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The Use of a Microwave Electromagnetic Field for Sintering Polymineral Compositions from Clay Raw Materials

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Abstract. An analysis of the results of using an electromagnetic field for processing inorganic compositions of various compositions is presented. A noticeable change in the properties of materials is shown (decrease in defectiveness of metal oxide powders, increase in strength and toughness of traditionally brittle materials). The problems of technology due to the selectivity of heating in the microwave field of multicomponent mixtures are shown. The results of sintering of polymineral compositions based on clay raw materials, the phase composition, the presence of nanosized phases and a large amount of glass phase in samples fired without defects are presented. The role of fusible salt fluxes is shown. The influence of the energetics of the endothermic process of decomposition of the raw material composition on the quality of the sintered material is noted. The need to study the features of the process of sintering of polymineral compositions in a high-frequency electromagnetic field, the importance of the results obtained for the development of an ecological, energy-efficient technology for sintering ceramic materials is shown.

INTRODUCTION

A significant number of works have been devoted to the processing of inorganic compositions in a microwave field. Particular interest in this direction is caused by the possibility of obtaining a material with improved properties. The increased rate of solid-phase reactions in the entire volume of the material ensures the formation of a highly dispersed sintered composition with special, often extreme properties. It was found that the treatment of crystalline oxide materials in a microwave field made it possible to obtain oxide powders of low defectiveness [1]. Data on increased fracture toughness for traditionally brittle materials such as ceramics are important [2, 3].

The selectivity of heating in a microwave field creates problems in the sintering of multicomponent mixtures, which include natural aluminosilicate, mainly polyoxide raw materials [4 - 6]. In this way, you can modify, design the structure of the material.

The results of studies on the synthesis of nanosized materials have shown that the treatment of suspensions with electromagnetic high-frequency radiation leads to the formation of a special high-strength structure, which is formed during the sintering of the material [7, 8]. This is of particular importance in the development of technology for sintering natural aluminosilicates, which are used to obtain clay-based ceramic and refractory materials. The study of the features of sintering of clay compositions in the microwave field has a great innovative potential and makes it possible to obtain data for the development of an ecological sintering technology, an alternative to the traditional ceramic technology by convection.

As the thermodynamic analysis of clay compositions shows, when heated in the temperature range of 400-600 °C, the initial components of the mixture decompose, fusible fluxes melt, and high-temperature phases begin to form. In the microwave field, sintering begins in the interfacial region and is enhanced in the presence of a liquid phase due to diffusion [9].

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The sintering process is influenced by the mineral composition of the clay composition, the presence of a flux additive, which increases the appearance of a liquid phase, chemical reactions and diffusion processes are enhanced throughout the entire volume of the material, and uniform sintering of the material [10] is achieved.

In the ceramic, glass and metallurgical industries, fusible salts, alkali and alkaline earth metal halides are used as fluxes to reduce the melting temperature of the charge. Reducing the temperature, the duration of heating the charge and increasing the intensification of sintering is possible when exposed to an electromagnetic field of high frequency [2, 11].

It is believed that dipole polarization, electronic and ionic conductivity are the main mechanism in the interaction of matter with the microwave field [12, 13]. The presence of polar molecules in salt solutions of clay compositions determines the mechanism of processes during heating in a microwave field. The magnitude of energy absorption by this mechanism can be associated with the freedom of movement of molecules, ions [13]. The use of salt fluxes in clay compositions involves the introduction of salt solutions into the composition. In this case, the absorption mechanism is realized, due to the conductivity due to the presence of ions, the size of which may be important during their migration and the release of thermal energy associated with an alternating electric current [13]. Predominantly ionic conductivity is typical for double and triple flux systems [14].

In works studying the thermodynamics of solid-phase reactions of formation of high-temperature phases during sintering, the dependence of the enthalpy of dehydration of a clay composition on the presence of exchange cations of a clay mineral [15, 16] has been established. The determination of the cation-exchange capacity of the mineral, the enthalpy of dehydration of clay was carried out using synchronous thermal analysis [15, 17].

Analysis of the results and directions of research into the mechanism of sintering of inorganic substances in an electromagnetic field showed the need to study the features of sintering of multicomponent mixtures, such as natural aluminosilicate raw materials.

The aim of the work was to study the peculiarities of sintering of clay raw materials and the effect on the quality of the sintered material of additives of salt fluxes, which are widely used in the metallurgical, ceramic and glass industries [17].

