Development of composite ceramic material using cullet

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Abstract. The research presents the results of the charge development for producing ceramic composite material, where ceramic particles of the crystalline structure serve as filler, and vitreous amorphous phase obtained by the introduction of the cullet and the flux into the charge at different firing temperatures serve as a binder. Herewith the cullet is used as a flux-strengthening additive, which is a source of vitreous phase, and the flux reduces the amount of the formed vitreous phase. Boric acid, feldspar, and dolomite separately have been used as fluxes in the current research. In the conducted experiments, the charge basic component was low-plasticity clay, which can be used for producing high quality products only with the introduction of functional additives. Basing on the obtained data, it has been stated that higher values of strength and lower values of water absorption for the developed material can be achieved at the introduction of 30 wt. % of the cullet and 2.5 wt.% of boric acid as a flux at the highest firing temperature of 1050°C. The developed charge composition facilitates broadening the construction materials production resource base due to the usage of low-demand low-plasticity clay and glass works waste. The material produced on the basis of this charge corresponds to the requirements for the construction materials used for indoor and outdoor facing of facades, socles of the buildings and facilities.

1 Introduction

Nowadays composite materials and composites are becoming more widely spread in many spheres of human activity. These materials should include two and more components, the components amount must be correlated and cause the formation of the required structure and properties. Herewith one of the components, called matrix or binder, composes solid phase in which other components, called fillers are spread. Composite materials advantages are the ability to combine the properties of the binder and the filler thus increasing their advantages and reducing disadvantages of the both components and entire composite material.

The correct selection of the binder, the filler and the production technology helps to produce composite materials for manufacturing the products with actual properties for the required application.

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This research considers the possibility to develop ceramic composite material for outdoor and indoor facing of the walls in buildings and constructions. For the mentioned application the material is to possess low water absorption, frost-resistance and good strength. In case of composite materials binder is to fill the pores and interstices in the material depth, reducing its water absorption and uniting filler particles into a solid frame. In composite materials amorphous vitreous phases serve as a binder and particles of crystal phase serve as a filler.

To receive the structure consisting of the alternating amorphous and crystal phases it is necessary to reach liquid phase sintering during ceramics firing. This problem is solved by the introduction of the functional additives into the charge and by the firing at the temperature, required for the transition of charge components into the melt. In this case the functional additives include flux-strengthening additives which are the source of the vitreous phase during firing, and the fusing agents which refer to the fusible substances in which melt other ceramics components can dissolve. Thus the flux application promotes liquid phase caking at much lower temperature thus decreasing production energy consumption, and lux-strengthening additives promote receiving considerably large amount of the vitreous phase.

To reduce raw materials expenses and to enlarge the resource base for the construction materials production it has been suggested to use low demand and low plasticity clay, cheap fluxes and cullet as a flux-strengthening additive as the charge components. Moreover cullet usage, which is a widely spread waste in the Vladimir region (up to 10% of the total waste [1]), will help solving the problem of the cullet accumulation.

The research authors previously conducted the research concerning the application of low plasticity clay together with the anthropogenic waste in the Vladimir region [1-4], and the development of the cullet utilization ways. In the course of the research the charge compositions for producing environmentally safe materials with rather high operational characteristics were developed. In the previously conducted research boric acid was used as a flux, which beside its principle function facilitated self-glazing effect [1, 4] of the produced ceramics.

The current research objective was the selection of charge composition and firing temperature for the ceramic composite material development for the production of the facing materials with high strength and low water absorption.

2 Materials and Methods

The clay of the Suvorotskoye field in the Vladimir region has been used as a basic component of the developed charge having the following composition (wt. %): $\text{SiO}_2 = 67,5$; $\text{Al}_2\text{O}_3 = 10,75$; $\text{Fe}_2\text{O}_3 = 5,85$; $\text{CaO} = 2,8$; $\text{MgO} = 1,7$; $\text{K}_2\text{O} = 2,4$; $\text{Na}_2\text{O} = 0,7$ [2]. Aluminum, calcium and magnesium oxides contained in the clay reduce its plasticity and consequently its plasticity index, determined by the standard method equals 5,2, and as a result refers to low-plasticity clay according to GOST 9169-75 [1]. Thus, without using these functional additives in the charge, based on the clay, the products possessing good strength and water absorption cannot be produced. Besides the products, made of low plasticity clay, possess low crack resistance and consequently in order to use this clay it is necessary to improve charge composition.

