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Structural and Thermomechanical Properties of Stove Tile Ceramics

Anton TRNÍK [1, 2*], Igor ŠTUBŇA [1], Gabriel VARGA [1], Martin KEPPERT [2], Peter BAČÍK [3]

[1] *Department of Physics, Constantine the Philosopher University, 94974 Nitra, Slovakia*
[2] *Department of Materials Engineering and Chemistry, Czech Technical University, 16629 Prague, Czech Republic*
[3] *Department of Mineralogy and Petrology, Comenius University, 84215 Bratislava, Slovakia*

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The thermomechanical and thermodilatometric behavior of fired heatproof stove tile ceramic material Letovice, which contains quartz, mullite and small amounts of feldspar and glassy phase, was studied while increasing temperature up to 1100 °C. Young's modulus was measured using the non-destructive sonic resonant method mf-TMA. To find actual dimensions of the sample, thermodilatometry was carried out at the same temperature regime as mf-TMA. A significant increase in Young's modulus was observed in the region of the $\alpha \rightarrow \beta$ transformation of quartz. This can be explained by the healing effect of the induced radial stresses around the quartz grains on microcracks. The presence of glassy phase caused a small decrease of Young's modulus at temperatures above ~950 °C.
Keywords: heatproof ceramics; Young's modulus; thermomechanical analysis (mf-TMA); thermodilatometry (TD).

1. INTRODUCTION

Traditional kaolin-based ceramics used in the ceramic tile industry are usually fired at 1000 °C – 1400 °C. The ceramic samples contain quartz and mullite as main crystalline phases and a certain amount of the glassy phase and pores [1]. Mechanical properties of these ceramics are significantly influenced by the size and concentration of the quartz grains. It is known that residual quartz grains have a negative influence on the strength of porcelain [2 – 5]. The reason is the presence of microcraks that are formed because of the stress generated by the thermal expansion mismatch during cooling [2 – 4].

It may be assumed that the microcracks, observed by SEM, around quartz grains are particularly important. Their origin is typically attributed to $\beta \rightarrow \alpha$ transformation of quartz during cooling. However, in [6] it was found using acoustic emission that microcraks are created in the temperature range of 900 °C – 800 °C, but not at 573 °C. Results obtained by the sonic resonant technique in the cooling stage of the firing [7] revealed that microcracking begins after the glass transformation (~800 °C) and is completed at the room temperature.

The presence of quartz in a fired product is frequently investigated by XRD, SEM and thermodilatometry. Measurement of Young´s modulus using the sonic resonant technique during thermal treatment of the tested sample, called modulated-force thermomechanical analysis (mf-TMA) demonstrates itself as a valuable tool for studying mechanical properties of ceramics. The mf-TMA method is non-destructive, sensitive, and requires relatively little material.

The focus of this research is the experimental study of the mechanical behavior of the ceramic material used for making stove ceramic tiles during its heating. In our previous work [8] we dealt with green ceramic material for stove tile manufacturing during its firing. Now, in the present work, we show results for X-ray diffraction analysis (XRD), thermodilatometry (TD) and modulated force thermomechanical analysis (mf-TMA) obtained on the fired stove tile ceramics.

2. EXPERIMENTAL

2.1. Samples

Green ceramic material for stove tiles in the form of a water slurry was delivered from the ceramic plant Keramika Letovice. The material was a mixture of four commercial clay materials (26.2 mass% of Unanov, 14.5 mass% of Znojmo, 7.7 mass% of Puritan-Vaton and 13.6 mass% of LVK) containing kaolinitic clays and quartz as well as small amount of mica, feldspar, Ca and Mg carbonates and minerals containing Fe and Ti. The minerals were mixed with a milled fired waste (8 mass%), kaolin (7.4 mass%), water and a plasticiser (sodium silicate Na_2SiO_3). The chemical composition of the raw mixture is identified in Table 1.

A set of 12 samples was prepared from the water slurry by casting into a gypsum mould. After open air free drying at room temperature for 6 days, the samples were fired in the air with heating rate of 5 °C·min^{-1} up to 1100 °C without soaking at the highest temperature and then freely cooled in the furnace. After firing and cooling the samples were tested during linear heating with rate 5 °C·min^{-1} up to 1100 °C. The dimensions of sample were (12 × 11 × 135) mm for mf-TMA and (12 × 11 × 50) mm for TD.

