INFLUENCE OF THE BURNING PARAMETERS ON THE STRUCTURAL PARAMETERS OF CERAMIC BODY

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Abstract. The dependence of the main and derived structural parameters on the maximal burning temperature and its exposure period is analyzed in the article. Following the defined plan, the samples produced from the selected formation masses were burned at various burning temperatures for a certain exposure at the maximal temperature. The structural properties of the ceramic bodies, produced after the burning, are very different. The main dependencies of the properties of the ceramic bodies on the main technological burning parameters were analyzed. The influence of the burning temperature and exposure at the maximal temperature on the characteristics of the ceramic body is estimated during the tests. It is described in the research what formation masses must be selected in order to create the ceramic bodies with the frost resistance sufficient for the environmental conditions of average and high aggressiveness.

Keywords: clay, burning temperature, structural parameters, reserve of pore volume, low porosity constructional ceramic.

Introduction

Frost resistance is the main characteristic of low porosity constructional ceramic products. Frost resistance of the products can be predicted by considering the structural parameters of the ceramic body (Mačiulaitis and Žurauskienė 2007). One of the parameters is a water absorption which in general characterizes the effective porosity of the ceramic body (Žurauskienė et al. 2009). Other parameters characterize the water filling level of the volume of product’s pores and capillaries and remaining reserve of pore volume.

During the technological production cycle it is possible to manufacture the products that are more frost resistant by properly selecting the burning mode, i.e. rate of the temperature rise, maximal burning temperature and its exposure period. The selection of the maximal temperature depends on the content of the mineralogical raw material, melting temperature and sintering range, quality of the preparation of raw material, type of the furnace, where the products are burned. It is important that high quality semi manufactures, that have minimal quantity of cracks after the drying, are provided for the burning (Mačiulaitis et al. 2007). It is necessary to note that, in order to produce the ceramic body with high quality content and structure, the exposure period at the maximal burning temperature is important as well (Žurauskienė and Nagrockienė 2007).

When the burning temperature is increased up to a certain level, the compressive strength of the ceramic body increases and effective porosity decreases. According to the dilatometric and differential curves of the formation masses formed from the low-melting alkaline clays it is possible to determine that the average radius of the pores and capillaries increases when the temperature is increased up to 900 ºC, but the average radius of the pores and capillaries decreases if temperature is increased further (Mačiulaitis and Žurauskienė 2007). Liquid, or, sometimes, gas, phases, created at certain heating temperatures, are important factors determining the ratio and structure of the chemical transformations. Newly created chemical combinations, with more dense arrangement of the atoms in a crystal than in the initial materials, cause the shrinking of the reacting mixture. At the same time the variation of the parameters of the crystal lattice due to the polymorphic transformations causes the expansion or shrinking of the material. When temperature and contact surface of the crystals increase, the bonds of the powder mixture strengthen and the porous sintered ceramic body is created (Mumenthaler et al. 1995). Due to the increase of the contact surface of the body, its density is increased and porosity decreases. During the normal course of the sintering processes, no over-high amount of liquid phase or especially melt should be created in the body (Žurauskienė and Nagrockienė 2007).
During the analysis of the creation of the ceramic body in high temperature, the sintering of the masses and increase of the density in the ceramic body is considered (Mačiulis and Mačiulaitis 2004). Usually, the change of the specific density of the material is related to the change of mass and volume rate, and density is a function of these values. Volume change during the burning is mathematically described through the variation values of the porosity, density and mass (Sadūnas 1999). Sintering is noticed externally by the change of the dimensions and properties of the sintered body (Mačiulaitis and Mašiškienė 2009). When sintering degree of the products is increased, their density, strength, hardness, volume stability in high temperatures, chemical resistance, heat conductivity increases, gas and water penetrability decreases etc. In the research works of majority authors (Kpyna et al. 1995, Kizinievič et al. 2004) the possibility to add high-melting kaolinite clays to low-melting hydromicaceous clay for the extension of the sintering interval and improvement of physical and mechanical properties is analyzed. Such additive, according to the authors (Sedmale et al. 2001), improves the compressive strength even up to 46–58 MPa. However, it shall be ascertained whether such high positive effect is caused by this high-melting clay additive.