Flux-strengthening additive in the developed charge composition is a sheet window cullet of the following composition (wt. %): $\text{SiO}_2 = 73,5$; $\text{CaO} = 7,4$; $\text{MgO} = 1,9$; $\text{Na}_2\text{O} = 11,1$; $\text{K}_2\text{O} = 5,2$; $\text{Al}_2\text{O}_3 = 0,9$ [2]. Beside the mentioned above problem of the accumulation of this waste type in the Vladimir region the window glass has been chosen due to its low amount of impurities, including color impurities, which may influence color and characteristics of the produced materials.

Boric acid B type 2 (GOST 18704-78) - basic substance of weight content 98,6%, feldspar PShS 0,30-20 (GOST 13451-77) and dolomite DK-18-0,25 (GOST 23672-79) have been

used in the current research as fluxes. Boric acid has been chosen due to its good flux properties and it could considerably change the properties of the developed materials in the previously conducted experiments [1-4].

Feldspar has been chosen because at the temperatures over 900°C it produces a melt in which quartz and other minerals are dissolved [6]. As for dolomite it decomposes at the temperature of 700-900°C producing calcium and magnesium oxides which at the temperature over 1000°C form fusible compounds with the clay components [7].

The used feldspar was characterized by the following composition (wt. %): $\text{SiO}_2 = 62$; $\text{Al}_2\text{O}_3 = 24,4$; $\text{K}_2\text{O} = 8,1$; $\text{Na}_2\text{O} = 5,2$; $\text{Fe}_2\text{O}_3 = 0,3$. Dolomite in its turn had the following composition (wt. %): $\text{CaO} = 32,5$; $\text{MgO} = 18,8$; $\text{SiO}_2 = 2,4$; $\text{Al}_2\text{O}_3 = 1,2$; $\text{Fe}_2\text{O}_3 = 0,2$; $\text{CO}_2 = 55,1$.

The developed material samples were produced according to the semi-dry pressing technology [2]. The clay was preliminary dried up to the constant weight, then the clay, dolomite and cullet were grained with the further fraction size selection of max 0,63 mm. Afterwards the charge components were selected and mixed in dry state in the required by the experiments ratios. Then the mixture was wetted and mixed again to produce the molding compound of humidity 8 wt. % to produce the samples under the specific pressure of 15MPa and firing temperature of 1050°C for the further study of the researched properties. The samples based on the researched compositions were produced in batches by three samples each.

To define the charge components ratio and to assess the research results, density (ρ , kg/m^3), compressive strength (σ_{cs} , MPa), porosity (P, %), water absorption (W, %) and frost resistance (F, cycles) were studied according to the standard methods for ceramic materials of the obtained samples.

3 Results

To assess flux-strengthening impact of the cullet on the property of the developed material, initially the samples were produced on the basis of the studied clay with the addition of glass cullet up to 35 wt.% in every 5 wt. %. The results are presented in Fig. 1.

The received data proves that when the cullet amount in the charge increases up to 20 wt. % the properties begin to change intensively: compression strength increase and water absorption reduction. Further increase of the cullet amount causes less considerable changes of the considered properties. It might be connected with the fact that 20 wt.% of the cullet is enough to fill most of the pores and voids in the material and serve as a binder of the ceramics particles. The decrease of the compression strength when cullet amount exceeds 30 wt.% depends on the excess of the vitreous phase causing distancing of the ceramics particles. Meanwhile, the impact of the less solid and more fragile vitreous phase on the material strength increases. It should also be stated that at the excess of the vitreous phase the meltback of the samples edges and their deformation occurs.

