The Microwave Electromagnetic Field is the Basis for Environmentally Friendly Technologies for Energy Generation and Production of Firing Material

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Abstract. Literature information about the problems in the energy and technology of firing materials is given. The possibility of sintering aluminosilicate clay raw materials, traditional for the production of clay and oxide ceramics, is established. The results of firing samples of natural aluminosilicates in microwave and muffle furnaces are considered. The data on the microwave field effect on aqueous solutions of hydroaluminosilicates, the mechanism of microwave energy absorption and the possibility of its use in hydrogen power engineering are considered. Prospects of aluminosilicate clay raw material as a raw material for hydrogen storage ceramic material are considered. The influence of the microwave field on the structure and properties of the material is shown. The phase compositions of fired materials made of refractory and bentonite clay with NaCl have been determined. Influence of mineral structure of clay raw material and fluxing salt on the sintering process is established. The presence of nanoscale phases was found for the compositions fired in the microwave field Samples with nanoscale phases showed the greatest strength. Samples from the mass with the addition of NaCl show high quality and increased strength of the samples. Samples with the addition of marl and NaCl salt showed high strength and sintering quality.

INTRODUCTION

Without energy costs, most material processing and production facilities cannot operate. First of all, it concerns productions related to the use of energy obtained from the combustion of carbon fuel. The environmental side of such productions becomes a priority problem. At present, compliance with environmental, energy and resource-saving requirements is a priority side of any promising material production technology.

Similar problems arise for energy producers. Since energy is currently the basic foundation of most production processes and the life of society, the progress of the economy of modern society is associated with an increased demand for environmental energy resources, which in our time are represented by natural fuels. A comprehensive solution to environmental problems is associated with the reorganization of both production and energy technologies.

The search for new technologies in power engineering went in parallel with the development of promising technologies in the production of fired materials. The need to develop the technology for the production of materials with improved performance properties was related to the demands of space, nuclear power, microelectronics, and nanotechnology for materials with special material properties that cannot be achieved by traditional technology. The solution to the problem was found in the technology of firing in a high-frequency electromagnetic field. The properties of the materials obtained by high-speed sintering in the microwave field, associated with the formation of nanoscale material structure, were characterized by special, extreme properties [1-6].

Energy transfer rate during interaction with the substance is one of the most important parameters of the ultrahigh-frequency energy of the electromagnetic field. This results in the separation and leveling of surface defects, reduction of grain and defective material structure sizes, formation of material structure with increased fracture strength and toughness [7-11].

Heating the composition in the microwave field leads to an increase in the temperature of the material caused by the accelerated movement of ions, electrons to higher energy levels, an increase in the reaction rate in the interfacial region, obtaining a microcrystalline structure of the material. Energy transfer with high speed leads to the formation of a special phase composition of the material, determining its final, often extreme properties. The increase in the rate of reaching the sintering temperature and its lower values is associated with an increase in the temperature gradient in the interphase region due to dielectric losses. The heating of the substance to phase transformation temperatures is especially important for reactions requiring large activation energies and is possible in the microwave electromagnetic field.

Studies of the sintering process with high heating rate in the electromagnetic field showed the possibility of obtaining material with unusually high density and strength [12-13] and super elasticity and ductility [14], which is especially important for traditionally brittle ceramics and composites based on it.

The results of studies of the sintering process in the microwave field showed the prospect for the development of environmental technology for firing materials.

Simultaneously with the research in the field of technologies of sintering compositions in the microwave electromagnetic field, research on new technologies in the field of energy was developed. First of all, we should talk about developments in the field of renewable energy sources, among which the transmission of energy by microwave radiation without wires and hydrogen energy are considered the most promising technologies.

The efficiency and advantages of wireless energy transfer by means of microwave beams over traditional technologies caused an increased interest in research in this area, the Center of Excellence on Sustainable Energy System was established at Kyoto University in Japan. A dynamically developing area was research in the field of SPS, project Solar Power Satellite (SPS2000) [15]. Significant progress has been made by Russian scientists, who have a method of wireless energy transfer using ceramic dielectrics [16].

The creation of the environmental production technology of the future is hard to imagine without hydrogen fuel. The efficiency factor of the hydrogen engine is higher than that of the internal combustion engine. This is a definite plus compared to traditional natural energy sources [21-25]. Currently, a lot of research is devoted to the problems of hydrogen production and storage [17-20]. In this regard, the experience of using SOFC (Solid Oxide Fuel Cells), which indicated the prospects of using ceramic material as a solid ion-conducting electrolyte, operating at temperatures of about 1000 °C [26] - the average sintering temperature of clay ceramics, is important.

Materials, that are capable of releasing hydrogen by splitting water when absorbing energy, can potentially be considered as raw materials in the technology of hydrogen fuel production. Hydrated aluminosilicates widespread in nature, whose crystalline and pore structure includes water, can become such materials. Dehydration of such minerals is completed on average by 600 °C, accompanied by decomposition of their crystalline structure and the beginning of formation of high-temperature phases of sintered material.

The presence in the interlayer space of aluminosilicates of water vapor in a wide range of temperatures and active metals for its decomposition [22-25] can provide under conditions of activating water microwave electromagnetic field [27] the process of hydrogen formation with simultaneous sintering and formation of highly porous structure of ceramic material for its storage.

Thus, the peculiarities of the structure of hydrated aluminosilicates make them a promising raw material for the simultaneous use of hydrogen fuel in the ecological technology of obtaining a wide class of fired materials, as well as the development of ecological hydrogen technology in the energy sector.

