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INTENSIFICATION OF CERAMIC MASS DECARBONIZATION WHEN SINGLE-FIRING OF TILES

The article is devoted to researches in the field production of ceramic tiles for interior wall covering for single firing technology. The formation of ceramic crock is parallel with the fusing of the glaze by single firing, which causes the appearance of defects on the surface. Found that the use mineralizes-shifts the decomposition of dolomite at low temperatures, creating favorable conditions for the formation of glaze coating.

Introduction. The production of ceramic tiles which are one of the main types of finish materials due to their performance and aesthetic properties is well developed in the Republic of Belarus. The production of tiles is energy-intensive and is based on the use of both local raw materials and imported ones. Due to the constant price increase for fuel and energy resources the enterprises in the building materials industry face challenges of introduction of new energy-saving technologies. At the same time produced product should remain profitable and competitive.

Traditional technology of tile production includes the following main stages: slurry production, press-powder preparation, pressing of products, drying, the first firing, glazing and decoration, glaze firing. During the first firing various physico-chemical processes occur (water removal, ceramic body decarbonization, polymorphous transformations, the formation of new crystal phases), as a result of which dried semi-finished product takes on physico-mechanical properties which are necessary for further production stage (water adsorption, mechanical strength). The formation of glaze coating takes place when glaze firing.

Today the leading producers of ceramic tiles for inside facing of walls (Spain, Italy, Germany) use single-firing technology (monoporosa), which allows not to use second-firing and at the same time the finished product retains the whole range of required properties (mechanical strength, water absorption, thermal resistance).

Existing studies in foreign practice cannot be fully used in the organization of tiles production by single-firing technology at enterprises in the Republic of Belarus, as their issue is based on local mineral raw materials which are characterized by peculiarities of chemical and low shrinkage properties and dimensional stability. However, in the process of single-firing, they are the main source of defect formation on the glaze coating, mainly "pinholes" mineralogical composition and conditions of geological formation [1–3].

Due to the fact that when single-firing the formation of ceramic crock runs parallel with facing glaze processes, if technologic parameters of firing and composition of ceramic body and glazes are wrong selected a large number of defects are formed, leading to down grading of product.

The study of technological parameters that influence on the formation of glaze coating and the quality of facing tiles produced by single-firing technology is of great scientific and practical interest.

Main part. In order to produce ceramic tiles a system that contains, %*: clay "Gaydukovka" 42.5–52.5, clay Kurdyum-3 – 5–15, dolomite – 5–15, kaolin KZ-1 – 10; quartz sand – 10;granitoid screening – 17.5 was investigated. Press-powder was made by thermal dewatering of slurry after mixed grinding of components in a ball mill of SPEEDY-1 brand (Italy). Tiles pressing was carried out at a maximum specific pressure of (25 ± 2) MPa. Sample firing was carried out at a temperature of (1,100 ± 5) °C, then after that their physico-chemical properties were determined.

As a result of studies optimum ceramic mass were selected, which lie in the range of compositions with dolomite content from 10.0 to 12.5% in the following ratio, %*: clay "Gaydukovka" – 42.5–47.5; clay Kurdyum-3 – 7.5–10.0; kaolin KZ-1 – 10; quartz sand – 10; granitoid screenings – 17.5. Together with nonplastic material, high carbonate content provides low shrinkage properties and dimensional stability. However, in the process of single-firing they are the main source of defect formation on the glaze coating, mainly "pinholes".

Samples obtained from the body of the optimal compositions satisfy the requirements of normative and technical documentation [4] and have the following set of properties: total shrinkage – to 1%, water absorption – 13.5–15.5%, density – 1,945–1,960 kg/m^3, porosity – 26.7–29.5%, the thermal expansion coefficient (CTE) – 7.43–7.47·10^{-6} K^{-1}, the mechanical strength in bending – 17.5–20.7 MPa.

* Hereinafter, unless otherwise indicated, weight percentage is given.

Ceramic body was investigated in order to intensify the process of body decarbonisation and its displacement in lower temperatures. In its composition fluoriteCaF_2 was administered in the amount of 1-2% as a mineralizer. The choice of a mineralizer was based on the wide use of fluorine-containing compounds in various industries to accelerate physico-chemical processes.

