

Influence of Mineralogy of Clays on Structural and Textural Features of the Heat Effective Composite Material

Irina Anatolevna Ivleva, Pavel Vasil'evich Besedin,
Igor Ivanovich Nemets and Sergey Viktorovich Andrushhak
Belgorod State Technological University Named after V.G. Shukhov,
Kostyukova Street 46, 308012 Belgorod, Russia

Abstract: The study presents the results of thermal efficiency of composite materials for construction purposes on the basis of clays of different mineralogical composition and glass porous component research. It is shown that the clay minerals such as kaolinite, montmorillonite and hydrous micas affect not uniformly the composite structure formation processes. X-ray diffraction and optical-visual analysis methods of new growth crystallization temperatures in composites based on mono and multimineral clays are set. It is revealed that the beginning of the interaction between clay minerals and glass porous component particles depends on the corresponding mineral crystal lattice destruction. The fragmented porous structure of the composites microreinforced with new growths provides high physical and mechanical properties of the materials. The influence of the mineralogical composition of raw clay on formation porosity composites formation is shown. The porous structure with predominance of open macropores is formed in composites based on kaolinite and mesopores in the presence of montmorillonite and hydromica.

Key words: Glass porous component, structure, porosity, new formation, crystallization, the micro reinforcing

INTRODUCTION

Clay raw materials, consumption of which is continuously increasing are used in the production of ceramic wall materials. This imposes the use of low grade rocks, excluding their technological properties. It does not allow products that meet both in appearance and physical-mechanical properties.

The mineralogical composition of clay raw materials affects the synthesis of crystalline and amorphous phases in the process of silication, forms composite material. Its structural and textural features are characterized by the phase composition, size and shape of the pores, their distribution and phases in-touch capabilities at interphase borders (Klyuchnikova *et al.*, 2003, 2004; Klyuchnikova and Lumar, 2005a, b, 2006; Klyuchnikova, 2007, 2012a). Directed synthesis in silication processes provides products with a given structure (Klyuchnikova, 2012b, 2013).

One of the common methods of creating thermal efficient materials is porization of their structure. Porous aggregates introduction unlike most common porization methods increases the products strength up to 20 MPa. A very effective method of the material strengthening is its micro-reinforcement (Besedin *et al.*, 2005; Ivleva *et al.*, 2012; Nemets and Ivleva, 2009).

PROCEDURE

This study presents the results of thermal efficiency of composite materials research using Glass Porous Component (GPC-foam glass production waste), performing the role of porous forming, inert and agglomerating component in clay-containing mixtures of different mineralogical composition. The GPC chemical composition represented, mass. %: SiO₂-71.6; Al₂O₃-2.7; Fe₂O₃-0.3; CaO-8.2; MgO-1.1; K₂O+Na₂O-14.7; SO₃-0.4. Optimal GPC grain size from 0.1-2.5 mm, a bulk density of 260 kg/m³. Pre-dried and ground clays were sifted through a sieve with 1.00 mm diameter holes. Clays and GPC were batched according to the formulation, mixed in a laboratory screw mixer while adding water in accordance with mass mixing moisture content. The plastic mass was formed by a hydraulic press under the specific pressure of 2-3 MPa.

Molded samples (blocks 30×30, 50×50 mm, cylinders with a diameter and a height of 50 mm) were dried to a residual moisture content of 2% and then kilned in an silit oven at 950, 1050 and 1150°C at a rate of temperature rise 2-3°C/min and ageing the sample when the highest temperature 2 h. After cooling the samples strength, water absorption, porosity, thermal conductivity, density and shrinkage during drying and firing as well as cold resistance were determined.

THE MAIN PART

For the study of the new growths synthesis using X-ray diffraction, differential thermal analysis and petrographic analysis methods were used. Proceeding from the assumption that the type of crystalline lattice and hence one or another type of clay minerals affects the processes of structure formation during the firing. Phase transformations occurring during sinterin mixtures of kaolin, bentonite, hydrous micas with and without the addition of GPC were investigated.

Laws of GPC influence and the clay mineral species on structure formation and properties of the composites were studied in monomineral GPC and GPC-polymineral clay systems.

Initial charge components differ in mineralogical and granulometric content. Chibisovskaya clay is kaolinite-hydromicaceous, Shebekinskaya is montmorillonite-hydromicaceous high-muscovite (25 wt.%) Gorodishchenskaya is montmorillonite-hydromicaceous. GPC number in charge with monomineral and multiminerall clays varied from 0-40 wt.% (Table 1).

Mineral formation processes in GPC monomineral systems, GPC-polymineral clays were investigated at

firing temperatures 950, 1050 and 1150°C. With X-ray phase and optical visual analysis methods temperatures of the new growth crystallization in GPC-monomineral and GPC-polymineral clay systems have been established.

