A study on sintering of ceramic bricks made from waste coal

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Abstract. The results of the study on phase transformations and structure formation during firing of bricks made from wastes of coaly argillite processing. The effect of firing temperature on the processes of mineral formation and changes in the quantitative content of amorphous phase and brick porosity was defined. It was found that at 950-1050 °C the sintering takes place providing a solid brick structure.

1. Introduction

Wastes generated by coal extraction and processing can be utilized as a raw material in the production of building materials including bricks but in Russia they are hardly used worsen the environment in the coal-mining regions. Wastes of Korkino lignite open-cut in Chelyabinsk region, Russia, are represented by argillites, aleurolites, coaly argillites, sandstones and shales [1]. Production of ceramic bricks of high quality made of waste coal is possible on the basis of the method developed by the authors [2]. This method of manufacturing ceramic matrix composites allows various types of technogenic and natural materials with low plasticity to be utilized in the building ceramics [3].

Firing of building ceramics is one of the most important factors that determines the properties of the product [4]. In the production of ceramic materials drying and firing consume the greater part of energy resources. Rational modes of heat treatment allows a brick with the required physico-mechanical properties at low cost to be obtained [5, 6].

The aim of the present research was to determine the firing temperature and study the processes of brick sintering made from processing of coaly argillites.

2. Methods and materials

At the first stage to determine the optimum firing temperature for bricks, made of coaly argillites with corrective additive of loam, we prepared a number of laboratory samples.

X-ray fluorescence (XRF) of coaly argillites and clay loam was performed with the use of spectrometer Shimadzu XRF 1800. The chemical composition is given in Table 1.

| Raw material                                      | Oxide content in % of dry substance |
|---------------------------------------------------|-------------------------------------|
| Processing wastes of coaly argillites from Korkino deposit | SiO₂  43.85  TiO₂  1.03  Al₂O₃  16.9  Fe₂O₃  9.97  MnO  0.2  MgO  2.8  CaO  3.35  R₂O  2.7  LOI  19.2 |
| Loam from Novokuznetsk                          | SiO₂  59.9  TiO₂  0.9  Al₂O₃  15.3  Fe₂O₃  5.7  MnO  0.2  MgO  2.4  CaO  5.4  R₂O  4.8  LOI  5.4 |
The study of the phase composition according to the data of the X-ray diffraction (XRD) showed that the coaly argillites consist of quartz, kaolinite, chlorite, siderite, and muscovite. It also includes dolomite, hematite and feldspar (Figure 1). Mineralogical composition of Novokuznetsk loam corresponds to the group of polymineral clays of kaolinite-montmorillonite-hydromica type. XRD of coaly argillites and clay loam was carried out using spectrometer Shimadzu LabX XRD-6000.

XRD data confirmed the results of the thermal analysis (Figure 2) done on the derivatograph Setaram Lab Sys Evo.

Loam is medium plastic (11.5), low disperse with low content of large and medium-sized inclusions, refers to low-melting, low temperature, non-coking raw material.

Figure 1. XRD of processing wastes of coaly argillites.

Figure 2 shows the TG, DTA and DTG data of processing wastes of coaly argillites. The mass loss is as follows: 100-120 °C dehydration of free water; 470-560 °C dehydration of the clay mineral; 740-780 °C decomposition of carbonates.

Total mass losses after the heating up to 1000 °C amounted to 22.64%, which indicates a high content of carbon dispersed mass.

Figure 2. TG, DTA and DTG curves of processing wastes of coaly argillites.
The laboratory ceramic samples from processing wastes of coaly argillites with an additive of loam were prepared by the patented method [2]. The mixture preparation included drying of raw material up to 2 ÷ 3% and grinding to class -300 µm. Particle size distribution after grinding was analyzed using laser diffraction granulometer Malvern Mastersizer 2000. The results showed that the content of fractions was (%): less than 0.005 mm – 28%, 0.05÷0.005 mm – 50%, 1÷0.05 mm – 22%.

The grinded argillites belong to low plastic materials (plastic index ≈ 6.0); non-caking, non-sensitive to drying (the coefficient of drying sensitivity <1) [7].

From the dried and grinded raw materials in the intensive mixer we prepared the molding powders of the following composition (%): processing wastes of coaly argillites 70; loam from Novokuznetsk 30. From the granulated powder at 20 MPa of compaction pressure the samples of cylindrical form 50 mm in diameter and height 45 ÷ 50 mm were made. Firing was conducted at various temperatures from 600 to 1200 °C.

3. Results and discussions
XRD of samples (Fig. 3) fired at a maximum temperature from 600 to 900 °C shows a sharp decrease in chlorite and minerals of carbonate group at a temperature 800 °C, which completely disappear above 900 °C. With the temperature rise starting at 900 °C the content of mineral phases of hematite and augite increases sharply. This indicates the hematitization processes and is confirmed by the characteristic red color of the samples.