Table 1. Chemical composition of the green ceramic mixture [mass%]

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	L.O.I.
23.08	62.4	1.47	0.68	1.5	0.4	0.72	2.45	7.3

*Corresponding author. Tel.: +421-37-6408616; fax: +421-37-6408556.
E-mail address: *atrnik@ukf.sk* (A. Trník)

2.2. Measurement methods

Vibration methods are useful to investigate dynamical mechanical properties, e. g. Young's modulus, over a wide range of temperatures. A convenient vibration method is the resonant technique during which a test specimen vibrates in a fundamental flexural mode. The resonant frequency is measured and employed with specimen geometry and mass to calculate Young's modulus [9]. Young's modulus E may be calculated for a prismatic sample with a uniform square cross-section as follows [9]

$$E = \left(0.97286 \frac{l^2 f}{d} Q \right)^2 \rho \ , \qquad (1)$$

where f is the resonant frequency of the fundamental mode, ρ is the volume mass, l is the length and d is the thickness of the sample. The parameter Q is a correction coefficient, which should be used if $l/d < 20$ and is also a function of Poisson's ratio. Since the ratio for the used samples $l/d = 11.25 < 20$, the correction coefficient was calculated, using Poisson's ratio 0.2, and its value is $Q = 1.0401$. After substituting the value of Q in Eq. (1) and by acknowledging that the mass of the sample, m_0, does not change, the volume mass $\rho(t) = m_0 / [l(t) d^2(t)]$. The values $l(t)$ and $d(t)$ are the length and thickness of the sample at the temperature t. They were obtained from the TD results. We assume an equal relative linear thermal expansion of the sample in both directions, axial and transversal, thus $\varepsilon = \Delta l(t) / l_0 = \Delta d(t) / d_0$, where the values l_0, d_0 are the initial length and thickness at the room temperature respectively. If $f(t)$ is the measured resonant frequency at temperature t, then Young's modulus

$$E(t) = 1.02388 \frac{m_0 l_0^3 f^2(t)}{d_0^4 (1+\varepsilon)} \ . \qquad (2)$$

The mf-TMA was applied with the apparatus designed by the authors [10] based on the construction described in [11, 12].

The XRD analysis was performed by the diffractometer Bruker D8 Advance with Cu anticathode ($\lambda\alpha_1 = 1.54060$ Å), accelerating voltage 40 kV and beam current 40 mA. Data were obtained by the Bruker LynxEye detector.

The flexural strength of the set of 12 samples (with dimensions $(12 \times 11 \times 100)$ mm) was measured with the three-point-method. The length of the support span was 80 mm and the loading force was raised 2 $N \cdot s^{-1}$ [13].

A picture of the fracture area was obtained with a scanning electron microscope Tescan Vega 3 SBH at a voltage of 20 kV.

The total porosity was calculated by the help of experimentally determined bulk density and matrix density. The bulk density was obtained by means of size and weight measurement of prismatic samples. The matrix density was measured by helium pycnometry (Pycnomatic ATC, Porotec). The pore size distribution was measured by mercury intrusion porosimetry (Pascal 140+440, Thermo). This method detects only pores smaller than 100 μm in diameter, hence the porosity measured by mercury porosimetry is lower than the total porosity.

The thermodilatometric analysis was performed on the sample with the length of 40 mm with a heating rate 5 °C/min using a dilatometer described in [14].

3. RESULTS AND DISCUSSION

The results of the XRD analysis of the sample fired at 1100 °C showed quartz, mullite and feldspar as main crystalline phases (see Fig. 1). The volume of other phases was insufficient to detect them by the X-ray diffraction.

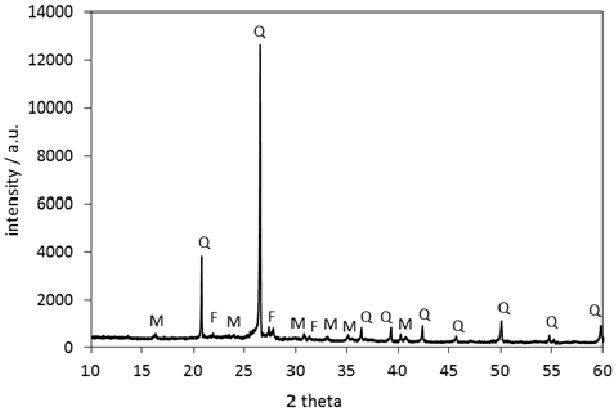

Fig. 1. XRD pattern of the tile ceramics fired at 1100 °C. Q – quartz, M – mullite, F – feldspar

The dilatometric curve (see Fig. 2) is nearly linear in the most important temperature region, i. e., from the exploitation point of view, between 20 °C – 500 °C. The average coefficient of the linear thermal expansion is 5.1×10^{-6} K^{-1} in this temperature interval. Similar results were obtained for porous clay ceramics [15]. Thermal expansion of the quartz grains caused the typical step at 573 °C on the dilatometric curve.