MATERIALS AND METHODS

For the manufacture of samples, clays of similar chemical composition were chosen, wt. %: 56-58 SiO_2, 20-30 Al_2O_3, 4-8 Fe_2O_3, 2-4 CaO + MgO, 1-2 K_2O + Na_2O. Clays with a similar content of basic minerals: bentonite clay (60% montmorillonite, 5% mica), refractory clay (60% kaolinite, 5% mica). Sodium salts with different structure and anion polarity used in the ceramic and glass industries were chosen as salt fluxes: $Na_2B_4O_7$ (Russian Federation State Standard GOST 8429-77) and NaCl (Russian Federation State Standard GOST 51574-2000).

A Samsung M 1711 NR microwave oven with an output radiation power of 800 W and an operating frequency of 2.45 GHz was chosen for sintering the samples. The furnace is equipped with a muffle insulated with mullite-silica insulation and a thermocouple with a radiation-protective coating. The thermocouple junction is installed in the immediate vicinity of the samples. The rate of temperature rise in the microwave oven - 30 min. Heat treatment was carried out to a temperature of 1000°C with holding at the maximum temperature for 5 min. Samples 20x20x20 mm in size were made using plastic technology from pre-ground clay moistened with saline. Without preliminary drying, the samples were fired in the muffle of a microwave oven. The behavior of each composition of the clay-salt composition during heating was studied by the method of synchronous thermal analysis (STA) on the device of a synchronous TG - DTA / DC analyzer (quadrupole mass spectrometer QMS403C) - equipment of the Tomsk Materials Science Center for Collective Use, which is part of the Tomsk Regional Center for Collective Use NU TSU. X-ray phase analysis was carried out on a Shimadzu XRD 6000 diffractometer in CuKα radiation (PDF 4 + base, POWDERCELL 2,4 full-profile analysis program), sample fractures were recorded on a system with an electron and focused ion beam (Quanta 200 3D).

RESULTS

Samples with the addition of fluxing salt sintered without damage. Thermal analysis was used to study the energetics of processes occurring in the temperature range of destruction of the main components of clay-salt compositions and the beginning of the formation of high-temperature phases.

The results of thermal analysis of clay compositions in the temperature range of decomposition of clay minerals are shown in Fig. 1. The combined endothermic reflections of the differential thermal curves of the compositions are presented in the temperature range of the appearance of surface defects of prototypes during heating in a microwave field. It can be seen that the dependence of the energy value of the endothermic process on the type of salt modifier is traced with a shift in the maximum of the endothermic process to the region of low temperatures.

The greatest endothermic effect is observed in compositions based on refractory clay. A sample of refractory clay was split, with the addition of $Na_2B_4O_7$ - had single surface cracks, with NaCl salt was fired without destruction. Samples based on bentonite clay had no defects after firing.

In the temperature range of 400-600 °C, the mineral constituents of clays and fluxes are destroyed, and the formation of liquid and high-temperature phases begins. Analyzing the curves, it can be assumed that this process is affected by the structural features of the clay mineral and the fluxing salt.

In clays in the temperature range of 400-600 °C, the destruction of the crystal structure of clay minerals (hydroaluminosilicates), the release of crystallization water and the formation of high-temperature phases [11, 15, 16] begin. For formulations with added salts, water vapor can initiate the formation of liquid and high-temperature phases (Table 1). It can be seen that the compositions based on bentonite clay have the highest percentage of glass phase.

The endothermic effects of samples based on bentonite clay are characterized by low energy and low weight loss. This phenomenon may be related to the cation exchange capacity, which is high for montmorillonite of bentonite clay [15, 17]. The composition of burnt samples of bentonite clay includes crystalline phases of different composition and a large percentage of amorphous glass phase (Table 1).

For samples based on bentonite and refractory clay with the addition of NaCl salt, endothermic processes occur at almost the same temperature, but with significant differences in process energy and mass loss. This may be due to differences in the mineral composition of clays. For refractory clay in a number of compositions: clay without flux - clay with $Na_2B_4O_7$ - clay with NaCl, the energy of the process and the temperature of the endothermic process decrease, and the mass loss increases. For compositions based on bentonite clay (clay without flux - clay with $Na_2B_4O_7$) the energy of the process increases, the maximum reflex temperature of the endothermic process and mass loss decrease.

TABLE 1. Phase Composition of Samples Fired in Microwave.