On a ternary diagram of CaO-Al₂O₃-SiO₂ state the temperature of initial appearance of the melt, the amount and composition of the liquid and crystalline phases were theoretically determined. The mineralogical composition of the samples calcined at 950 and 1050°C and the data obtained from the study in Table 2.

With optical and scanning electron microscopy methods in the microstructure of the samples (4 k, 4 m, 4 gs) of monomineralic clays containing GPC high isotropic glass phase and new growths in the form of needle and prismatic crystals have been identified. The structure of the composites is represented with fragments consisting of spherical pore sized <0.1-300 microns, the contact layer and interfragmentary space (Fig. 1).

New growths penetrate the glass phase and form a felt-like grid microarming the inner surface of the pores (Fig. 2), the contact layer between glass porous component and clay matrix (Fig. 1b) and inter fragmentary space (Fig. 1a, b).

The fragmented porous structure microreinforced with new growths of anorthite, wollastonite, diopside, (alpha)-tridymite improves the physico-mechanical properties of ceramics as compared with the control formulation (0 k, 0 m, 0 gs).

While increasing calcination temperature from 950-1150°C in the samples of (2 k, 4 k, 2 m, 4 m, 2 n, 4 gs) an intense anorthite crystallization is being contemplated dissolving simultaneously quartz in the glass melt. Anorthite reduces composites firing shrinkage. Oxides CaO, MgO, K₂O, Na₂O, inserted with glass pourous

Table 1: Mixtures compositions and ciphers

Components	Components and mixtures of components identifier by weight (%)					
	0 k	4 k	0 m	4 m	0 h	4 h
Kaolin	100	60	-	-	-	-
Bentonite	-	-	100	60	-	-
Hydromica	-	-	-	-	100	60
GPS	0	40	0	40	0	40
Ciphers	0 sh	4 sh	0 gs	4 gs	0 ch	4 ch
Shebekinskaya clay	100	60				
Gorodishenskaya clay			100	60		
Chibisovskaya clay					100	60
GPS	0	40	0	40	0	40

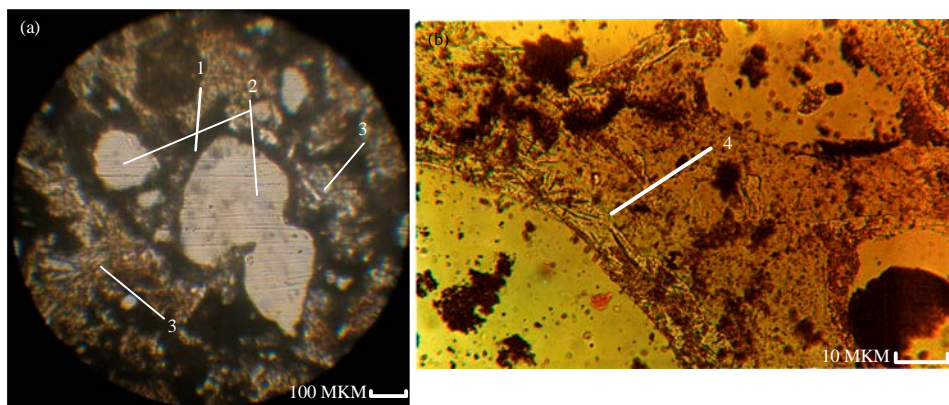


Fig. 1: Photomicrographs of fragmented microreinforced porous structure (T_{firing}-1050°C); a) composition (4 gs); b) composition (4 k): 1: fragment of the structure; 2: pores; 3: interfragmentary space crystallization; 4: treads microreinforced with plated needles

Table 2: The mineralogical composition of composites samples

		New growths and their denominations													
Clays	Identifier mixture	The firing temperature (°C)	Quartz	α -cristobalite	α -tridymite	Anorthite	β -wollastonite	Diopside	Mullite	Hematite	Kaolinite	Illite	Montmorillonite	Muscovite	
			(Qv)	(cr)	(tr)	(An)	(wol)	(D)	(Mul)	(H)	(K)	(Il)	(m)	(Mus)	
Monomineral	0 k	950	+								+				
	4 k		+		+	+	+		Sl						
	0 m	950	+	+						+			+		
	4 m		+	+				+		+					
	0 h	950	+										+		
Multimineral	4 h		+		+	+							+		
	0 sh	1050	+		+									+	
	4 sh		+		+		+							+	
	0 gs	1050	+							+					
	4 gs		+		+		+			+					
	0 ch	1050	+							Sl					
	4 ch		+					+		+					
	Theoretical phase composition of calcine mixtures (defined by the state diagram of the system CaO-Al ₂ O ₃ -SiO ₂)														
	Clays	Identifier mixture	The temperature of appearance of a liquid phase (°C)	Composition of crystalline phases											
				Tr	An	Wol	Mul								
Monomineral	0 k	1345	++	+	-	+++									
	4 k	1345	+	++	-	++									
	0 m	1345	++	+	-	++									
	4 m	1165	+	+	++	-									
	0 h	1345	+	++	-	++									
Multimineral	4 h	1165	++	+++	+	-									
	0 sh	1345	++	+	-	+									
	4 sh	1165	++	++	+	-									
	4 gs	1345	++	+	-	+									
	4 gs	1165	++	+	+	-									
	0 ch	1345	++	-	-	+									
	4 ch	1165	+++	++	+	-									

