Wall ceramic products based on aluminum silicate materials

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Abstract. The paper focuses on wall ceramic products modified by vitrified aluminosilicate microspheres. It is shown that during phase transformations occurred in firing polyminerallized clays and vitrified microspheres, the formation of mullite- and anorthite-like compounds and gehlenite is observed within the 950–1050°C temperature range. The formation of such phases provides a synthesis of a strong aluminosilicate scaffold for ceramic materials.

1. Introduction
New standards for thermal protection of buildings require the creation of new wall materials possessing improved thermophysical properties. It is therefore necessary to develop construction materials, which would meet the specific requirements for their application in severe climatic conditions.

The development and implementation of advanced ceramic wall materials having high mechanical- and physical and thermophysical properties with the addition of industrial waste, is an urgent challenge for the modern materials science in construction. The presence in ashes of vitrified microspheres with a spectrum of the most important properties, allows them to be used in the production of wall materials.

The integrated use of clay materials in compositions with vitrified microspheres allows producing fired wall materials with high mechanical-and-physical and thermophysical properties and low thermal conductivity [1–5].

The aim of this work is the development of compositions for ceramic construction materials based on different clay minerals and vitrified microspheres using justified conditions of the structure formation.

2. Experimental
Natural and man-made raw materials are studied to synthesize ceramic wall products. Clays from Kemerovo, Novosibirsk and Tomsk regions are used as natural materials for the manufacture of fired wall materials.

A large amount of waste has accumulated in the Siberian region. Most waste is produced by mining, metallurgical and heat power industries [6]. On the territory of the Kemerovo region, several ash-disposal areas store hundreds of thousands of tons of waste. Vitrified ash microspheres are chosen as a research object.

Sampling materials from four mineral deposits were explored, namely: Rodionovskoe in the Tomsk region, Belovskoe and Egozovskoe in the Kemerovo region and Verkhnii Koen in the Novosibirsk region.
region. Their chemical, mineral and grain-size compositions were studied to evaluate the possibility of application in manufacturing ceramic construction materials.

Table 1 summarizes the chemical composition of clay materials. The oxide content includes 12.75–14.17 % aluminum oxide, 3.33–5.56 % iron oxide, 4.3–9.10 % calcium oxide, and 0.50–2.9 % magnesium oxide.

**Table 1. Chemical composition of clay materials.**

| Deposits         | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | R₂O | TiO₂ | Ignition loss |
|------------------|-------|-------|-------|------|------|-----|------|--------------|
| Belovskoe        | 58.80 | 13.77 | 5.56  | 9.10 | 0.50 | 1.09| -    | 11.18        |
| Egozovskoe       | 66.44 | 12.75 | 4.36  | 6.25 | 1.4  | 1.88| -    | 6.92         |
| Verkhnii Koen    | 65.2  | 12.9  | 4.9   | 4.3  | 2.9  | 4.1 | 0.8  | 4.9          |
| Rodionovskoe     | 66.0  | 14.17 | 3.33  | 5.2  | 2.08 | 2.67| 0.63 | 7.26         |

Using the data from Table 1, the clay materials can be grouped according to their industrial applications as depicted in Fig. 1. The mole ratio between Al₂O₃ and SiO₂ and a sum of moles of fusing agents are accepted as clay material indicators.

**Figure 1.** Industrial application of clays depending on their chemical composition: ● – Egozovskoe deposit; ○ – Belovskoe deposit; ■ – Verkhnii Koen deposit; ▲ – Rodionovskoe deposit.

As can be seen from Fig. 1, clays from Belovskoe deposit can be used in the production of clay tiles, whereas clays from Egozovskoe, Rodionovskoe and Verkhnii Koen deposits can be used in both brick and clay tile production.

In terms of the grain-size composition, all the clays relate to a coarsely dispersed raw material. Moreover, they have a low content (less than 1%) of coarse-grained inclusions. These clays can be used in the brick and clay tile production. The low degree of dispersion provides these clays with low
plasticity and sensitivity to dehydration. The plasticity index of clays varies from 8.0 of Verkhnii Koen deposit to 12.25 of Belovskoe deposit. The dehydration sensitivity coefficient ranges between 1.026 and 1.31. Clays from all the four deposits possess a medium plasticity, and the dehydration sensitivity coefficient is nearly 1.

In Fig. 1 imaging points of the clay compositions lie in the elementary triangle of anorthite–cristobalite–silica, with the eutectic point at 1100 °C.

Kaolinite–montmorillonite composition is favorable for sintering clay minerals as it is characterized by a wider increase interval of the melt.

Vitrified microspheres are considered as a man-made raw material which remains after coal burning in furnaces and is stored in ash-disposal areas using a hydraulic method.

