The investigation of the matrix structure of ceramic brick made from carbonaceous mudstone tailings

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Abstract. The study of the matrix structure of ceramic brick made from carbonaceous mudstone tailings of Korkinsky coal opened pit mine is presented in the current paper. This study includes a thin sections analysis by the polarizing microscope, X-ray, SEM and infrared spectra investigations. It has been discovered that processes of solid- and liquid-phase sintering with the formation of new mineral phases occur inside and on the surfaces of granules during firing. It is shown that a liquid phase is formed in the matrix. It fills inter-grain gaps and connects mineral particles between themselves. It has been found that the advanced physical and mechanical properties of ceramic bricks obtained by creation of the matrix ceramic crock structure, intensive forming of a glass phase on the boundary of the section medium of ceramic composite and temperature reduction of the processes of solid-phase sintering.

1. Introduction

The waste after coal extraction and cleaning can be a valuable raw material for production of construction materials such as wall ceramics. Up to the present moment, however, it has not been widely utilized and bulk anthropogenic wastes worsen the environment in coal-mining districts \cite{1, 2}. Utilization of such waste is especially crucial for Chelyabinsk region where the biggest in Europe Korkinskiy brown coal open pit mine is located. During the period of its operation since 1934, hundreds of millions т�x tons of waste, that contain argillites, siltstones, coaly argillites, sandstones and shales, have been accumulated in the disposal areas \cite{3}.

The constraint factors of use of waste from Korkinskiy open pit coal mine in the wall ceramics technology are unstable, the content of carbon and non-plasticity of anthropogenic raw material are often increased. This problem could be solved via reducing the coal content in the rock \cite{4, 5}, the application of semi-dry pressing technology and directed formation of the spatially-organized structure of a ceramic crock for non-plastic raw materials \cite{6}.

The formulated technological idea was verified in industrial conditions of a brick plant LLC ‘Krasniy Kirpich’ of semi-dry pressing (Krasnoyarsk Region) \cite{7}. Physical-mechanical tests of the ceramic brick lot produced from coaly argillites of Korkinskiy open pit coal mine showed that the new method of burden preparation, which includes waste granulation with subsequent powdering of granules by clay, makes it possible to obtain high-quality ceramic products according to the Russian State Standards.
The purpose of this work is to carry out the petrographic study of the formation mechanism of a strong structure of a ceramic brick pilot lot produced from coal mine waste with the coal content below 11 %.

2. Raw materials selection

The tailings of the brown coal (carbonaceous mudstones) from Korkinsky coal opened pit mine have been investigated as the initial raw for ceramic bricks production. In this mine the coal content is from 10 up to 18 %, depending on the size of the wastes. Coal mine wastes are not soaked in water, the stone-like clay material is made as a result of compression, hydration and cementation of clays deposited in the coal thickness and is not ductile in the natural conditions.

The chemical composition (see the Table) of the waste belongs to the semiacid group of a raw material (Al₂O₃ more than 16 %), with a high content of coloring oxides (Fe₂O₃ + TiO₂ more than 10 %). The study of the phase composition according to the data of the X-ray powder diffractometry showed that the waste consists of quartz, kaolinite, siderite, muscovite, there is also dolomite, hematite, and field spar.

| SiO₂ | Al₂O₃ | Fe₂O₃ | MnO | TiO₂ | MgO | CaO | R₂O | LWF* |
|------|-------|-------|-----|------|-----|-----|-----|------|
| 40.8-42.8 | 16.2-17.9 | 9.97-12.6 | 0.2-0.26 | 0.8-1.4 | 2.5-2.8 | 2.1-4.4 | 1.9-2.2 | 17.8-19.2 |

*LWF – loss when firing.