Research analyses how structural properties of the ceramic body change when the mixtures of the ceramic raw materials are burned at the selected highest burning temperatures with various exposure periods at this temperature.

Research materials and methodology

Chemical composition of the raw material was determined by the classical methods of chemical analysis for silicate materials (Mandeikytė and Šiaucūnas 1995). Physical properties of burned ceramic samples were defined according LST EN 771-1 and LST EN 772-16. During the tests carried out in accordance with LST EN 771-1 the requirements, provided for HD (high density) group of products, were followed. Water absorption after 72 h ($W_{72}$, %), water saturation of samples in the vacuum process ($W_{vac}$, %), specific density ($\rho_s$, g/cm$^3$) was determined by the special methodology (Mačiulaitis 1996). According to the results of water absorption (after 72 h, after vacuuming) these parameters were calculated: effective porosity ($W_e$, %), total open porosity ($W_{oc}$, %), reserve of pore volume ($R$, %) and water absorption by capillaries under normal conditions (g/cm$^2$) after 30 minutes, 60 minutes and after 120 minutes (Mačiulaitis et al. 2008).

Investigation the frost resistance of samples by volumetric freezing – heating, the samples was put in the freezing chamber, where the forced ventilation took place the temperature was automatically regulated according LST 1272-92.

The fusible hydromicaceous clays were selected for investigation (clay a and clay b). After the X-ray phase analysis of the Devonian clay a, it was estimated that the main minerals of the clay are as follows: hydromica (0.99, 0.498, 0.447, 0.256, 0.20, 0.15 nm), kaolin (0.714, 0.356, 0.20, 0.15 nm), and the following minerals dominate: quartz (0.425, 0.335, 0.245, 0.228, 0.224, 0.213, 0.199, 0.182, 0.167, 0.166, 0.154, 0.145 nm), feldspar (0.324, 0.30, 0.18 nm), dolomite (0.37, 0.288, 0.238, 0.22, 0.20, 0.179 nm). The X-ray analysis of the clay b has shown that the following is identified: hydromica (0.99, 0.498, 0.448, 0.256, 0.199 nm), kaolin (0.71, 0.355, 0.99 nm), chlorite (1.41, 0.71, 0.355 nm), and the following minerals dominate: quartz (0.425, 0.335, 0.245, 0.228, 0.224, 0.213, 0.182 nm), feldspar (0.324 nm), dolomite (0.288, 0.24, 0.219, 0.179 nm), calcite (0.305, 0.249, 0.209, 0.191, 0.188 nm).

High-melting clay (clay c) was used in the analysis. According to the X-ray phase analysis, the main minerals of clay c are as follows: hydromica (1.0, 0.499, 0.448, 0.256, 0.20 and 0.15 nm), kaolin (0.717, 0.359, 0.239, 0.235, 0.20, 0.199, 0.149 nm), Other dominating minerals are quartz (0.425, 0.335, 0.245, 0.228, 0.224, 0.213, 0.182, 0.167, 0.166, 0.154 nm), feldspar (0.321 nm), dolomite (0.289 nm). Iron is found in a form of goethite minerals (0.419, 0.270 nm).

In order to determine the physical properties and the structural parameters, samples were made in a plastic formation way from the formation mixes presented in Table 1. Granulometric composition of formation mixtures presented in Table 2. Chemical compositions of the mixtures presented in Table 3.