Table 2 presents the chemical composition of vitrified microspheres, which shows that it is an aluminosilicate material. A significant amount of aluminum oxide, fusing agents and iron oxide promotes the formation of both liquid and crystal (mullite, fayalite) phases, which improve the product strength. The presence of carbon residue and fusing agents lowers the temperature of the liquid phase formation and saves the fuel.

| Oxide content, wt.% | SiO₂ | Al₂O₃ | FeO  | CaO  | MgO  | R₂O  | Total |
|---------------------|------|-------|------|------|------|------|-------|
|                     | 62.80| 24.40 | 5.04 | 4.60 | 1.82 | 1.34 | 100   |

The mineralogical composition of vitrified microspheres shows that the amount of amorphous aluminosilicate and crystalline materials is 91 % and 9 %, respectively. The crystal phase consists of 84–85 % of silica and 15–16 % of mullite and hematite.

The obtained mineralogical composition is supported by the X-ray diffraction (XRD) patterns presented in Fig. 2.

![Figure 2. XRD patterns of vitrified aluminosilicate microsphere.](image)

According to our morphological observations, the shape of vitrified microspheres is fully spherical due to their formation from the gas-containing melt [7].

It should be noted that the chemical and mineralogical compositions of vitrified microspheres depend on the ash composition and is determined by the composition of the initial fuel (coal, shale) they are produced from [8].
A study of the properties of vitrified microspheres shows that they mostly consist of hollow spherical particles. Therefore, the properties of the end composite product will depend on the shape and properties of vitrified microspheres.

The great difference in the bulk density of vitrified microspheres and clay material can be explained not only by their dispersion degree and mineralogical composition, but above all, by the fact that vitrified microspheres mainly consist of the vitreous phase. These microspheres are filled with flue gases comprising carbon oxide, an uncomplete combustion product.

In firing the ceramic material, gas in microspheres burns, thereby promoting the temperature increase inside the final ceramic material. Additionally, they consist of carbon particulates in the form of coke, the amount of which can be rather large.

Based on this information, it is hypothesized that the structure of the ceramic material generates from a mixture of clays and vitrified microspheres. At the initial stage of sintering, during the uncomplete combustion of residual fuel with CO formation, the created reducing conditions provide the transfer of iron oxide to ferrous iron in clay minerals and the temperature decrease of the primary melt due to the formation of low-temperature eutectics. This melt creates conditions for the intense sintering of interacting particles and the increase in the liquid phase amount due to the dissolution of the vitreous phase, feldspar and clays in the primary alkaline ferrous melt. The sintering process is accompanied by the pore formation conditioned by the liquid phase swelling by gaseous products resulting from burning of carbon oxide and carbon particulates and the removal of chemically-bound water from clay fractions. The appeared pores are mostly closed, with walls strengthened by wetting of the vitreous phase. The sintering process in the presence of the liquid phase intensifies the mullite crystallization, thereby hardening the obtained product due to a complete structure formation [9].

A composition of 80 wt.% clays and 20 wt.% aluminosilicate microspheres was used to investigate phase transformations in firing the ceramic material. The specimens 120×60×15 mm in size were prepared and fired at a temperature of 1000 and 1050 °C.

The XRD patterns of the fired clay and aluminosilicate microsphere composition is given in Fig. 3. One can see the formation of mullite crystals $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which has a positive effect on the mechanical strength of the obtained ceramic composite.

The XRD analysis of the fired composition proves the presence of such crystal phases as silica, wollastonite, gehlenite, albite, cyanite, and mullite- and anorthite-like compounds.
Figure 3. XRD patterns of specimens fired at 1000 °C: a – clays; b – clays and vitrified aluminosilicate microspheres in the ratio of 80:20.

Observations of the composite specimen microstructure performed on a scanning electron microscope (SEM) show that it is homogeneous, with both closed and interconnected pores (Fig. 4). There is a slight spread in values of the pore size. The shape and size of the structural elements in the obtained material are more regular than in conventional material with the granulated structure. In porous materials, the strength parameter is determined by the grain size, shape and size of interparticle necks, and their spatial orientation.
Figure 4. SEM images of the specimen consisting of clays and vitrified aluminosilicate microspheres.

In Fig. 4, the contact layer is well defined around the microspheres. It is formed during sintering the clay material and vitrified microspheres. This demonstrates that the obtained melt of the clay minerals envelopes the microsphere surface and partially hardens the aluminosilicate scaffold of the ceramic material.

3. Conclusions
Based on the investigation results of phase transformations occurred during firing polymineral clays and vitrified microspheres, it can be stated that mullite- and anorthite-like compounds and gehlenite formed within the temperature range of 950–1050°C. The formation of such phases provided a synthesis of a strong aluminosilicate scaffold for the ceramic material. The firing temperature of 1000°C was detected to be enough for the production of the effective wall materials, because it provided the formation of mullite- and anorthite-like phases between the vitrified microspheres and clay minerals.

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