Influence of process parameters of firing clay materials on phase composition and structure of ceramics

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Abstract. The article describes the influence of the technological impact the firing process has on ceramics structure. The process of forming a ceramic crock is described, which is represented by crystalline phase and glass phase. The dependences of the end product properties on the phases constituting its structure are described. Using X-ray phase analysis and electron microscopy, the authors studied ceramics produced from three types of clay materials with different content of clay minerals (kaolinite and montmorillonite). The change in the phase composition of the ceramic crock depending on the firing temperature is described. A conclusion was made on the fact that the structure is mainly glass phase with crystalline impurity inclusions. A necessity has been revealed for producing ordered structure for mullite.

1. Introduction
Building ceramics and its manufacture is one of the priority trends in the development of the Russian construction complex [1,2].

The main properties of ceramic products (strength, fire resistance, and frost resistance) are explained by the peculiarities of the composition and structure of this material. Forming of the composition and structure happens at the stages of geological and technological history. The biggest influence on the structure is made by the conditions of green firing [3].

A ceramic crock consists of two main structural components: crystalline phase and glass phase (melt) [4].

The crystalline phase is represented by crystalline impurity minerals, quartz mostly, and by aluminosilicate compounds. Most often these are $\text{Al}_4\text{O}_3[\text{AlSi}_2\text{O}_5]_2$ or $\text{Al}_6[\text{Al}([\text{Si}_2\text{Al}]\text{O})_{13}]$ mullites. As a rule, mullite has acircular habitus. The protruded form of mullite crystals forms a microreinforced structure. This structure better resists tension stresses. It is good for the strength indices in case of stretching and bending. For structural ceramics the bending strength is very important. The enhanced bending strength logically improves the frost resistance of the end products. Meanwhile, the density of the end products does not increase due to not-highly-packed crystals of mullite. This predetermines efficient thermal performance of the ceramic crock [5-7]. The amorphous phase forms because of baking of ceramics during firing and includes glass-forming oxides. Also, X-ray amorphous components may include certain types of clay impurities and metakaolin, which is generated during heating of kaolinite. The glass phase composition, which forms after baking, depends on the type and composition of clay. The volume of the glass phase in the ceramic crock may reach 60%. Thanks to
the glass phase, the compression strength forms. Namely thanks to the presence of the glass phase, minor elastic deformations are observed in the ceramics which are followed by brittle fracture. Excessive baking leads to big firing shrinkage and density increase. This is undesirable when manufacturing efficient walling ceramics [8,9].

In general, it is widely agreed that the process of forming of the structural phases in ceramics (without consideration to the processes in the impurity components) may be described as follows. At the temperature of clay mineral decomposition (925 °C for kaolinite), silicon-aluminum spinel is formed (exothermic reaction), which turns into mullite at the temperature of 1100 °C. Meanwhile, silicon oxide is generated [10]. In this case, the scheme of the process of mullite forming is as follows: kaolinite → metakaolinite → spinel type phase → mullite phase → proper mullite propagation. That is, at the temperature of 925 °C the layers of metakaolinite shrink and form the spinel type phase with generation of silicon oxide. When raising the temperature up to 1050...1100 °C, the spinel type structure transits to the mullite phase, and silicon oxide in the form of cristobalite is generated at the same time. At the temperature interval of 1200...1400 °C, cristobalite and mullite propagation continues [11,12]. The process is accompanied by shrinkage phenomena, and when the temperature of 1300 °C is reached, cristobalite dissolves in glass. After that cristobalite in the form of melt fills the pores formed in the crystalline grid. This phenomenon explains the firing shrinkage [13,14].

Thus, the ceramics properties can be controlled. It is possible when targetedly changing the ceramic cork structure through the ratio of the structure-forming phases, mostly, by means of changing the process parameters of firing. Meanwhile, the efficiency of the impact methods will differ depending on the initial phase composition of clay.

2. Materials and methods

The objective of the presented research includes the assessment of the efficiency of thermal influence on forming of the ceramic cork structural elements from clays of various origins.