When heated the behavior of ceramic body that contains $CaF_2$is studied by differential scanning colorimetry (DSC). Traditionally, the presence of the first endothermic effect is observed in the temperature range of 60–120°C with a maximum at 90°C, which is associated with the removal of physically-bounded water by clay minerals (Fig. 1). The second endothermic effect is observed in the temperature range of 450–550°C with a maximum at 500°C. This effect is due to a loss of hydroxyl groups by crystal lattice of kaolinite and its decomposition into metakaolinite and water. Exo-effect at 320°C corresponds to the temperature of decomposition of the organic impurities.

In the composition with the content of fluorite in the amount of 2% carbonate decomposing temperature is 760°C which is by 20°C lower than that of the composition without the additive of a mineralizer.

The mechanism of fluorite action, as may be supposed is in the formation at the initial stage of the intermediates that have relatively low melting points, which then involve in silicate-forming reaction dolomite, accelerating carbonates decomposition processes.

An intensification of decarbonization processes is shown by the estimated values of the activation energy that make 125.3 kJ/mol for the ceramic body without additive,for the masses with a content of 1% CaF_2 – 98.4 kJ/mol, with a 2% CaF_2 – 65.2 kJ/mol. The decrease in activation energy in 2 times increases the speed of decarbonization in the temperature range 660–750°C.

It should be noted that two endothermic effects can be clearly identified on DSC curve of a compound with the additive of 2% of fluorite. The first effect at a temperature of 720°C corresponds to the dissociation of magnesite $MgCO_3$. The differentiation of endothermic effects points to an active participation in the reactions of silication $MgCO_3$. Formed crystalline phases are magnesium silicates, as evidenced by X-ray phase analysis of samples hard-burned at a temperature of 700°C (Fig. 2b).

With increase of heat treatment temperature the intensity of magnesium silicate peaks increases, while dolomite decreases, and at a temperature of 800°C peaks corresponding dolomite are absent (Fig. 2a).

Typical for clay systems exotherm effect is observed in the temperature range 880–980°C with a maximum at 920°C which is due to lattice rearrangement of metakaolinite, transition of amorphized structure to cryptocrystalline.

