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Investigation of the transition layer of the core–shell of ceramic matrix composites based on coal waste

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Abstract. The study results of the chemical, particle size, and mineral compositions of the raw materials of ceramic samples (coal waste and clay) are presented. A model of the transition layer between the shell and the core of the ceramic matrix composite is provided. The technique for preparing multilayer ceramic samples imitating the phase boundary of a ceramic material of a matrix structure is described. The differentiated studies of the phase composition and microstructure of multilayer ceramic samples are presented. The interaction of the products of the core and the shell in the transition layer in ceramic materials of the matrix structure during firing is established.

1. Introduction

In the 20th century, the world development was provided mainly due to hydrocarbon energy. Large-scale mining and burning of coal led to the formation of hundreds of millions of tonnes of coal waste and ashes of combined heat and power plants (CHP) [1]. Such industrial wastes are aluminosilicates according to the mineral composition [2]. Therefore, it is important to use them as technogenic raw materials for the production of building materials [3-5]. Construction and technological waste management will help to save natural resources, conserve nature and improve the environment on the earth [6, 7].

There is positive experience in the production of ceramic bricks from the ash of CHP plant or coal wastes. The amount of waste in the ceramic mass is from 70 to 100% [8-11]. Since the days of the USSR, brick factories were built and successfully operated in Novokuznetsk (Kuzbass), Yermak (Kazakhstan) and other cities. Currently, brick is not produced in these plants for various reasons [12, 13].

The classical technology of plastic molding of bricks is not suitable when using coal waste [14]. Wastes do not have good ductility and mass cohesion. They have a high content of carbon particles and impurities (up to 18-25%). Therefore, the development of brick technology from coal waste with high structural strength (structural quality coefficient) is relevant.

It is necessary to develop new methods for preparing the molding material from waste and to select corrective additives to form a rational structure of the material [15-17].

The authors developed a technology for wall ceramic materials of a matrix structure from technogenic and natural raw materials [18]. The matrix structure of ceramics has two main components: aggregate (cores) – the product of firing granules from industrial waste; matrix is a product of firing a clay shell around granules. The clay content in such structure in the composition of the mixture does not exceed 20-25% by weight and ceramic products have the required performance properties. The manufacture of ceramic matrix composites from coal wastes has its own characteristics. The high carbon content in the waste can lead to the destruction of contacts at the borders of the granules during firing. To solve this problem, it is necessary: to press hollow products with a wall thickness of 8-12 mm; create an oxidizing environment for burning carbon inside the brick; reduce the amount of carbon particles in the press mass, etc.

Thus, it is necessary to establish and optimize the mixed and technological factors of the new ceramic technology to obtain strong and durable ceramic matrix composites from coal waste. An important criterion is the mechanical compatibility of the matrix and cores of the ceramic material.

The aim of the current investigation was a differentiated study of the transition layer of the core–shell ceramic materials of the matrix structure based on coal waste.

2. Methods and research objects

Raw materials were investigated in accordance with GOST 21216-2014 “Clay raw materials. Test methods” and GOST 9169-75 “Clay raw materials for the ceramic industry. Classification”. The chemical composition was determined by X-ray fluorescence dispersive wave analysis (ShimadzuXRF-1800 spectrometer). The particle size distribution was determined by the method of laser diffraction of suspensions (laser analyzer Mastersiser 2000). The structure of the layers of model ceramic samples was studied by optical and electron microscopy. The phase composition was determined by powder x-ray diffractometry (X-ray diffractometer ShimadzuXRD-6000).

Coal wastes were studied as objects – dry enrichment of coaly argillites (Korkinsky brown coal section, Chelyabinsk region), clay raw materials were taken from the Novokuznetsk deposit (Kuzbass) and multilayer ceramic samples made from them. The chemical composition and particle size distribution of the raw materials are shown in table 1, 2.

Table 1. The chemical composition of raw materials.

Name of raw materials	The content of oxides on absolutely dry matter, %										
	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaO	MgO	TiO_2	MnO	K_2O	Na_2O	S
Coal waste	51.26	21.62	14.47	-	4.64	2.52	1.26	0.12	2.13	0.62	0.34
Clay	64.85	17.09	7.02		3.26	2.34	0.87	0.19	2.73	0.78	0.006

Table 2. Granulometric composition of raw materials.

Name of raw materials	The content of fractions in microns, %				
	>0.06	0.06-0.01	0.01-0.005	0.005-0.001	<0.001
Coal waste	58.2	9.2	8.6	11.6	12.4
Clay	-	2.6	64.2	5.1	28.1

Coal wastes belong to the group of semi-acid raw materials with a high content of coloring oxides by chemical composition. The granulometric composition of the waste was determined after preliminary two-stage grinding in a jaw crusher and laboratory runners. According to the results of granulometric studies, coal wastes are classified as coarse raw materials with a predominance of sand fraction (table 2).

