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Thermomechanical analysis of quartz porcelain in temperature cycles

Igor Štubňa *, Anton Trník, Libor Vozár

Department of Physics, Constantine the Philosopher University, A. Hlinku 1, 949 74 Nitra, Slovakia

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Abstract

Samples made from a mixture of 50% kaolin and clay, 25% quartz and 25% feldspar were tested by non-destructive sonic resonant method, which is sensitive to the structure defects. Sound velocity and Young's modulus of the green samples were measured during a cooling stage of the firing from temperature 1250 °C. Fired samples were also measured in temperature cycles 20–800–20 °C to reveal a role of the quartz grains in porcelain structure. A microcracking was begun in the cooling stage at the glass phase transformation point (∼760 °C) and continued to room temperature as a consequence of different thermal expansions of phases. A sharp drop of the mechanical strength (∼25%) measured during cooling between 600 and 500 °C confirms an important function of the β → α transformation of quartz. Unsolved quartz grains decrease their volume and generate tensile stress in their close surroundings, which causes the microcracks. Sound velocity and Young's modulus of the fired samples evidenced hysteresis on heating and cooling, attributed to microcracking during cooling and healing the microcracks during heating in the region of the α–β transformation of quartz. Given those conditions, there follows a rapid change of the sound velocity (∼21%) and Young's modulus (∼46%).

Keywords: Resonant method; α–β Transformation of quartz; Young's modulus; Sound velocity; Mechanical strength; Quartz porcelain

1. Introduction

Although alumina electroporcelain has some advantages, particularly higher mechanical strength, a quartz electroporcelain is still manufactured because of its lower price. Its electrical and mechanical properties are convenient for high-voltage and low-voltage insulators in electric power distribution networks. The major influence on mechanical properties of quartz porcelain comes from its microstructure where unsolved quartz grains play an important role. It is recognized that residual quartz grains have a negative influence on the strength of the porcelain. The primary problems associated with quartz in electroporcelain and the ways to decrease the negative effects of quartz were recently described by Liebermann [1–3].

It is apparent that the relatively large volume change accompanying β → α transformation of the unsolved quartz grains ($\Delta V/V = -0.68\%$ for free quartz grain) is the basic source of microcracking. The circumferential microcracks and microcracks in quartz grains observed by electron or light microscopy at room temperature are a result of releasing the mechanical stress caused by the difference in thermal expansion between the quartz grains and glass matrix. A significant source of the mechanical stress is β → α quartz transformation, which occurs at 573 °C in the cooling interval of the firing [2,4–9]. It was also noted that the large size of quartz particles results in a high density of microcracks [10]. On the other hand, the effect of addition of fine-grained quartz powder increases the bending strength of porcelain because sub-micron particles dissolve into a feldspatic liquid phase. An important way of strengthening porcelain is to reduce the content of coarse quartz particles [11]. Both mechanical strength and Young's modulus increase if the quartz content decreases [12]. However, there are other than the glass phase and unsolved quartz grains in the quartz porcelain body. Mullite and pores participate in the body. The microcracks are formed because of the stress generated as a consequence of phases thermal expansion mismatch during cooling [1–10,13]. A high firing temperature helps to solve quartz grains but it did not lead to higher mechanical strength because of the creation new pores in the porcelain body [14].

* Corresponding author.
E-mail address: istubna@ukf.sk (I. Štubňa).

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A different explanation of the influence of the quartz grains size as well as creation of the cracks around grains was proposed in Ref. [5]. That is, the glass phase has a saturation limit which when exceeded, results in no further dissolution of quartz. The amount of quartz that dissolves into the glass phase is not controlled by quartz particle size, but rather by the glass phase composition. Smaller quartz grains may dissolve more rapidly than larger grains, but for sufficiently long firing cycles the saturation limit of the glass phase is reached, regardless of dissolution rate.

Experiments have shown that cracking (due to the thermal expansion mismatch between quartz grains and surrounding glass phase) takes place circumferentially around quartz grains upon cooling of the sample (e.g. Ref. [2]). In Ref. [5] it is assumed that the stresses that act on the quartz grain are radially tensile and tangentially compressive. It is also assumed that the strength of the pristine glass is significantly greater than that of quartz. Therefore, the forces acting on the grains would result in a crack within the particle before any cracks in the glass would form. Circumferential cracking that is often recognized around quartz grains in micrographs is most likely an artifact of sample preparation or a misidentification of a crack residing within the grain itself.