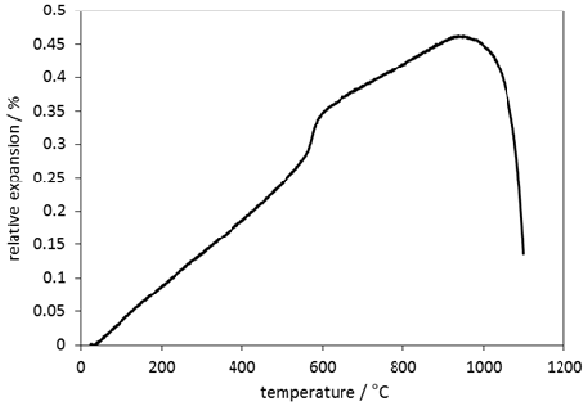

Fig. 2. Relative linear thermal expansion of the fired sample

Above ~950 °C, a contraction of the sample was noted and recorded. The contraction was caused by the pressure of the push-rod dilatometer's rod on the sample because the sample contained some part of glassy phase which decreases its viscosity at higher temperatures. Thus this contraction is not a real property of the measured material [15].

The results of the mf-TMA method are illustrated in Fig. 3. From thermodilatometric results, the actual values $\varepsilon(t) = \Delta l(t) / l_0$ were determined. Substituting these values

as well as m_0, l_0, d_0 and the resonant frequency $f(t)$ into Eq. (2), the Young's modulus was calculated.

In the temperature range of 20 °C – 573 °C neither chemical reactions nor phase transitions were evident in the sample. So in this case, a monotonic decrease of Young's modulus should be expected. However, the opposite relationship between Young's modulus and temperature was observed. This result may be caused by improving the contacts between phases of the ceramic material as a result of their different linear thermal expansion coefficients (for mullite $\alpha_{20-450\,°C} = 5.4 \times 10^{-6}\ K^{-1}$ [17], for quartz $\alpha_{20-450\,°C} = 13 \times 10^{-6}\ K^{-1}$ [18], for glassy phase created in kaolin based ceramics $\alpha_{20-450\,°C} \approx 6 \times 10^{-6}\ K^{-1}$ [6]).

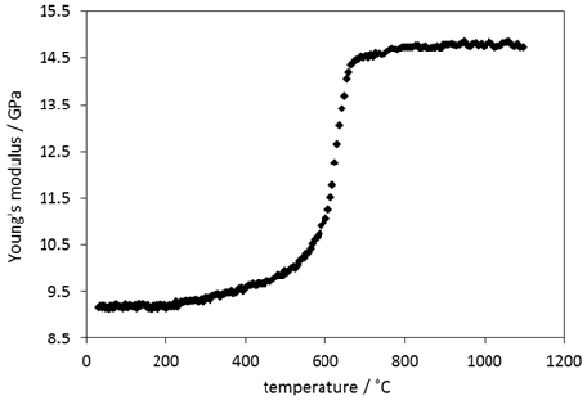

Fig. 3. Young's modulus of the fired sample

A steep relative increase in Young's modulus $100[E(650\,°C) - E(500\,°C)]/E(500\,°C) \approx 45\,\%$ was observed in the range of 500 °C – 650 °C. The $\alpha \rightarrow \beta$ transformation of quartz takes place at 573 °C, which is the temperature within this interval. If the quartz grains are free and can change dimensions without obstructions, their relative volume change is +0.68 % [18]. The quartz grains are not free in the ceramic structure but are surrounded with the products of the firing. Therefore, the quartz grains generate compressive stresses in their close surroundings as they expand. That leads to a healing effect, that is, some of the microcracks located in the close vicinity of the quartz grains vanish [7]. Since quartz grains have circumferential microcracks around them, the consequence is the rapid increase of Young's modulus. Similar results were obtained on a quartz porcelain sample [7, 19].

An existence of the glassy phase leads to the softening of the material at temperatures above ~950 °C and to a contracting of the sample caused by the press in the dilatometer (see Fig. 2). Generally, the glassy phase has a dampening effect, which decreases the amplitude of the sample resonant vibration as well as the resonant frequency. But this is not reflected in the course of Young's modulus, and its values are approximately constant at temperatures above ~800 °C.