<table>
<thead>
<tr>
<th>Marking</th>
<th>Composition of forming mixtures, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>80 % a clay, 20 % b clay</td>
</tr>
<tr>
<td>II</td>
<td>70 % a clay, 30 % c clay</td>
</tr>
</tbody>
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<thead>
<tr>
<th>Mixture marking</th>
<th>Sand particles &gt; 0.05 mm, %</th>
<th>Dust particles (0.05-0.005) mm, %</th>
<th>Clay particles &lt; 0.005 mm, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>19.06</td>
<td>27.53</td>
<td>53.41</td>
</tr>
<tr>
<td>II</td>
<td>17.20</td>
<td>30.38</td>
<td>52.42</td>
</tr>
</tbody>
</table>

At first, formation mass was mixed dried, manually, and then moistened up to the moisture suitable for the formation. The sufficient amount of water is added for the formation mass to form well. Then this mass is stored for three days at (95±5 %) relative humidity environment to have the humidity evenly distributed in the formation mass. After three days of storage the laboratory semi manufactures were burned at the size of 70×70×70 mm were formed. Firstly, the formed semi manufactures were dried at natural conditions, in the laboratory, then they were dried in an electrical stove for three days and the temperature was increased gradually by reaching (105±5) °C temperature at the last day.
Table 3. Chemical compositions of the forming mixtures

<table>
<thead>
<tr>
<th>Mixture marking</th>
<th>Chemical composition, %</th>
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<tbody>
<tr>
<td></td>
<td>SiO₂</td>
</tr>
<tr>
<td>I</td>
<td>63.03</td>
</tr>
<tr>
<td>II</td>
<td>63.24</td>
</tr>
</tbody>
</table>

* L.o.l. in 1000 °C.

During the research the dependence of physical, mechanical and structural properties on the maximal burning temperature of the samples and exposure period at the maximal burning temperature was analyzed. Maximal burning temperature of the samples and exposure period at the maximal burning temperature was chosen on the basis of earlier studies and planned according to the received data (Mačiulaitis and Žurauskienė 2007). The marking of the samples, depending on their maximal burning temperature and exposure period at the maximal temperature, is shown in Fig 1. The burning period of the samples varied from 32 to 43 hours. The exposure period of the samples at the maximal burning temperature varied from 0 to 10 hours. The burning was carried out by increasing the temperature at the rate of 2 °C per minute, up to 570 °C temperature, and at the rate of 3–4 °C per minute up to the maximal burning temperature. The examples of the burning curves of the samples are shown in Figs 2 and 3 by considering the limiting points A, E, J and R. Every sample’s characteristic provided in the article is an arithmetic mean value estimated after testing of six samples.

Research results and discussion

Frost resistance of the ceramic products during exploitation especially depends on the water filling level of the volume of their pores and capillaries or on the remaining reserve of pore volume (Mačiulaitis 1996). On the parameters, that characterizes the water filling level of the pore and capillaries the best, is the absorption of the ceramic body. The absorption of the ceramic body is estimated in several ways during the ceramic research works: by following the way described in a standard (LST EN 771-1 2005) when samples are soaked at natural conditions for 24 hours, or by increasing the soaking period to 72 hours (Mačiulaitis 1996). During the analysis the absorption of the ceramic body was estimated when the samples were soaked in water at natural conditions and the absorption was tracked after 72 hours.

The dependence of the reserve of pore volume of the samples produced form the formation mass I on water absorption after the soaking in water for 72 hours is shown in Fig 4. Additionally, this figure shows the capillary rate of mass flow at normal conditions towards the freezing after 2 hours of testing. Value of the capillary rate of mass flow at normal conditions towards the freezing is conditionally indicated as the size of the sphere. Two areas α and β are separated in the diagram (Figure 4). Water absorption of the samples belonging to the area α is higher than 6 %, and their reserve of pore volume is lower than 40 %. Water absorption of area β is lower than 6 %, and reserve of pore volume is higher than 40 %. Samples of area α should crack foremost during the freezing, i.e. they must be frost resistant at least during the exploitation conditions. This would be the general prediction of frost resistance during exploitation of these samples.
The data of Fig 4 was used to deduce the direct reliance of reserve of pore volume on the absorption of the samples with the following equation:

\[ R = -0.218 \cdot W_{72} + 14.81 \]  

(1)

with the coefficient of correlation \(-0.979\), where \( R \) is reserve of pore volume, \%; \( W_{72} \) is water absorption after 72 h. In Fig 5 the important area \( \beta \), which corresponds to the requirements of low porosity ceramics, is shown separately. It can be noticed from the figure that by considering three parameters analysed (water absorption after 72 h \( W_{72} \), reserve of pore volume \( R \) and capillary rate of mass flow \( g \)) samples I K, I L and I P satisfy the requirements of the low porosity of ceramic body the most.