3. Experimental procedure

The production of the ceramic bricks with matrix structure from raw material has been partially described in paper [8]. Dispersed particles are aggregated into granules, clayey material covers their surface, and samples from these granules are pressed and fired. The spatial cellular carcass is formed as a result of such process, it serves as disperse medium after bricks pressing. Disperse medium produces a liquid-phase during firing. This phase is introduced into a peripheral zone of disperse medium (a boundary layer) and forms a strong matrix structure after crystallization.

The granulated molding powder for ceramic brick production was prepared by granulation of fine-dispersed coal waste and subsequent powdering of granules by the mixture of loamy clay and crushed glass. The burden composition (mass %) was the following: coal mining waste – 65; Novokuznetsk loamy clay – 25; crushed glass – 10.

4. The investigation of the ceramic bricks matrix structure

The macrostructure study of a ceramic product burnt at 900...1000 °C (Figure 1) revealed the presence of spatial surfaces of phase boundaries in the common body of the material distinguished by a more intensive brown color and forming a regular continuous carcass with the directed orientation of cells, allows to refer it to the class of ceramic matrix composites [9]. The matrix of the composite material is formed from the clay component of the burden, which plays a role of the disperse medium after pressing and burning of products, and the disperse phase is formed from the coal mine waste with addition of crushed glass.

The disperse phase has a concentric-zonal structure, the granule body is represented by mono- and poly-mineral fragments of minerals (Figure 2). Mono-mineral fragments of quartz preserve their isometric angulated shape; some of them are of a ditrigonal form and remain almost unchangeable during sintering. Small and fine fragments on the surface of large crystals transit into crystobalite or tridimite. Large polygonal fragments of field spar decay and re-crystallize during sintering. Predominantly, solid-phase reactions result in the formation of anorthite-bytownite plagioclases and potassium-sodium field spars.
Figure 1. A macrostructure of ceramic bricks produced from coal wastes
a – experimental samples; b – fracture of brick; c – thin section, transmitting light, × 20; d – polished section, reflecting light, × 5; 1 – boundary layer between granules; 2 – granule body

Figure 2. Micrographs of the matrix structure of ceramic bricks produced from coal wastes
a – nics III, × 25; b – nics III, × 100; c – nics III, × 100; 1 – fritted quartz particles; 2 – field spar; 3 – ore minerals; 4 – pores; 5 – complex pyroxene with inclusions of cryptocrystalline minerals covered with the brownish coat

During the analysis of thin sections by a polarizing microscope, ore minerals of a spherical, oval, or sometimes polygonal form can be seen due to dehydration, dissociation, and re-crystallization of initial components during sintering, that is especially typical for sulfide minerals. Ore minerals are partially fused, which is proved by the evident isometric shape of limonite crystals (Figure 3b, e). In the periphery large fragments are covered by a brownish coat. The gaps between large fragments are filled with the cryptocrystalline and amorphous-glassy substance forming the cementing mass, a crystal phase of which is represented by pyroxenes of a variable structure (Figure 3e), quartz and field spars, sometimes by olivines and decomposed garnets. Thus, the granule body has a fine-brecciated texture and consists of relict minerals and newly formed crystal phases bound into a comprehensive whole by the glass phase.

Figure 3. Micrographs of individual parts of the disperse phase in the composite material: a – thin section, transmitting light, nics II, × 50; b – nics II, × 70; c – nics X, × 200; d – nics X, × 50; e – nics X, × 70; f – nics II, × 100; 1 – augite; 2 – ore minerals; 3 – field spar; 4 – rhombic pyroxene
The X-ray (Figure 4а) and microscopic investigations of the disperse phase vindicate the solid-phase mechanism of sintering with the formation of new mineral phases. Decoding of diffraction patterns enabled identification of quartz, hematite, field spars, mullite-like phase, and augite in the granules. In the plane-polarized light, the pyroxenes are mainly represented by augite of the variable composition (Figure 3с, d), sometimes by diopside and newly formed pseudo-wollastonite. From the X-ray point of view, the powdering layer after sintering is represented by quartz, hematite, mullite, field spars, and spinel.