-. Not available; +: little; ++: much; +++: lots of

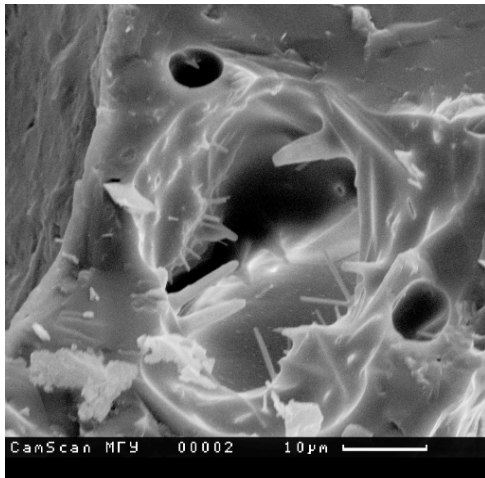


Fig. 2: Micrograph of composite sample (Tfiring-1050°C) growth of crystals in the pore structure (4 m)

component weaken the crystallization of cristobalite formed from degradation products of montmorillonite and reduce expansion of composition (4 m). In hydromica samples with GPS (4 gs) compressive strength is 70 MPa as a result of co-crystallization of anorthite α -tridymite and diopside.

Analyzing the location of compositions points of (Table 1) on the diagram of the CaO-Al₂O₃-SiO₂ system we can conclude that the introduction of foam glass reduces the temperature of melt appearance ~180°C down changes the composition and proportion of crystalline phases. Crystallization of β -wollastonite creates conditions for increasing the amount of anorthite. Starting interaction between the clay minerals and the foamed glass particles depends on the degradation temperature of the respective crystal lattice of the clay mineral which rises in a series of bentonite, hydromica kaolinite.

Glass porous component in compositions with multimineral clays, promotes the dissolution of quartz and cristobalite in product structure, increases the amount of crystalline phase not prone to polymorphism at respective burning temperatures. The structure of materials is also fragmented, microreinforced with α -tridymite, anorthite β -wollastonite, diopside, hematite crystals. It improves the physical and mechanical properties of composites. Samples of Chibisovskoy kaolinite hydromica clay composition after 4h firing at 1050°C showed a compressive strength-32 MPa, flexural strength-6.3 MPa, the thermal conductivity coefficient-0.370 W/m·K at a density of 1360 kg/m³.

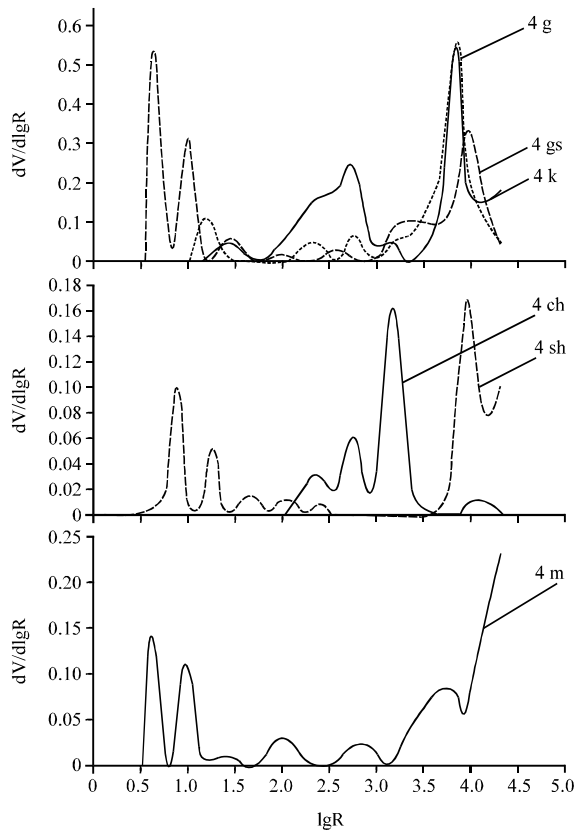


Fig. 3: Differential distribution of pores in the samples based on mono- and multiminerals with foam glass (mercury porosimetry)

According to mineralogical calculation, the optimal ratio in Shebekinsky clay forming minerals, wt.%: Montmorillonite-20, glauconite-15, muscovite-25, silica-32, Calcite-9, provides a composition with a GPS high physico-mechanical properties of the composites 4 Sh: compression strength-44 MPa, flexural strength-12 MPa, heat transfer coefficient-0.268 W/m·K at a density of 1030 kg/m³ due to intense crystallization of anorthite β-wollastonite α-tridymite, diopside.