To perform this research, 3 samples of clay raw materials were taken from the Chelyabinsk Region fields:

- Severo-Kruglyanskoye field featuring raw materials containing both main clay minerals, kaolinite and montmorillonite, in approximately equal proportions;
- Poletaevskoye field, and namely crude kaolin composed of mixed monomineral clay (kaolinite) and nonassociated quartz (up to 50 %);
- Yuzhno-Sychevskoye field featuring clay raw materials mostly composed of montmorillonite.

The main impurity mineral in all the clays under study was quartz, and also small amounts of carbonate inclusions in the form of calcite were present.

The samples for studying were prepared to testing by the powdering process, in compliance with GOST 32026-2012 [15].

The prepared samples of raw clay materials underwent firing at the temperatures of up to 1100 °C (the maximum temperature of 1100 °C was chosen based on economic efficiency when firing walling ceramics). The firing conditions were as follows: raising the temperature at the rate of 150 °C/h and holding the temperature of 573 °C during 30 min. for all samples. After that, the temperature was raised to the maximum one at the same rate. Once the maximum temperature was reached, isothermal holding followed, and after that – cooling, also at the rate of 150 °C/hour. Further on, the X-ray phase analysis was performed for the burned samples using ДРОН-3 X-ray diffractometer (the interplanar spaces, intensiveness of peaks, their areas, and the halo areas were determined using DIFWIN and PDWin software packages), as well as the microscopic study using JEOL JSM-6460LA electron focused-beam microscope with Oxford Instruments INCA-350 X-ray microanalyzer. The ratio of the X-ray amorphous and crystalline phases in the samples was defined by correlating the areas of ha-los and peaks of crystalline compounds using the working technique based on British Standard BS 6699:1992; the obtained values were used as a comparative (not absolute) characteristics to determine
the differences between the clays [16]. The degree of the mullite crystallinity was assessed against the size of crystallites (as per the coherent scattering zone) in the direction of h-k-l 1-1-1 (angle of scattering as per scale 20 was 35.3 degrees, interplanar space was 2.54 Å), using Scherrer-Selyakov formula.

3. Results
The influence of the maximum firing temperature on the composition of the crystalline phases is shown in Figure 1.

![Figure 1. Changing the number of crystalline phases depending on the temperature of thermal processing for different clays.](image)

The obtained dependencies reveal that the plotted curves are of similar character. Before the decomposition begins, the percent of the crystalline phases is permanent and is represented both by the main clay minerals and the impurity ones. After the clay minerals begin to decompose (around 500 – 600 °C), the number of the crystalline phases logically starts decreasing, which is also facilitated by the decomposition of the impurity minerals (carbonates in particular), meanwhile the main impurity mineral quartz maintains its crystalline structure throughout the whole interval of studies. Once the minimum is reached (800 – 925 °C), the newgrowths, including mullite, start crystallizing, the number of which evenly increases as the temperature rises [17].

The number of newgrowths containing mullite is calculated as the difference between the minimum quantity of the crystalline phases and its quantity at 1100 °C; and the theoretically possible quantity of mullite is calculated as per the stoichiometric equation of decomposition of the initial clay minerals. The results are given in Table 1.
Table 1. Quantity of Newgrowths during Thermal Processing of Clays.

| Field                      | X-ray amorphous compounds (%) | Crystalline phases (%) | Crystalline newgrowths, including mullite (%) | Theoretically possible quantity of mullite (%) |
|----------------------------|-------------------------------|-----------------------|-----------------------------------------------|-----------------------------------------------|
| Severo-Kruglyanskoye field | Initial Value | Extreme Value | Value at 1100 °C | Initial Value | Extreme Value | Value at 1100 °C | Initial Value | Extreme Value | Value at 1100 °C |
| X-ray amorphous compounds  | 19,2                         | 35,9                  | 29,3                                           | 80,8                                         | 64,1                               | 70,7                                           | 6,6                                      | 30,8                                      |
| Crystalline phases (%)     | 80,8                         | 64,1                  | 70,7                                           |                                              |                                    |                                                |                                              |                                           |
| Crystalline newgrowths,    |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
|   including mullite (%)    |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
| Theoretically possible     |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
|   quantity of mullite (%)  |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |

Poletaevskoye field

| X-ray amorphous compounds  | 32,9                         | 46,6                  | 37,4                                           | 67,1                                         | 53,4                               | 62,6                                           | 9,2                                      | 48,8                                      |
| Crystalline phases (%)     | 67,1                         | 53,4                  | 62,6                                           |                                              |                                    |                                                |                                              |                                           |
| Crystalline newgrowths,    |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
|   including mullite (%)    |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
| Theoretically possible     |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
|   quantity of mullite (%)  |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |

Yuzhno-Sychevskoye field

| X-ray amorphous compounds  | 17,2                         | 34,8                  | 25,2                                           | 82,8                                         | 65,2                               | 74,8                                           | 9,5                                      | 22,1                                      |
| Crystalline phases (%)     | 82,8                         | 65,2                  | 74,8                                           |                                              |                                    |                                                |                                              |                                           |
| Crystalline newgrowths,    |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
|   including mullite (%)    |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
| Theoretically possible     |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |
|   quantity of mullite (%)  |                              |                       |                                                |                                              |                                    |                                                |                                              |                                           |

The values given in Table 2 are not obviously related either to the composition of the initial clays, or to the ratio of crystalline and X-ray amorphous compounds in the clays. We may unequivocally conclude that during clay firing at the temperature below 1100 °C (this temperature is typical for production of walling ceramics), only small part of the initial raw materials transforms into mullite. The remaining major part is glass generated as a result of baking, as well as impurity components. The size of mullite crystallites at the maximum firing temperature (1100 °C) is given in Table 2.

Table 2. Mullite Crystallites Size as per the Coherent Scattering Zone in the Direction of h-k-l 1-1-1.

| Name of Clay Raw Materials Field | Line Intrinsic Broadening in the Diffraction Pattern, in Degrees of Scale 2θ | Mullite Crystallites Size (nm) |
|----------------------------------|---------------------------------------------------------------------------------|--------------------------------|
| Severo-Kruglyanskoye field       | 0,1974                                                                          | 44                             |
| Poletaevskoye                    | 0,3714                                                                          | 23                             |
| Yuzhno-Sychevskoye field         | 0,3625                                                                          | 24                             |

The obtained data show that at the maximum temperature of 1100°C the mullite crystallites only begin to grow, are characterized with nanosize, and cannot provide reinforcement for the ceramic crock at the microscale by blocking opening of cracks in case of stretching and bending loads.

The results of the structure studying are confirmed with microphotographs given in Fig. 2a, 2b, 2c. On microphotographs it is not possible to get a visual image of the mullite crystallites due to their small size. The structure of the ceramic crock is mostly represented by the glass phase with crystalline impurity inclusions.

Thus, the reserves of clay raw materials are not used in the walling ceramics to their fullest. We may assume that by intentionally increasing the ratio between mullite and glass it is possible to significantly improve the properties of the ceramic crock. It may be fulfilled by creating favourable conditions for mullite crystals growth by varying the process parameters, in particular the time of holding at the maximum temperature, or by using other methods, for instance, through the use of crystal seeds [3,17].
4. Conclusion
In general, the performed research revealed that, as matters stand, in the walling ceramics technology (using of the local kaolin, montmorillonite clays, and the firing conditions under 1100 °C) the ceramic crock forms mainly from the glass phase generated during baking, as well as from inclusions of crystalline impurity minerals. The mullite mineral forms in a small quantity and is characterized with nanosize, what does not facilitate improvement of the ceramic crock properties, such as bending and...
fracture strength, as well as frost resistance. To improve these indices through the raw materials’ reserves and without changing the firing parameters, the methods of targeted forming of the mullite crystals should be used.

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