At the second stage of the research, additionally selected before the experiment fluxes were introduced in the amount of up to 5 wt. % into the charge, based on low plasticity clay, containing 30 wt.% of the cullet (fig. 2).

Fig. 1. The impact of the cullet on the compression strength (a) and water absorption of the studied ceramic material.

Fig. 2. Fluxes impact on compression strength (a) and water absorption (b) of the researched ceramic material.

The obtained data indicates that the highest strength and the lowest water absorption are achieved when boric acid was used as a fusing agent. Meanwhile water absorption is gradually decreasing with the increase of the flux amount in the charge composition, but the compression strength reaches its peak when 2,5 wt. % of boric acid is applied but with the further increase of the considered additive it starts to reduce. Similar effect can be explained by the fact that boric acid melts and starts to perform fusing role at considerably lower temperatures (170,9°C), but the feldspar forms less liquid melt than boric acid and even at higher temperature (starting with 900°C [6]). The bigger part of dolomite is evaporated as carbon dioxide as a result of decomposition, the remained calcium and magnesium oxides form easily melted compounds at the temperature over 1000°C and the melt amount is much lower in comparison with the other two fluxes. Besides it should be noted that during

dolomite decomposing pores and voids appear, which at a certain moment reduce strength and increase water absorption.

The third research stage was devoted to the to the study of the dependence of the developed material properties on the firing temperature of the three different compositions: the charge without any additives, the charge including 30 wt. % of cullet, and the charge containing 30 wt. % of cullet and 2,5 wt. % of boric acid.

The research results show that the developed composition, containing flux-strengthening additive and a flux, possesses higher strength and lower water absorption. All compositions are characterized by their maximum strength at 1050°C with the further decrease of the considered property. It is connected with the fact that at higher temperature the excess of the vitreous phase is observed, thus leading to the strength reduction, as it was previously mentioned. As for the composition without additives its strength reduction and water absorption increase depends on the occurrence of the inner crystallization pressure [8] causing cracking.

Fig. 3. Firing temperature impact on the compression strength (a) and water absorption (b) of the studied ceramic material.

For the comparative assessment of the charge development results at the selected firing temperature the main operational characteristics have been determined for the three considered above compositions, presented in the table.

Table. The properties of the studied ceramic materials.

Additives, wt. %		ρ, kg/m³	σcs, MPa	P, %	W, %	F, cycles
Cullet	Boric acid					
-	-	2099	14,3	6,9	7,5	41
30	-	1687	25,6	4,8	5,2	51
30	2,5	1866	30,2	2,8	2,9	58

From the table it is clear that additives introduction sufficiently facilitates strength increase and water absorption decrease in comparison with the ceramic material, produced basically only on the studied clay.

4 Conclusions

The results of the carried out research demonstrate that the developed charge composition allows producing composite ceramic material where the filler includes the particles of the ceramics crystalline phase and the binder is a vitreous phase, received after the introduction of the cullet and boric acid into the charge. Herewith the cullet is a flux-strengthening additive which increases material strength and reduces its water absorption, but boric acid is a flux, which reduces the temperature of the liquid phase sintering of the produced material and increases the quantity of the obtained vitreous phase and consequently the increased impact on the structure and property of the composite ceramic material.

The basic components of the charge are low-plasticity clay (67,5 wt. %) which cannot be used without the introduction of the functional additives for producing high quality products and cullet (30 wt. %), which is a waste requiring utilization to reduce environment pollution. The application of the specified components for the constructional materials production helps to reduce expenses for the high quality initial resources and to widen raw materials base of the enterprises, producing construction materials.

The properties of the produced composite material allow using it for the production of the facing materials. The material density is comparatively low and it means that it will not provide high load on the basement and bearing structures. The material water absorption is low and frost-resistance consequently is rather high to be applied for outdoor facing of the facades and socles of the buildings and facilities. The strength of the developed material is considerably high and the received effect of the surface self-glazing not only reduces water absorption, but makes it possible to use this material for producing facades with self-cleaning property, when it rains and snows.

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