Porosity studies were conducted on a porosimeter of low pressure created by Leningrad Institute of Technology and Visual-Optical Methods. As control compositions, samples manufactured from raw batches of Table 1 were applied.

According to the International Union of Pure and Applied Chemistry (IUPAC) classification according to largest hydraulic radius: submicropores with r_{eq} to 0.2 nm micropores, r_{eq} from 0.2-1.0 nm mesopores from 1.0-25 nm and macropores more than 25 nm (Strelov, 1972). Maximum number of macropores with a hydraulic radius 26-325000 and 20 nm mesopores is characteristic for samples of 4 k.

At a total open porosity of 32% ratio between macro and mesopores is 31.64 and 0.36%. Differential curve character (Fig. 3) of 4 m composition indicates an increase in the number of pores with a smaller hydraulic radius. The 7.9-15.7 nm pores is 7.43% of the total, 40.39% are pores 39-312500 nm. The ratio of open to the total porosity is 0.51 indicating that elevated levels of closed pores contents. Samples based on hydromica and foam glass are characterized by a significant content of pores with sizes ranging from 4-20 nm to 26-325000. In total open porosity of 38.6%, pores with sizes <20 nm are 11.54%, the remaining 27% occupy macropores. The total 4 gs composite porosity is 52% of which 15.5% are mesopores and 36.5% are macropores. The ratio of $P_{open} : P_{total}$ - 0.74. Closed porosity was 14%. However, it should be noted that when preparing the samples (6×6×1.5 mm) for mercury porosimetry internal surface of the samples is renovated which increases the open porosity. The open porosity of the initial samples of 4 gs composition (1150°C) - 2.4% against 38.6% after preparation for porosimetry.

When analyzing the results of samples from porosimetry multiminerals with foam glass it is noticed the influence of clay minerals on porosity ratio. For Shebekinskaya clay samples with a high content of montmorillonite, glauconite and muscovite the mesopores equivalent radius is 4-20 nm (11.5%), similar to the mesopores in hydromica and montmorillonite. Macropores number is 26-375.000 nm 37.5% when the total porosity is 49.0% and open porosity is 29.5%.

When the content of 40 wt.% Foam glass in Chibisovskoy samples of kaolin-hydromica clay total porosity amounted 32.69% and an open porosity - 14.89% mesopores in these specimens were not observed. Number of macropores with a hydraulic radius from 154-280000 nm is 100%. Ratio of $P_{open} : P_{total}$ - 0.57.

For samples of Gorodyschenskaya montmorillonite hydromica clay the presence of small mesopores with hydraulic radius from 4-20 nm is peculiar. Maximum on porosity distribution curve corresponds to the hydraulic radius of 14.12 nm.

RESULTS

It has been thus established that the mineralogical composition of the clay material influences the formation of ceramic texture. Texture with a predominance of open macropores is formed in the samples (4 k) on the basis of well-crystallized kaolinite. Increased content in the bentonite leaf-fine particles of montmorillonite and a significant amount of melt in hydromica causes the formation of closed mesopores in samples (4 m) and (4 gs) after firing.

Clayey material fraction content of <1 micron (44%) increase in Shebekinskaya hydromica montmorillonite clay contributed formation of a significant amount of closed mesopores in samples (4 sh). In this regard, the ceramic composition samples 4 m, 4 sh and 4 gs had the lowest water absorption and high strength ratios 31, 44, 70 MPa, respectively.

Starting interaction between clay minerals and glass porous component depends on the destruction temperature of the clay mineral crystal lattice which rises in a series of montmorillonite-hydromica-kaolinite.

CONCLUSION

Glass porous component activating effect on processes of phase and structure formation during the firing of the composite material obtained on the basis of clays of different mineralogical composition and glass porous component has been revealed. It is shown that the introduction of glass porous component to the initial clay mass structure promotes firm porous fragmented structure formation. During the sintering process microreinforced of the pore inside surface of the contact layer and inter fragmentary space with non-isometrical elongated crystals of anorthite, wollastonite, albite, diopside α -tridymite, mullite takes place.

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