Coal wastes consist of argillites, siltstones, carbonaceous mudstones and shales by terms of material composition. This is a mixture of mineral particles with a dispersed carbon mass (the content of carbon particles is 12-15 wt.%).

According to the mineral composition, coal wastes consist of quartz, kaolinite, siderite, hydromuscovite, dolomite and feldspar. The amount of free quartz is 50-53%.

In terms of plasticity, crushed coal wastes are low-plastic (plasticity number ≈ 6.0); by drying properties – insensitive to drying (sensitivity coefficient to drying < 1); by sintering degree – non-sintering technogenic raw materials.

Clay is a clayey rock (silty loams) typical of Western Siberia [19] belongs to semi-acidic raw materials according to its chemical composition (table 1). As for granulometric composition, it refers to low-dispersed raw materials with a low content of large and medium inclusions (table 2).

Clay belongs to polymineral rocks by the mineral composition, according to the group of clay minerals it belongs to the type: montmorillonite-hydromica. Clay belongs to a moderately plastic raw material according to its technological properties. It has a high sensitivity to drying and is a low-melting raw material of low temperature sintering.

3. Results and discussion

A model of the transition layer between the shell and the core of the ceramic matrix composite was developed to study the phase composition and structure of the ceramic material at the phase boundary (figure 1, a). Taking into account the chemical composition of the carbon waste according to the method of [20], multilayer samples were prepared without a plug to prevent swelling of the inner zone of the samples (figure 1, b, c). The number and composition of the raw components of the layers are given in table 3.

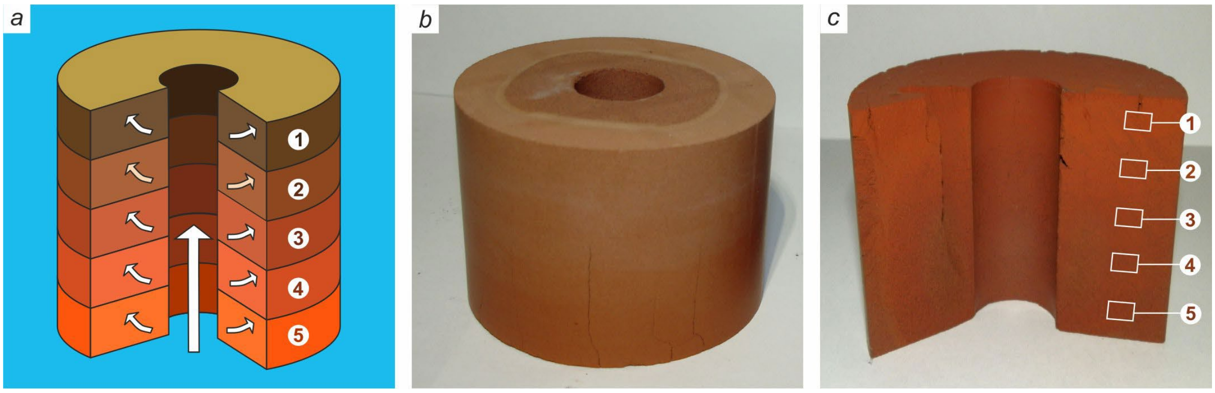

Figure 1. Model of the transition layer (a), appearance (b) and cross section (c) of a model multilayer ceramic sample from coal waste, clay and their mixtures: 1 – core; 2 – transition zone from the core; 3 – the central region of the transition zone; 4 – transition zone from the side of the shell; 5 – shell.

Table 3. The composition of the raw components of the layers of the model sample.

Name of raw materials	The content of the component in the mixture in%, the number of the layer of the sample				
	1	2	3	4	5
Coal waste	100	75	50	25	-
Clay	-	25	50	75	100

3.1. Features of the preparation of multilayer samples

Accurate dosing of the press powder by volume was provided for each layer. The layer thickness was 7-10 mm. The moisture content of the raw materials for each layer was controlled. The crushed components were dried to constant weight. The raw materials were thoroughly mixed and the mixture was passed through a sieve with a mesh of 0.63 mm. The exact amount of water was calculated to moisten the mixtures of each layer. It was equalized the moisture content of the prepared press. Wet mixtures for each layer of the model sample were simultaneously kept in a desiccator for at least 5-6 hours. The relative humidity of the press powders of all layers was the same. Humidity was in the range of 9-10% by weight.

Multilayer samples were pressed at a pressure of 15 MPa. The pressing was carried out on a hydraulic press with a smooth increase in pressure. It was applied the two-stage pressing mode with a ratio of preliminary and final pressures of 1:4. A one-sided method of applying press force was selected. The samples were dried to constant weight in an oven at a temperature of 105 °C. Samples were fired in a muffle furnace in a stepwise mode with exposure at a maximum temperature of 950 °C.