Composition	Phases Identified	Weight Percent	Crystallite Size, nm
Bentonite clay + $Na_2B_4O_7$	SiO_2	18	72
	$NaAlSi_3O_8$	22	20
	$NaCaB_5O_9$	27	30
	$CaMgSi_2O_6$	20	68
	CaB_2O_4	4	27
		Amorphous glass phase 29 %	
Bentonite clay + NaCl	SiO_2	2	> 100
	$NaAlSi_3O_8$	23	35
	$Na_{7,5}(Al_{7,2}Si_{8,8}O_{32})$	37	30
	Al_2SiO_5	38	22
		Amorphous glass phase 40 %	
Refractory clay + $Na_2B_4O_7$	SiO_2	95	82
	CaB_2O_4	5	27
		Amorphous glass phase 26 %	
Refractory clay + NaCl	Al_2O_3	19	6
	SiO_2	63	63
	Al_2SiO_5	17	3
		Traces of the amorphous phase	

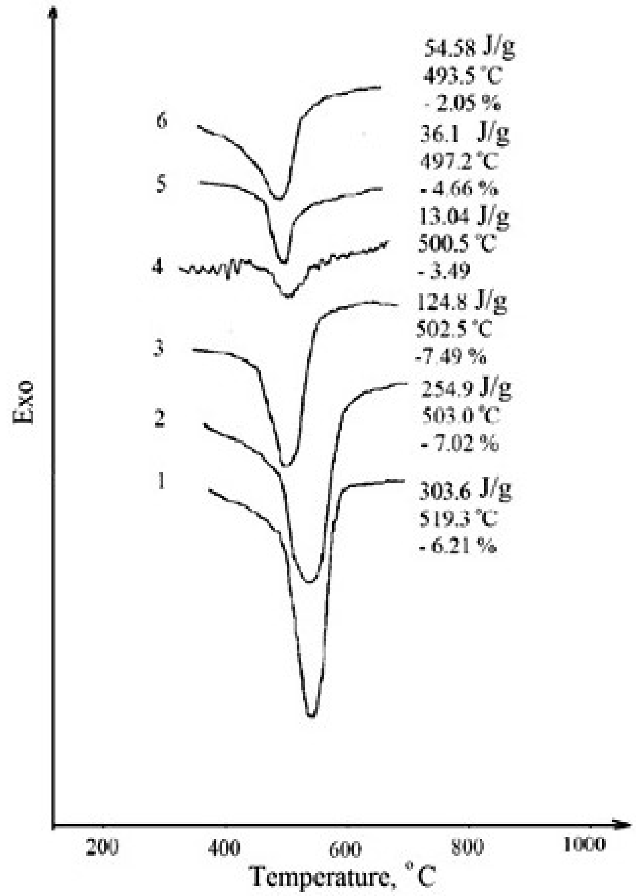

FIGURE 1. Endothermic effects of compositions based on: refractory clay (1), refractory clay and $Na_2B_4O_7$ (2), refractory clay and NaCl (3), bentonite clay and NaCl (4), bentonite clay (5), bentonite clay and $Na_2B_4O_7$ (6).

The energy of endothermic processes of refractory and bentonite clays with additives in the series NaCl , $Na_2B_4O_7$ increases. This may be due to the size of the [15] anion. With an increase in the size of the anion, the ability to diffuse decreases, which complicates the process of entry of the ion into the adsorption layer of the clay exchange complex [15].

The results of X-ray phase analysis of samples fired in a microwave field showed the presence of a crystalline phase of nanosized dispersion and the presence of an amorphous phase (Table 1). Compositions with $Na_2B_4O_7$ based on bentonite and refractory clays have a similar amount of glass phase (29 and 26%). The composition of the crystalline phase differs significantly. This affects the significant differences in the strength of the samples (Fig. 2).

Comparing the strength and composition of samples based on bentonite clay, it can be seen that the strength of the samples is mainly influenced by the composition and amount of the crystalline phase (Fig. 2). The sample based on bentonite clay and $Na_2B_4O_7$ contains fibrous crystals and shows high strength (Fig. 3a).

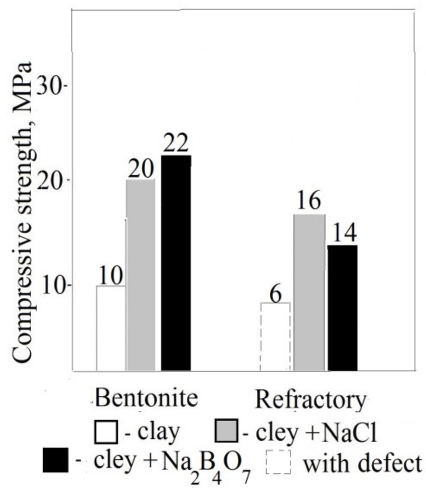

FIGURE 2. Compressive strength of fired samples molded from plastic masses based on bentonite clay (Bentonite), refractory clay (Refractory) with fluxes.