Young's modulus has a low value at the room temperature, i. e. 9.3 GPa, see Fig. 3. It is indirectly confirmed by the low values of the flexural mechanical strength at room temperature, the main value is 9.4 MPa. Low Weibull's modulus, $m = 10$, which is depicted in Fig. 4, can be caused by a relatively large variety of pores and cracks in the samples. The open porosity (measured with the mercury porosimeter) is 33.70 %, and the size distribution of the pore diameters is shown in Fig. 5. Small pores with diameter less than 1 μm predominate. The total porosity is 61.40 %.

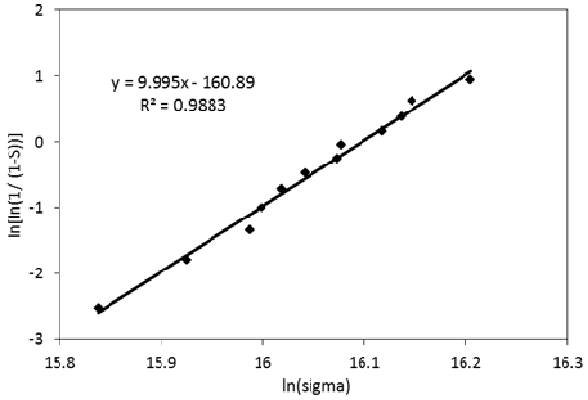

Fig. 4. Results of the Weibull's statistics for mechanical strength (in MPa)

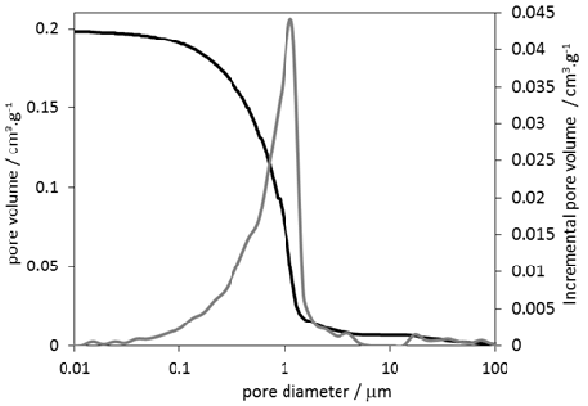

Fig. 5. The pore volume distribution (black curve) and the incremental pore volume distribution (grey curve) of the samples

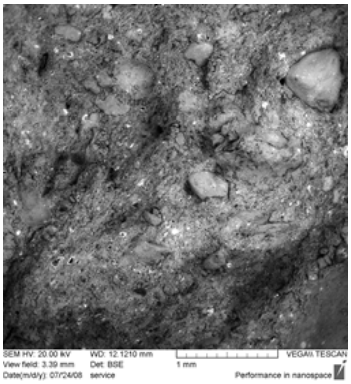

Fig. 6. Fired ceramics. The quartz grains with circumferential microcraks can be seen

Some causes of the low mechanical parameters can be:

- Weak mullitization and low content of mullite in the structure. This is confirmed by the XRD analysis where the mullite reflexions are weak.
- The maximum temperature of 1100 °C is not sufficient for completing the glassy phase creation, which confirms residual feldspar in the sample. The consequence is the very weak liquid phase sintering and enduring of the defect structure, see Fig. 6.

- High concentration of the cracks and high porosity. This is also evident in Fig. 4 and Fig. 6.

4. CONCLUSIONS

The mechanical behavior of the fired heatproof stove tile ceramic material Letovice was studied by the non-destructive sonic resonant method mf-TMA. To determine the actual dimensions and volume mass of the sample, TD was carried out in the same temperature regime (20 °C – 1100 °C, 5 °C.min^{-1}) as the mf-TMA.
The following information was obtained:

- Different thermal expansions of the phases can partially remove microcracks between crystals and, subsequently, slightly improve mechanical properties of the sample during heating from 20 °C to 550 °C.
- The $\alpha \rightarrow \beta$ transformation of the unsolved quartz grains induces a radial stress with a healing effect on microcracks. That leads to a rapid increase of Young's modulus.
- The sample contains a certain amount of the glassy phase, which causes a very low descent of Young's modulus at temperatures above ~950 °C.
- Processes taking place on the boundaries between phases play more important roles in the mechanical behavior of the samples than processes inside the phases. It is a consequence of the different thermal expansions of glass, mullite and quartz.
- Young's modulus and flexural strength have low values, 9.3 GPa and 9.4 MPa respectively, which is caused by the high porosity.

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