The results described in Refs. [1–11,13] are based on investigations of the porcelain samples (a) at room temperature, (b) from scanning electron microscopy or from optical microscopy of the porcelain surface and (c) from measuring the mechanical strength of samples prepared with different contents of quartz with different grain size. The cracking is typically attributed to: (a) an abrupt contraction accompanied by the phase transformation of quartz at temperature of 573 °C and (b) to differences between thermal expansion coefficients of the phases in porcelain body. The origin of the cracking has not been often studied experimentally at relevant actual temperatures.

Important results can be obtained by in situ non-destructive measuring the mechanical parameter connected with concentration of cracks, e.g. sound velocity or Young's modulus, or by observation of the acoustic emission. This last method was employed in Ref. [15] to examine spontaneous cracking in porcelain samples during cooling. It was found out that acoustic emission signals were detected in the temperature range of 900–800 °C and never at temperatures less than 600 °C. At 573 °C, the measuring system did not detect acoustic emission signals, because of the small energy-emission rates. From the thermal expansion, it was determined that ∼850 °C was the glass transformation temperature. Thermodilatometry of mullite sample and glass sample of the same composition as glass phase in porcelain showed that both thermal expansions were approximately equal in the temperature range of 300–1000 °C. Consequently, the thermal stresses were introduced during cooling on the boundary between the quartz grains and the glass phase. The cracks often passed through the interface between the quartz grains and the glass phase that formed around the quartz. This indicated that the interface between the quartz and the glass phase was subjected to large thermal stresses or that the interface was weak.

Another, but different experiment was performed by the author and co-workers [8], where the sound velocity was measured in the cooling stage of firing via the help of the non-destructive sonic resonant method. Mechanical strength was also measured during cooling in Ref. [7], and its decrease ∼30% was found in the temperature region 650–450 °C. One conclusion is that the cause of microcracking is the relaxation of local stresses around the quartz grains during β → α quartz transformation based on the results in Refs. [7,8]. A possibility of the cracking other than this source was not taken into account. Samples used in Refs. [7,8] were made from the same mixture and by the same technology as those used in the work noted.

A resonant measurement of the sound velocity (or Young's modulus) as a non-destructive method is suitable for continuous testing of the sample in the large temperature interval, the base of the mf-TMA (modulated force thermomechanical analysis). The sound velocity is sensitive to defects in the structure (e.g. microcracks), thus it may be used for their identification.

A focus of this work is mf-TMA analyses of the quartz porcelain sample in the cooling stage of the firing, as well as the measuring of the fired sample around the α–β quartz transformation.

2. Samples and measurement method

Samples were made from a mixture of 50% kaolin and clay, 25% quartz and 25% feldspar. The mixture was ground and sieved on a 100 mesh/mm^2 sieve. A plastic material was made from this mixture. Then, cylindrical samples were made with the laboratory extruder. The green samples were heated in the mf-TMA apparatus in the air up to 1250 °C and measured during cooling. The temperature was increased and decreased linearly with the rate of 5 °C/min.

The final dimensions of one sample after firing, for example, were Ø 10.35 mm × 139.85 mm, and its weight was 27.40 g. The sample material density was determined from the sample weight and dimension. Its value was 2328 kg/m^3.

The fired samples were then used for mf-TMA in a temperature cycle 20 → 800 → 250 °C, performed with rate of 5 °C/min.

A measurement method used is described in Ref. [16]. Sound velocity was measured using the resonant flexural vibration of the sample with the apparatus described in Ref. [17]. Resonant frequencies were measured in temperature steps of 0.3 °C. Values of the sound velocity c_0 and Young's modulus E were calculated by formulae

$$c_0 = 1.12278\frac{l^2 f}{d}\sqrt{T}, \quad E = c_0^2\rho,$$

where f is the resonant frequency of the fundamental mode; l, d are the length and the diameter of the sample; ρ is the density of the material; $T = 1.02551$ is the correction coefficient for Poisson's ratio $\mu = 0.2$ and ratio $l/d = 14$, which is tabulated in Ref. [18] or calculated by the formula given in Ref. [16].

Values of the sound velocity can be measured by the sonic resonant method only when the solidity of the sample is

sufficient for maintaining the resonant vibration. But is not possible if a liquid glass phase with low viscosity is present in the sample. Therefore, the sample was put on the porous alumina table during heating from 20 to 1250 °C and cooling to 950 °C to prevent deformation of the sample by its weight. The sample was measured at temperatures below 950 °C.

3. Results and discussion

The results of the mf-TMA obtained during cooling are plotted in Fig. 1. Similar relationship was obtained with the more simple apparatus by the author and co-workers [8].