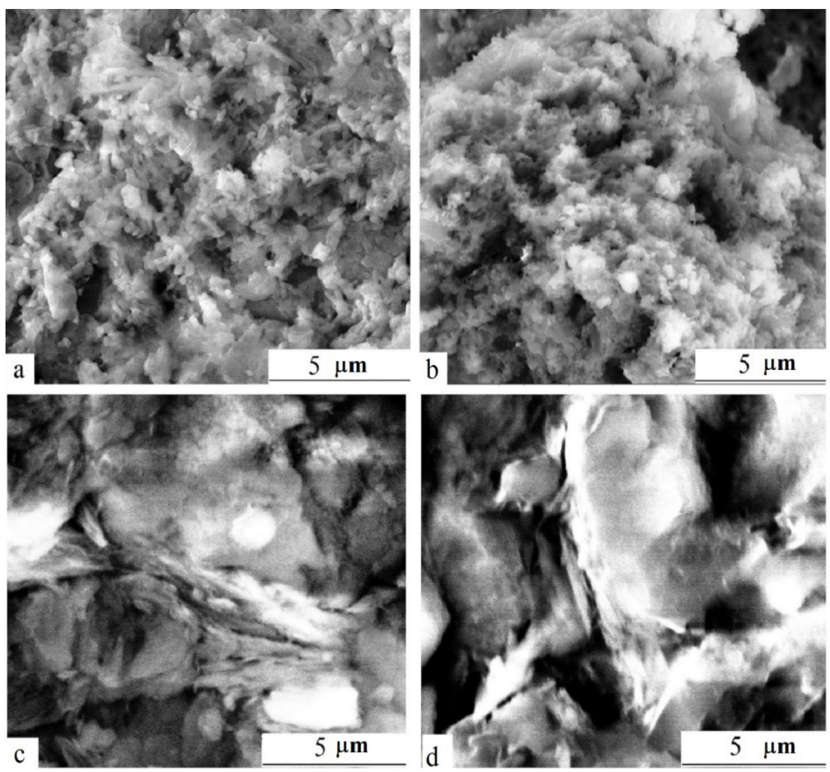

FIGURE 3. Fracture structure of samples fired in a microwave field based on bentonite clay and $Na_2B_4O_7$ (a), bentonite clay and NaCl (b), refractory clay and $Na_2B_4O_7$ (c), refractory clay and NaCl (d).

The microstructure of the fractures of the samples is shown in fig. 3. Compositions based on bentonite clay have a uniform structure. Fibrous inclusions of presumably calcium borates and calcium aluminosilicates (Table 1) are seen in the composition with the addition of $Na_2B_4O_7$. For compositions based on refractory clay, a dense structure is visible due to the large amount of quartz.

Analysis of the sintering process in the field of microwave clay compositions showed that in order to obtain high-quality samples, it is necessary to analyze the energy of the endothermic process in the temperature range of 400–600 °C.

DISCUSSION

The paper presents information about the results of the study of the structure and properties of materials obtained during the processing of inorganic compositions in the microwave field. The special properties of materials obtained under microwave sintering conditions and the problems that arise during the sintering of multicomponent mixtures due to the selectivity of heating in a microwave field are shown [4].

From this standpoint, the study of the features of sintering of clay compositions in a high-frequency electromagnetic field is promising both for understanding the sintering mechanism and for developing an environmentally, energy-efficient alternative to the traditional ceramic firing technology.

The results obtained in the present work make it possible to better understand the mechanism of sintering of a polyoxide composition during high-speed heating in a microwave field. The influence of the energy of the process in the zone of phase transformations of the clay composition, the mineral composition of the clay and the type of salt flux on the quality of sintering, the structure and properties of the fired material is noted. The study of the features of sintering of clay compositions in the presence of a salt flux makes it possible to supplement the idea of the sintering mechanism in a microwave field with experimental data, to note the influence of the physicochemical features of polar molecules of salt fluxes in clay compositions on the sintering process [12, 13]. The results obtained in the work can be useful for understanding the thermodynamics of the formation of high-temperature phases during sintering, choosing the optimal composition of the clay composition during sintering in a microwave field, and the possibility of designing the structure and properties of a ceramic material.

The results of the studies carried out can be used in the development of technology for obtaining traditional types of clay ceramic materials, such as high-strength building and refractory ceramics, as well as polyoxide catalysts [5], ceramic absorbers of microwave energy [18], solid oxide fuel cells [19], etc. The results of the work can be useful in developing the fundamentals of efficient ceramics technology.

CONCLUSION

According to the results of the research, it was established:

- The sintering process of samples from a polymineral composition based on natural clays in the microwave field is possible in the presence of salt fluxes;
- The quality of sintering samples depends on the mineral composition of the clay and the nature of the flux;
- The quality of sintering clay composition affects the value of energy of endothermic process in the temperature range 400-600 ° C;
- The presence of fibrous formations in the composition based on bentonite clay and $Na_2B_4O_7$ was established.

The results of the study of sintering in the microwave field of clay-salt compositions showed the prospect and direction of research on the development of the fundamentals of ecological technology for the production of ceramics and coincide with the results of the study of sintering in a high-frequency electromagnetic field of inorganic compounds.

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