continues. Young’s modulus slightly decreases. |

Table 1. Development of the mechanical stress on a quartz grain
stress is developed (see Fig. 8). This stress can be responsible for the cracking below the transformation temperature.

When the temperature further decreases, a dramatic increase of the tensile radial stress (Fig. 7) and compressive tangential stress (Fig. 8) is created on the grain surface when the grain quickly contracts at the $\beta \rightarrow \alpha$ transition of quartz. The glassy phase also contracts but moderately (Figs. 2 and 6). A firm contact between the grain and surrounding glass was supposed due to a wetting the grain with melted glass at the temperatures above 900°C. At temperatures below 600°C, the glassy phase is brittle, which could result in formation of circumferential cracks nucleating at the quartz particles, because the tensile stress can be bigger than the strength between the grain and glass. Such circumferential cracks are very often observed around the quartz grains as it is visible in Fig. 1 and reported in literature, e.g.6),35) According to Reinoso et al.,17) tensile stress inside the grain and in its very close vicinity is very high. It can reach $\sim 2.3$ GPa, which can be sufficient to break the microstructure.

According to Fig. 7, the compressive radial stress changes into tensile stress in the narrow temperature interval around the $\beta \rightarrow \alpha$ quartz transition. This stress step reaches $\sim 110–170$ MPa depending on the part of the quartz grain in the composite sphere. The tensile stress on the quartz grain surface increases with decreasing the quartz-glass volume ratio. The thick cladding (in the case of small grain) represents a big obstacle for deformation of the grain, consequently, the thick cladding makes radial stress bigger. At the temperatures below 560°C, the stress remains tensile down to the room temperature.

The tangential stress also changes dramatically around the $\beta \rightarrow \alpha$ quartz transition (Fig. 8). It changes into compressive stress and reaches $\sim 110–240$ MPa depending on the part of the quartz grain in the composite sphere.

### 3.2 Case of the isolated grain

When $\nu < 0.15$, the grain can be considered as isolat-
ed, i.e. surrounded with an infinite matrix. For this $R_2 \to \infty$ and $v \to 0$. Substituting $v = 0$ and $R_2 \to \infty$ into Eqs. (13)–(15), the radial stress for isolated grain can be obtained. The radial stress in the infinite matrix is $\sigma_{\infty}(r \to \infty) = 0$ which is obtained when $r \to \infty$ is substituted into Eq. (5). The zero radial stress gives also Eq. (1) when $r \to \infty$. The comparison of the radial stress calculated from Eq. (1) with the radial stress calculated from Eq. (5) for $v = 0.01$ is depicted in Fig. 9, in which strong similarities are visible. The value $v = 0.01$ represents a tiny grain inside a large cladding, which is close to the case of a grain in the infinite matrix.

The comparison of Selsing’s model with the “composite sphere” model confirms the conclusion in, which states that Selsing’s model is suitable if the content of quartz in ceramics is less than 10–15%.

3.3 The “composite sphere” model and experimental observations

Pictures of SEM taken from traditional ceramics (e.g. Fig. 1) and in-situ measurements of Young’s modulus and AE during firing of ceramics are suitable experimental techniques for a direct or indirect observation of the cracks and their development. The first AE signals appear in the cooling stage of the firing when the liquid glassy phase becomes solid. According to Fig. 7, the radial stress on the grain surface reaches 40–80 MPa (for 10–50% of quartz content) during cooling and before $\beta \rightarrow \alpha$ transition of quartz. Since this stress is compressive and decreases proportionally $1/r^1$ (when $r > R_1$), the critical place is located close to the grain. This radial compressive strength is hardly cause of the first cracks registered through AE signals. The cracks can arise from a tensile tangential strength on the grain surface. This crack creation results in the interruption of the increase of Young’s modulus and its small decrease which begins after glass transformation (see Fig. 3).

When the $\beta \rightarrow \alpha$ transition of quartz is reached, the radial stress changes itself from compressive to tensile, passing through zero value (Fig. 7). Very little or no AE signals were observed (Fig. 10), consequently very little cracks were formed and Young’s modulus passed through a sharp minimum (Fig. 3).

The presence of AE signals and decrease in Young’s modulus showed that the cracks formation resumed below $500^\circ C$. The tensile radial stress on the grain and in its close vicinity reached 100–180 MPa (Fig. 7) which is higher than tensile strength of the alkaline glasses (30–70 MPa). Cracks in glassy phase could be expected, but the cracks were formed directly around the grains as SEM pictures commonly show. Consequently, the weak point was boundary between the grain and glassy phase. When the cracks are formed in this place, the stress is released and a reason for cracking the glassy phase vanishes.

There are two temperature intervals in which tensile stress acts on the boundary between the quartz grain and glassy matrix. It is the tangential tensile stress above the $\beta \rightarrow \alpha$ quartz transition and radial tensile stress under this transition. These stresses are the source of the nucleation of the microcracks.

When the circumferential crack is formed, the tensile radial stress should fall down to very small value on the grain, but Fig. 7 does not show it because the boundary condition $u_{\text{g}}(R_1) = u_{\text{m}}(R_1)$ in Eq. (8) states that the mechanical contact between the grain and glassy phase is never interrupted.

4. Conclusions

If the volume fraction of quartz in traditional ceramics is higher than 10%, the use of Selsing’s formula is questionable. In this paper a model of the composite sphere, in which the inner sphere is a quartz grain and its spherical cladding is glassy phase, was shown. The development of the stress on the grain surface during the cooling stage of the firing was described.

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