A resonant flexural vibration develops in the sample if viscosity of the glass phase is high enough for propagation of the mechanical flexural wave. That condition appears at the temperature of ∼1000 °C. This temperature is higher than the glass transformation point of ∼800 °C given in Ref. [13], or ∼760 °C determined in the samples prepared from the same raw mixture as the samples used in this experiment [19]. Values of the sound velocity increase with lowering the temperature as long as the viscosity of the glass phase is high enough to that eliminate the easy release of the stress in the structure. From this point a creation of the microcracks may begin as a consequence of the releasing the stress between phases with different thermal expansion coefficients. This process is expressed by descending values of the sound velocity below ∼760 °C. Then, there is a rapid decrease of the values with a sharp minimum at ∼573 °C, which may be explained by tensile stress, which affects the surroundings of the quartz grains and other microcracks can be created. But a small recovery of the sound velocity (and Young's modulus) is evident during continued cooling. The recovery is accompanied by small, temporary increasing of the mechanical strength after its relatively wide minimum. This situation is illustrated in Table 1, which shows results from Ref. [7]. The cause of the recovery of the sound velocity and mechanical strength after $\beta \rightarrow \alpha$ quartz transformation is unclear. The last feature of the relationship in Fig. 1 is the progressive decrease of the sound velocity up to a value $c_0 = 4700$ m/s (or Young's modulus $E = 48$ GPa) at the room temperature. The least value of the mechanical strength is evenly detected at the room temperature, see Table 1. Generally stated, if no changes of the structure take place, a ceramic sample has a tendency to increase its mechanical properties during temperature treatment. However, in Fig. 1 and Table 1 there is evidence of an opposite effect. So it may be assumed, that small microcracking continues until the room temperature is reached.

Table 1
Mechanical strength during cooling

Actual temperature (°C)	Mechanical strength (MPa)	Standard deviation (MPa)
690	90.8	2.05
620	83.5	3.25
585	64.9	3.51
543	61.3	2.13
500	62.5	3.86
460	58.8	3.02
406	60.0	1.57
360	64.0	1.24
293	63.4	1.16
256	63.0	2.22
208	63.7	1.49
20	54.0	2.25

The results of the mf-TMA gained by testing the fired quartz porcelain sample are illustrated in Fig. 2. In the temperature range of 20–573 °C, only decreasing values of the sound velocity are expected because neither chemical reactions nor phase transitions are evident in the sample. Regardless of this assumption, it can be observed that the sound velocity increases from ∼330 °C. As noted in an earlier section of this paper, microcracks unfavourably influence the mechanical strength and, consequently, Young's modulus, and sound velocity. The extinction of some part of the microcracks may be responsible for changing the values of the sound velocity to decrease at ∼330 °C. The reason for that extinction may be the stress

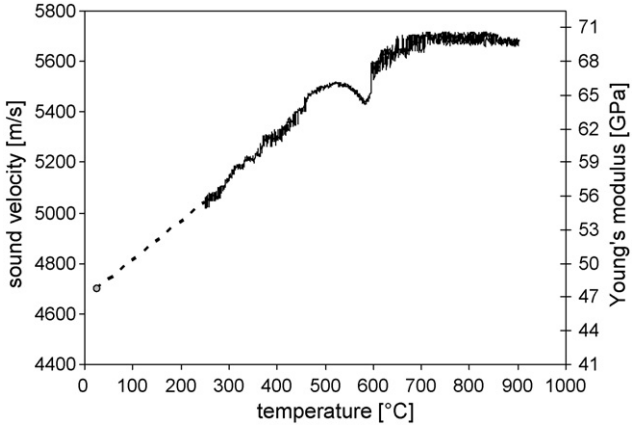

Fig. 1. Sound velocity and Young's modulus during cooling after reaching the highest firing temperature (1250 °C). Dashed line is estimated coarse, symbol (o) marks the final value at the room temperature.

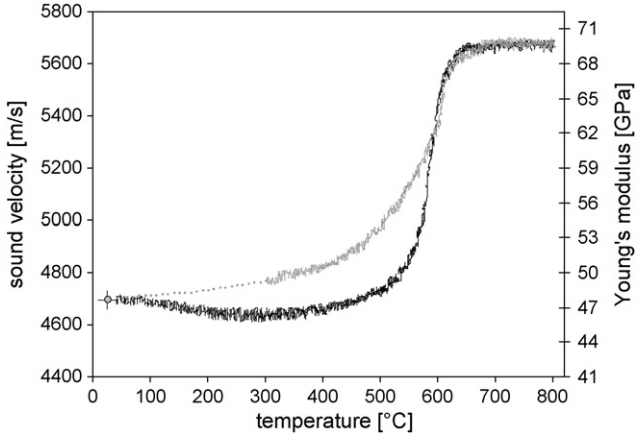

Fig. 2. Sound velocity and Young's modulus of the fired sample at heating–cooling cycle, where the black curve is for heating, the gray one is for cooling, and the dashed line is estimated course, marks (+) and (○) belong to values in the beginning and in the end of the cycle.

generated by differences between thermal expansion coefficients of the phases.