The dependence of the reserve of pore volume of the samples created from the formation mass II on water absorption after 72 hours of soaking in water is shown in Fig 6. Additionally, this figure shows the capillary rate of mass flow of the samples at normal conditions towards the freezing after 2 hours of testing. In the diagram (Fig 7) three areas \( \alpha \), \( \beta \) and \( \gamma \) are specified. In this figure, on the contrary than it is in Fig 4, third area is distinguished as well. The samples of this area have water absorption lower than 6 %, but reserve of pore volume in this area is lower than 40 %. Value of the capillary rate of mass flow at normal conditions towards the freezing is conditionally indicated as the size of the sphere.

The specific density of the samples was estimated during the research. Values of the specific density are shown in Fig 8. It can be noticed that the values of specific density of the ceramic bodies, formed from the different formation masses and burned, vary according to the same trend. Since only low-melting clays were used in one formation mass, and the mixture of low-melting and high-melting clays in the other formation mass, it can be noticed that up to 1050 °C of burning temperature the ceramic bodies, that, in comparison, are not of high density, are created. In case of higher burning temperature, the ceramic bodies with higher density are created. Longer exposure period at high limiting burning temperature influences the density of the ceramic body as well, and during this period not so dense and stiff compounds are created.

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Considering the references (Мачюлайтис 1997), the highest frost resistance during exploitation according to the estimated structural parameters should belong to the samples II P. The mean thickness of the walls of the con-
ditional pores and capillaries of these samples is equal to 4.85, and the mean value of reserve of pore volume is 49.05 %, effective porosity – 11.34 %, capillary rate of mass flow towards the freezing after 30 minutes and after one hour is the same and equal to 0.03 g/cm², and 0.04 g/cm² after 120 minutes. The samples created from the formation mass I should noted. According to the frost resistance during exploitation they should be the best. The mean thickness of the walls of the conditional pores and capillaries of these samples is equal to 3.4, and the mean value of reserve of pore volume is 0.17 g/cm², after one hour – 0.14 g/cm², and after 120 minutes is 0.11 g/cm².

**Conclusions**

It was found that the burning temperature of the ceramic body and exposure period at the maximal temperature has large influence on the properties of the produced ceramic body. In order to create low porosity ceramic, the burning must be carried out by gradually increasing temperature 2 °C per minute, up to 570 °C and 3–4 °C per minute up to the maximal burning temperature. The exposure period at the maximal temperature must be not shorter than 4 h for the formation masses created from the mixture of local low-melting clays or from the mixture of local low-melting and high-melting clays.

The additive of high-melting clay increases the obtained reserve of pore volume of the ceramic body, decreases the capillary rate of mass flow and the ceramic body with the properties of low porosity ceramics is created at the maximal burning temperature of 1050 °C.

During the research, the direct regression and correlation was used during the analysis of the data, direct relation of reserve of pore volume on absorption of samples was derived. The correlation coefficients of these regression equations are –0.979 and –0.853. Additionally, results of the analysis show that rate of mass flow at normal conditions after 120 minutes is important property characterising the structure of the ceramic body.

The most frost resistant samples of volumetric freezing – heating method, which were produced from the analysed ceramic formation masses, were burned at 1070–1090 °C maximal burning temperature regardless the exposure period at this burning temperature.

**References**


Mačiulaitis, R.; Malaiškienė, J.; Kčaitė, A. 2007. Influence of Drying on the Final Properties of Ceramics, in *The 9th In-