3.2. Investigation of the phase composition of multilayer samples

To study the phase composition of the layers of model ceramic samples, fragments of each layer were cut out (figure 1, c). In figure 2 the results of layer-by-layer x-ray phase analysis were presented. The numbering and designation of the layers corresponds to figure 1. On the X-ray diffraction patterns of the layers, the mineral phases were identified: quartz (d/n = 4.255; 3.343 Å); hematite (d/n = 2.69; 2.52; 1.697 Å); albite (d/n = 3.78; 3.196 Å); magnetite (d/n = 2.532; 1.616 Å) orthoclase (d/n = 5.88; 3.954; 3.31 Å).

A semi-quantitative assessment of the content of the main mineral phases in the layers of the model sample during a layer-by-layer transition from the core to the shell was carried out by changing the intensity of the mineral lines. The intensity of the diffraction maxima of the crystalline phase was estimated by the number of peaks per second (counts per second). In figure 3 it has been graphically presented the results of the curves analysis, which showed a decrease in the amplitude of crystalline quartz in the direction from the shell to the core. This is due to the higher silica content in clay. On the contrary, it was observed a layer-by-layer increase in the intensity of hematite lines towards the core (figure 3), due to a lower content of iron oxides in clay compared to coal waste.

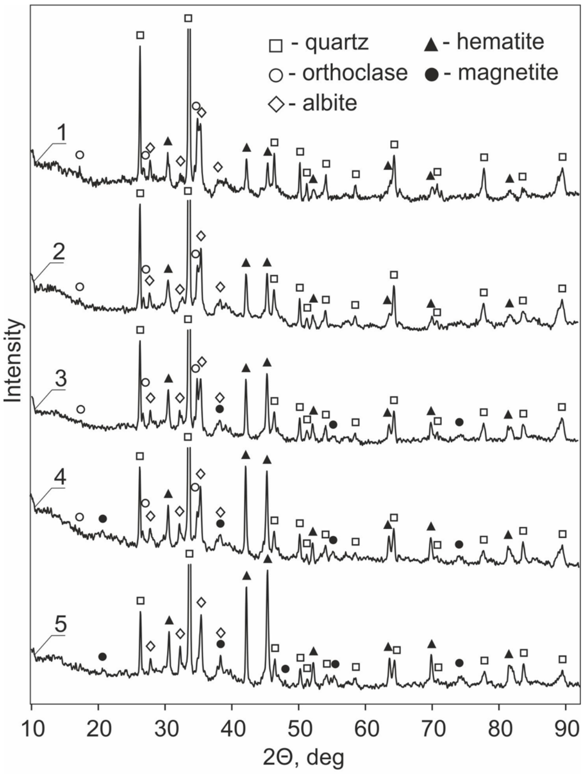

Figure 2. X-ray diffraction patterns of the layers of a model multilayer ceramic sample from coal waste, clay and their mixtures.

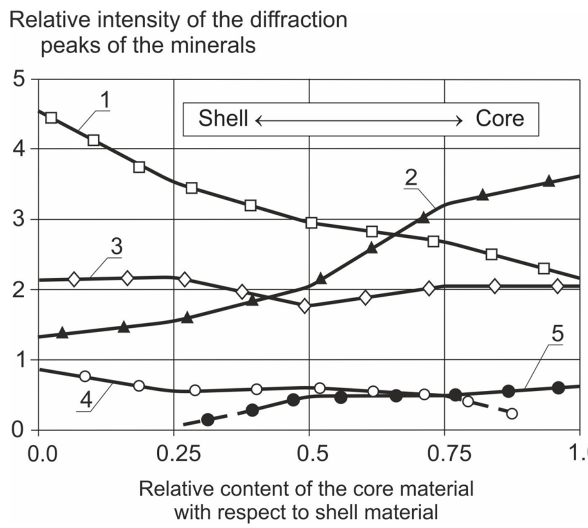

Figure 3. Changing in the intensity of the lines of minerals during a layer-by-layer transition from the core to the shell of a model multilayer ceramic sample from coal waste, clay and their mixtures: 1 – quartz; 2 – hematite; 3 – albite; 4 – orthoclase; 5 – magnetite.

The intensity of albite lines practically does not change from the core to the shell of the ceramic sample. The same content of sodium feldspar is due to the similar chemical composition of raw materials in terms of Na_2O. There is a decrease in the intensity of the lines of orthoclase, as well as its complete absence in the layer of coal waste with a decrease in the amount of clay in the composition of the layers after firing. Starting from the central layer of the transition zone (layer 3), magnetite lines are marked, and their intensity increases towards the core.

3.3. Study of the multilayer samples structure

Structural studies were carried out on Olympus GX-51 optical polarization microscope using polished sections in crossed and parallel Nicoles with magnification 15-75 times. The layers microstructure of model ceramic samples are shown in figure 4.