A steep increase in the sound velocity (∼21%) and Young's modulus (∼46%) can be noted in the range of 500–630 °C. The α → β transformation of quartz takes place at 573 °C, which is the temperature within this interval. If the quartz grains are free and can change their dimensions without obstructions, their relative volume change is +0.68%. But, the quartz grains are not free since they are encapsuled by the glass phase. The quartz grains increase their volume less than 0.68% and generate a compressive stress in their close surroundings.

Since many quartz grains have circumferential microcracks around them, the stress has a healing effect, which leads to the rapid increase of the sound velocity and Young's modulus. Their values reach nearly the maximum values, which occur during cooling stage of the firing (see Fig. 1). This fact can be explained by extinction of the most microcracks and that most microcracks are located in the close vicinity of the quartz grains. During cooling, these events occur in reverse order. The β → α transformation of quartz induces the gradual relapse of the original status of microcracks because of the tensile stress around the quartz grains. This assumption is assured by the equal values of the sound velocity (Young's modulus) measured at the room temperature at the beginning and end of the mf-TMA. The result of the cycle of heating and cooling is a hysteresis shape of the relationship between the sound velocity and the temperature. For example, thermal expansion also exhibits hysteresis on heating and cooling. These phenomena are attributed to healing the microcracks during heating and microcracking during cooling [20].

From the results in this research, it does not follow that circumferential cracking, which is often seen around quartz grains, is most likely an artifact of sample preparation as was noted in Ref. [5]. The sample for the mf-TMA is unimpaired, which is different from the sample for micrograph, where mechanical or chemical treatment (fracture or polishing or etching) alters the surface of the sample.

Acoustic emission used in Ref. [13] showed that no acoustic emission signal was detected at 573 °C, because of the small energy-emission rates. Therefore, only a very few or none of the cracks could create at β → α transformation of quartz. Thus, Fig. 2 and Table 1 demonstrate a major role of β → α and α → β transformation of quartz, which would not be possible without the presence of the microcracks in the vicinity of the quartz grains. The significant concentration of the microcracks only in these places could be created by two mechanisms:

(a) Stresses induced by the differences between thermal expansion of quartz grains and glass phase (and there are not stresses between glass phase and mullite because of the equality of their thermal expansion coefficients stated in Ref. [13]).
(b) During the β → α transformation of quartz in the cooling stage of the firing. This hypothesis is confirmed by the sharp minimum of the sound velocity (Fig. 1) as well as by the decrease of the mechanical strength (Table 1) at −573 °C connected with defects in the porcelain structure.

4. Conclusion

The results of the mf-TMA analysis based on the non-destructive sonic resonant method confirmed the sensitivity of the method to the presence of the microcracks in the porcelain structure as well as the pertinence of the method for surveys of the microcracking.

Two types of samples made from a mixture of 50% kaolin and clay, 25% quartz and 25% feldspar were tested: (a) green samples during cooling from the firing temperature of 1250 °C and (b) fired samples during temperature cycles 20–800–20 °C. Results obtained by the mf-TMA in the cooling stage of the firing revealed that microcracking begins at the temperature of the glass transformation and is completed at the room temperature. Almost all microcraks are located in the close vicinity of the quartz grains.

These results, when combined with results of the mechanical strength measured during cooling, showed that the β → α transformation of unsolved quartz grains play an important role in the microcracking.

The microcracking is a consequence of different thermal expansions of the phases. Unsolved quartz grains decrease their volume at 573 °C during cooling and generate tensile stress in their close surroundings. These conditions and relationships cause the microcracks around the grains.

Sound velocity and Young's modulus of the fired samples help identify the presence of those microcraks that change their values in a narrow temperature interval around α–β transformation of quartz. The result took place with sound velocity ∼21% and Young's modulus ∼46%. Both of these mechanical parameters exhibit hysteresis on heating and cooling. The hysteresis is attributed to microcracking during cooling and healing of the microcracks during heating, in the region of the α–β transformation of quartz.

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