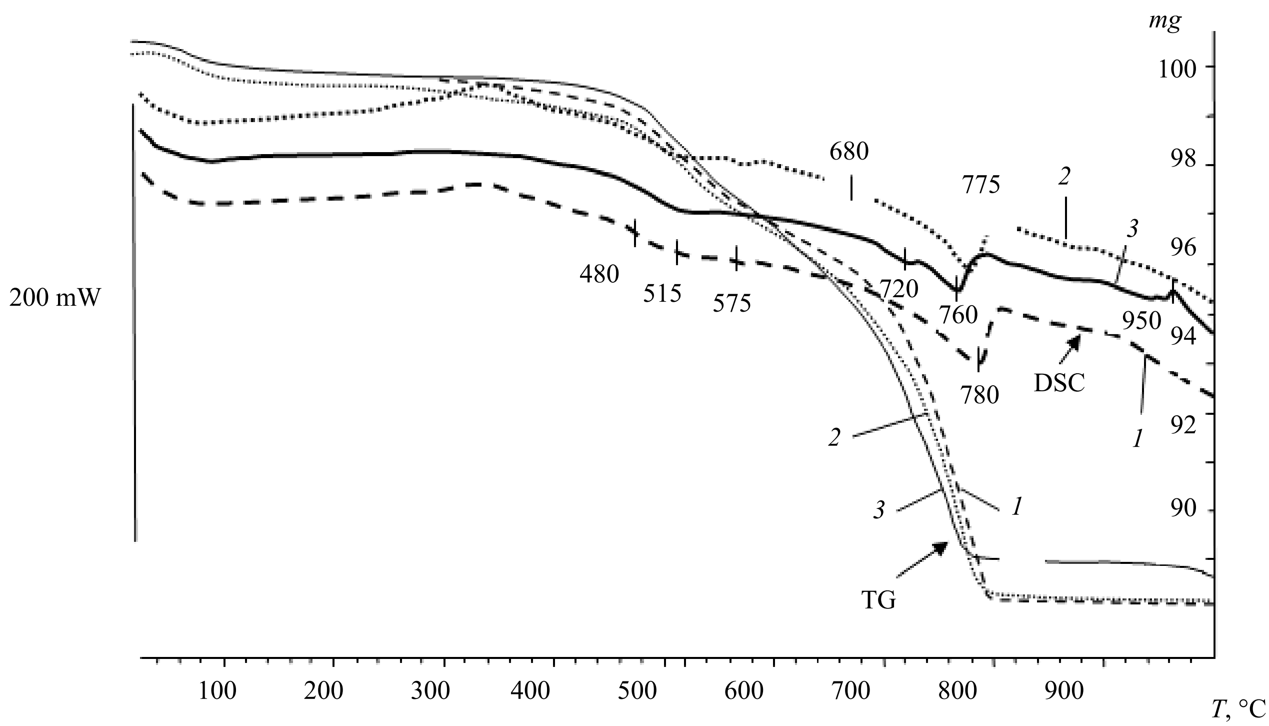
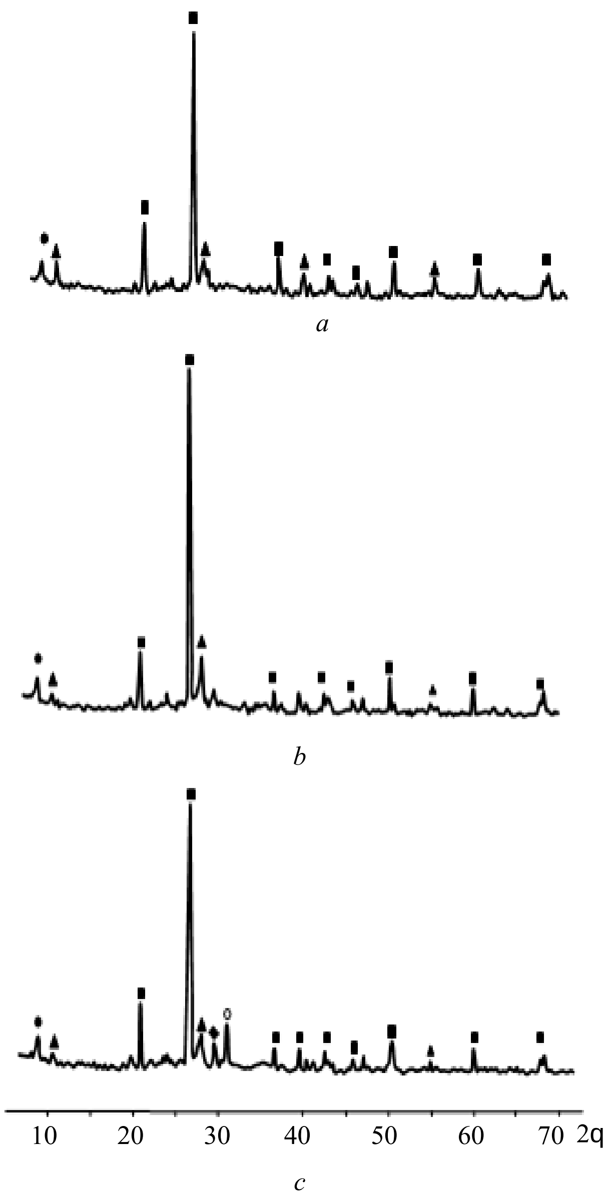


Fig. 1 DSC and TG curves of the investigated compounds:
1 – without additive; *2* – 1 mas.%CaF_2; *3* – 2 mas. %CaF_2



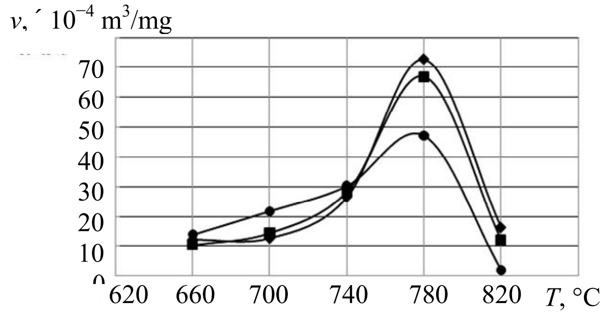
■ – SiO_2; ▲ – $MgSiO_3$; ○ – $CaMg(CO_3)_2$;
● – $KMg_3(Si_3Al)O_{10}(OH)_2$; ◆ – $CaCO_3$

Fig. 2. X-ray pattern of samples:
a– 800°C; *b* – 700°C; *c* – 600°C

When using fluorite in the amount of 2% the main volume of gaseous products evolves up to 750°C (Fig. 3). In the body without a mineralizer this process occurs mainly at temperatures above 750°C which is undesirable as it causes the formation of "pinholes" on the glaze coating.

The glaze applied when decorating, must meet certain requirements. Glaze sintering should occur at temperatures that facilitate the processes of degassing ceramic body, it must quickly spread and form a smooth surface for uniform coverage in a narrow temperature range of 1050–1100°C.