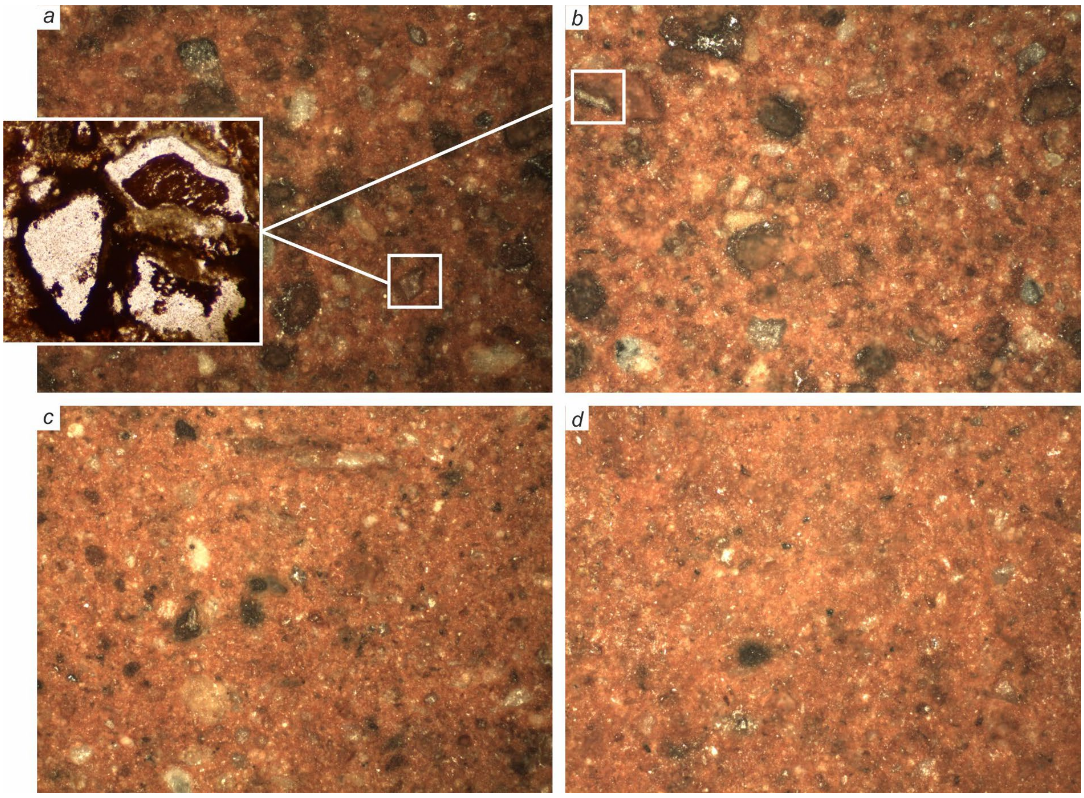

Figure 4. Structure micrographs of the core layers (a), the center of the transition zone (b), the transition zone from the side of the shell (c) and shell of the model multilayer ceramic sample (d). Polished section, reflected light: × 15: Nicoli II.

The layer formed from carbon waste (core zone) has a conglomerate structure and it is represented by mono- and polymineral fragments of minerals (figure 4, a). Monomineral fragments of quartz retain an isometric angular shape. Large polygonal fragments of feldspars undergo firing and recrystallization during the firing process. Mainly potassium-sodium feldspars are formed as a result of solid-phase reactions. Significant amounts of dark-colored minerals are spherical, oval, sometimes polygonal form. Large fragments from the periphery are covered with a brownish shell. The gaps between the large fragments are filled with cryptocrystalline and amorphous glassy matter. Its crystalline phase is represented by pyroxenes of variable composition, quartz and feldspars.

A layer formed from clay (shell zone) has a uniformly distributed cryptocrystalline structure (figure 4, d). Large fragments of minerals are completely absent. It consists mainly of microscopic crystals evenly distributed in the glass phase and fragments of transparent yellowish-white minerals, as well as finely dispersed cryptocrystalline aggregates, mainly brownish-red. The structure of the layers of the transition zone (figure 4, b, c) sequentially varies from partially conglomerate to cryptocrystalline in the direction from the core to the shell. This is due to a decrease in the amount of coal waste (table. 3).

4. Conclusion

As a result of the studies, it have been determined the dependences of the change in the mineral phases in the transition zone at the interface between the shell and the core of the composite. Identical crystalline phases were found in the core formed from coal waste, in transition layers and in the shell formed from clay. Thus, it was established the interaction of the core and shell products during firing with the formation of identical crystalline phases in the transition layer in multilayer ceramic samples from coal waste, clay and their mixtures. This eliminates the appearance of thermal stresses in ceramic materials of the matrix structure.

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