The dependence of the porosity changes in the samples on the firing temperature is given in Figure 4. At a temperature from 600 to 900 °C the total porosity in the samples increases in average by 10-14% due to activation of gas generation in the material. At a temperature 950-1050 °C a slight decrease 1-3% in the porosity occurs, which can be explained by the increase in the amount of pyroplastic phase and partial removal of gases from the material during sintering. Starting from the temperature of 1100 °C there is a melting and swelling of products. A significant increase in the glass phase is evidence of the process of liquid and solid phase sintering of samples [8]. Sintering and formation of a solid structure of ceramic material occur at 950-1050 °C; it is confirmed by high physico-mechanical properties (Table 2).
Table 2. Physico-mechanical properties of ceramic samples.

| No. | Firing temperature, °C | Bulk density, kg/m³ | W, % | Ytot, % | Rc, MPa | Strength-density ratio |
|-----|------------------------|---------------------|------|---------|---------|-----------------------|
| 1   | 600                    | 1771                | 18.0 | 1.3     | 6.0     | 3.4                   |
| 2   | 800                    | 1684                | 20.6 | 2.0     | 14.0    | 8.3                   |
| 3   | 900                    | 1683                | 19.9 | 2.7     | 21.4    | 12.7                  |
| 4   | 950                    | 1675                | 19.6 | 3.0     | 23.1    | 13.8                  |
| 5   | 1000                   | 1725                | 16.7 | 5.4     | 24.7    | 14.3                  |
| 6   | 1050                   | 1725                | 14.9 | 5.7     | 25.4    | 14.7                  |
| 7   | 1100                   | -                   | -    | -       | -       | -                     |

On the basis of research at the brick factory JSC “Krasny Kirpich” (Russia, Krasnoyarsk) a pilot batch of bricks made from processing wastes of coaly argillites was produced. The study of ceramic brick macrostructure (Figure 5) revealed the presence of a continuous ordered frame with the directed orientation of cells that can be attributed to the class of ceramic matrix composites. The matrix of the composite material is formed from a clay component of the mixture, and the aggregate – from processing wastes of coaly argillites.

Figure 5. SEM (a, b) and optical microscopy (c, d) of ceramic brick made from processing wastes of coaly argillites: 1 – the boundary layer between granules; 2 – aggregate.

During investigation of thin sections (Figure 6) under the polarizing microscope we observed ore minerals of spherical, sometimes oval or polygonal shapes, caused by dehydration, recrystallization and dissociation in the process of sintering. Partial melting of ore minerals confirmed by isometric form of brown iron crystals. Large fragments of initial minerals are covered with brownish shell, the spaces between them filled with cryptocrystalline and amorphous substance (Figure 5c, d; Figure 6).

Study of the microstructure by the polarizing microscope revealed that after firing the aggregate has a thin brecciated texture and consists of relic minerals and neoformations of crystalline phases.
connected by the glass phase into a single unit (Figure 6). The boundary layer of the composite matrix is formed from clay minerals in the process of sintering, is a cryptocrystalline aggregate continuously transiting from one granule into another.

Figure 6. Optical microscopy of the boundary layer of ceramic matrix composite: 1 – neoformations of hematite nature; 2 – pore edge; 3 – glass crystalline phase; 4 – ore minerals; 5 – complex pyroxene; 6 – pore; 7 – augite; 8 – quartz; 9 – rhombic pyroxene.

XRD showed in the aggregate quartz, hematite, feldspar, augite and a mullite-like phase; in the boundary layer: quartz, hematite, mullite, feldspar and spinel (Figure 7).

Figure 7. XRD of ceramic bricks made from processing waste of coaly argillites: 1 – boundary layer; 2 – aggregate.
By the pronounced x-ray amorphous halo we can judge about a significant amount of glasses in the dispersion medium (15-20%), which is consistent with the observation in thin sections. Particles of relic quartz and feldspar alongside with the minerals of neoformations are reinforcing matrix, having a fine disperse hematite nature. Infrared spectra of the ceramic matrix composite confirm the presence of the indicated mineral phases (Figure 8).

The increased pore content in the granule body is due to burn-out of disperse coal in the process of firing. In the boundary layer the porosity slightly increases due to air pressing during granulated molding mixture compression, as well as squeezing water into the dusting layer during adobe brick molding. Walls of pores in the boundary layer are formed by an amorphous glassy mass permeated by cryptocrystalline minerals.

6. Conclusions
As a result of the conducted research into process of sintering during firing bricks from processing waste of coaly argillites it was established found:
- content of main mineral phases remains almost unchanged during firing up to 1100 °C, which positively affects the structural and mechanical characteristics of the bricks;
- increase in the firing temperature above 1100 °C leads to overfiring of bricks;
- optimum amount of pyroplastic glass phase for brick sintering is formed at a temperature 950-1050 °C;
- high physico-mechanical properties of bricks are conditioned by the spatially organized matrix structure.

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