In this study we used glazes, synthesized in the system R_2O – RO – Al_2O_3 – B_2O_3 – SiO_2 (where R_2O – Na_2O, K_2O; RO – CaO, ZnO, MgO, BaO), the following component, mol. %: SiO_2 – 54.5–64.5; B_2O_3 – 5–15; CaO – 7.5–17.5; Na_2O, K_2O, BaO, ZnO, MgO, Al_2O_3 – the rest.



– without additive;
– 1 mas. % CaF_2; – 2 mas. % CaF_2

Fig. 3. The volume of evolved gases at different temperatures

The investigation of characteristic points of melting glaze coatings was carried out with the help of a heating microscope MNO-2 on powder glaze pressed cylinders (Fig. 4) and showed that for the formation of defect-free coating the temperature range between softening point and the formation of the hemisphere should be 70–90°C, and the glaze softening temperature should be shifted in the high-temperature region 1070– 1080°C. It facilitates carbonates decomposition processes that occur in the ceramic body, and it allows getting product with quality glazed coating.

As a result it is determined that the high content of calcium oxide in the compositions of glaze glasses in the amount of 10–15 mol. % shifts the temperature of coatings formation into high-temperature region 1060–1100°C and facilitates formation processes of glaze coating and ceramic crock. At the same time the nature of glaze viscosity change during cooling ceramic tiles in single-firing process promotes rapid solidification of glaze layer, creating favorable conditions for the formation of a quality defect-free coating [5].

Conclusion. According to the results of the research there is the following conclusion. When single-firing of tiles the main defects are "pinholes", caused by the inconsistency of the processes of ceramic body decarbonization and the formation of glaze coating. The presence of fluorite in ceramic body allows to intensify the process of dolomite decomposition and to shift it in the temperature range 670–700°C. As in the conditions of high-speed single-firing the processes of ceramic crock formation occur at high speed in a short period of time, the decarbonization temperature decrease by 20°C will create favorable conditions for the formation of a defect-free glaze coating.

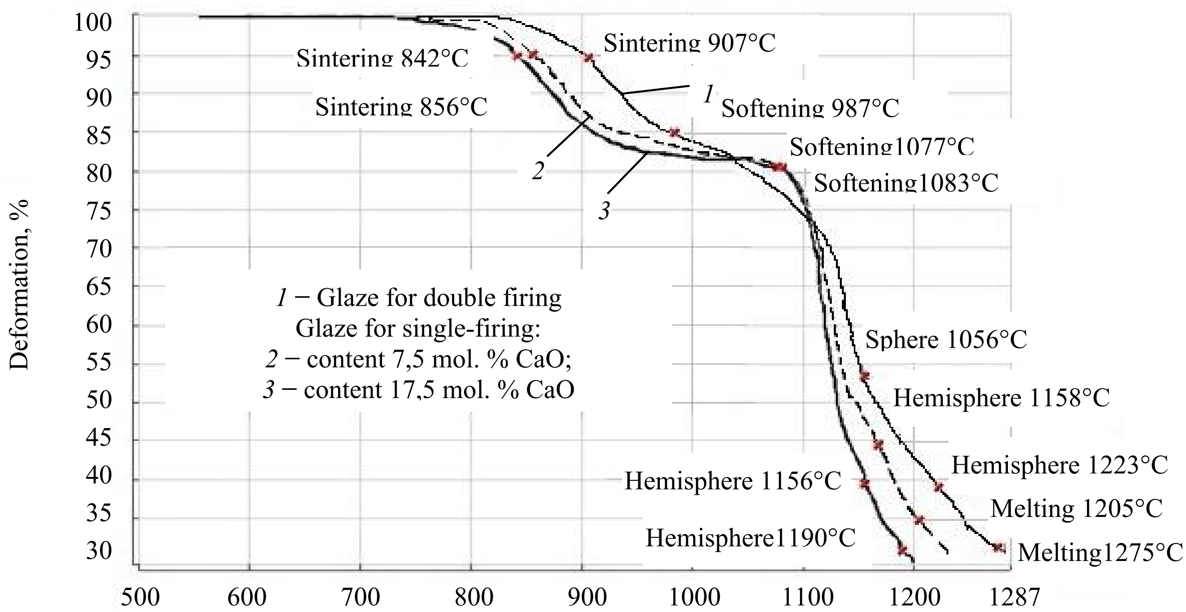


Fig. 4. Curves of glazes melting

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