Infrared spectra of absorption of the ceramic matrix composite based on coal waste prove the presence of the found mineral phases (Figure 4b). In the low- and intermediate-frequency areas of spectrum (up to 1.800 cm\(^{-1}\)) the composite material has the absorption maximums of 470, 545, 1090, 1170 cm\(^{-1}\) typical for hematite. The presence of quartz is confirmed by the characteristic doublet of 770, 790 cm\(^{-1}\). The absorption maximums (605, 1090 cm\(^{-1}\)) correspond to mullite. Spinel in the IR-spectrum of the disperse medium is registered at the peaks of 575, 710, and 1735 cm\(^{-1}\), augite in the disperse medium – at peaks of 560, 670, and 1490 cm\(^{-1}\).

![Figure 4. X-ray diffraction patterns (a) and infrared spectra (b) of the ceramic bricks from coal wastes: 1 – disperse medium; 2 – disperse phase](image)

The pores with the sizes from 0.1 to 400 m\(\mu\) are evenly distributed over the ceramic crock cross section. Normally, the pores are of a spherical form and have a rough uneven surface (Figure 5), and a significant quantity of them are of a cell shape (Figures 1, 2).

![Figure 5. SEM-image of the microporous structure in the boundary layer (a, b, c) and in the body of a granule (d, e, f) of ceramic brick from coal wastes 1 – disperse medium; 2 – disperse phase](image)
5. Results and discussion

It was experimentally established that the granule body has a fine-brecciated texture and consists of relict minerals and newly formed crystal phases bound into a comprehensive whole by the glass phase. The disperse medium (a granules boundary layer) of the matrix composite, formed by argillites during sintering, represents the cryptocrystalline aggregate continuously transiting from one granule to another. In the disperse medium, large fragments are not present. The medium consists mainly of microscopic crystals and fragments of transparent yellowish-white minerals evenly distributed in the glass phase; there are also fine cryptocrystalline aggregates, brownish-red in most cases (Figure 2c).

Expansion of the powdering layer results from the interaction with the boundary layer of the granules during sintering. Under oxygen deficiency, needed for burn-out of carbonic residual from the waste, the iron oxides recover into the protoxidic form and react with the amorphous silica, which are generated in the process of decomposition of clay minerals in the boundary layer. Thus, the glass phase is formed intensively on the granules boundary and it stimulates solid phase reactions and intensifies the cementing action of the cellular carcass.

The vividly expressed X-ray amorphous halo vindicates a significant quantity of glass in the disperse medium (up to 15...20 %) which agrees with the observations in the thin sections. Particles of remnant quartz and field spar, along with the new mineral formations, are the reinforcing carcass of the matrix, having a fine hematite nature.

The increased amount of pores in the granule body is explained by the burn-out in the process of dispersed coal mass burning. In the boundary layer the porosity increases to some extent, which is caused by the air compression as the granulated mass is compacted, and also by water squeezing-out into the powdering layer during adobe brick molding. It should be noted that pore walls in the boundary layer are formed by the amorphous vitreous mass veined with cryptocrystalline minerals (Figure 5c). Evidently such internal fusion of pore space walls increases the fraction of closed porosity and decreases the water absorption ability of the ceramic crock.

6. Conclusions

The petrographic analysis of the ceramic brick test lot produced from the wastes of Korkinskiy coal open pit mine shows that the advanced physical and mechanical properties result from:

– the matrix structure of the ceramic crock in which the disperse medium i.e. a re-crystallized bond of the amorphous and mineral phases fills inter-grain gaps and binds mineral particles to each other;
– intensive formation of the glass phase on the boundary of the disperse medium and the disperse phase which promotes solid-phase reactions and intensifies the cementing action of the matrix;
– reduction of the temperature of solid-phase sintering processes followed by the formation of anorthite-biotowne plagioclases, hematite, augite, spinel and other mineral phases.

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