The study of sintering peculiarities of widespread polymineral aluminosilicate raw materials under heating conditions in a high-frequency microwave electromagnetic field is necessary to create an environmental technology for obtaining a material with the effect of hydrogen accumulation in its honeycomb structure [28-30].

The development of ceramic microwave energy absorbers, which include SiO_2, Al_2O_3, CaO, MgO oxides - the main components of polymineral natural aluminosilicates are of interest. Volumetric absorption of microwave energy, its conversion into heat and dissipation of excess energy is the main requirement for such materials.31 Of particular interest are marls, containing a large percentage of carbonates, decomposing with the formation of a porous structure in the range of temperatures of hydrogen formation during water electrolysis.

Difficulties of sintering polymineral raw materials arise because of the different reaction of each component of the raw mixture to the electromagnetic field. Studying the process of activation of aluminosilicate suspensions in the microwave field were established structures, which at the subsequent firing even under conditions of convective heating form compositions with nanoscale formations, which have increased activity due to the high surface energy [31]. During sintering in the microwave field a completely nanoscale material structure is formed.

The mechanism of sintering in the microwave field involves starting the process in the interfacial region and spreading it by diffusion to the entire volume of the material [32-33].

The study of sintering in the microwave field of aluminosilicate compositions has shown the influence on the sintering process mineral composition of the clay composition and the presence of mineralization, which contributes to the formation of the amorphous phase in the interfacial space [33]. From these positions condensed microsilica, the main component of which is amorphous silicon dioxide [34], is of interest.

Currently, the technology of obtaining fired materials, such as clay and oxide ceramics, refractories, cement clinker is traditionally obtained by convection firing in furnaces. The study of the features of microwave sintering of polymineral compositions is of great importance for the development of the fundamental bases of the technology of obtaining materials with special properties under the influence of electromagnetic fields on the material structure.

The aim of the work was to study the peculiarities of heat treatment in the microwave field of polymineral aluminosilicate compositions from natural raw materials.

MATERIALS AND METHODS

In this work researches of sintering process in microwave field of samples from natural polymineral mixtures were carried out. The strength and quality of sintering of fired samples in the microwave field and the structure after convective firing in a muffle furnace were determined.

As natural raw materials were selected: Nizhne-Uvelsky refractory clay (60% kaolinite, 5% mica) with the content of basic oxides (mass %): 58.0 SiO_2, 30.2 Al_2O_3, 4.3 Fe_2O_3, 1.2 CaO + MgO, 0. 9 K_2O + Na_2O; Nurlatsky bentonite (60% montmorillonite, 5% mica) with the content of basic oxides (mass %): 56.4 SiO_2, 20.0 Al_2O_3, 8.1 Fe_2O_3, 4.39 CaO + MgO, 2.0 K_2O + Na_2O; marl-Maksimkovsky clay deposit composition in mass %: 33.2% SiO_2 , 11.4% Al_2O_3, 26.1% $CaCO_3$ + $MgCO_3$, 3.6% Fe_2O_3, 3.6% Na_2O + K_2O; diatomite (Inza) with the content of amorphous silica 60% and basic oxides (mass %): 98.7 SiO_2, 0.1 Al_2O_3, 0.05 Fe_2O_3, 0.3 CaO + MgO, 0.65 K_2O + Na_2O.

In clays the active component is montmorillonite (metastable crystalline structure), in diatomite - silica (amorphous structure).As an activator sintering - fluxing salt NaCl (Russian Federation State Standard GOST 51574-2000) because of its ability to form fusible mixtures with silicates and improve the sintering of polymineral natural mixtures.

To prepare the molding mixture, clay and diatomite were crushed, sifted through a sieve with a hole diameter of 1 mm, mixed with additives in a ball mill for an hour. The clay mass was moistened until a plastic dough was obtained, from which the 20 × 20 × 20 mm samples were molded for firing in a muffle and microwave oven. In the furnaces, the maximum rate of temperature rise was maintained: in the muffle furnace for 4 hours, and in the microwave oven for 30 minutes. Heat treatment was carried out to a temperature of 1000 °C with holding at the maximum temperature in the muffle furnace for 30 min, in microwave - 5 min.

Used for sintering muffle furnace PVK-1,4-17 and microwave furnace (Samsung 1711 NR) at the output radiation power of 800 W at the operating frequency of 2, 45 GHz. The magnetic field is created by current of industrial frequency of 50 Hz, which flows in the power supply system of the furnace. For sintering, a muffle of mullite-silica plates was installed inside the microwave furnace. The temperature was controlled by a thermocouple with a radiation-proof coated junction installed near the sample.

X-ray phase analysis of the annealed samples was performed on a Shimadzu XRD 6000 diffractometer in CuK - radiation (PDF 4+ base, POWDERCELL 2.4 full-profile analysis program), fracture imaging of the samples was performed on an electron and focused ion beam system (Quanta 200 3D) at the TSU Tomsk Regional Center for Collective Use.

RESULTS

During firing in a microwave oven samples with fluxing salt sintered without destruction. Samples that included a carbonate additive in the form of marl and amorphous silica in the form of diatomite had the highest quality appearance.

The greatest strength was obtained by sintering in the microwave field. Samples of refractory clay without salt had cracks on the surface, small splinters. Samples of marl without additives, fired in the microwave field, had small cracks on the surface. During convective firing, the samples burned without rupture, but showed a low level of strength. Samples with the addition of NaCl salt when sintered in the microwave field burned without destruction and had a higher strength compared to the samples fired in the muffle furnace.

The greatest increase in strength was obtained for the composition based on marl, diatomite and NaCl salt, which was fired in a microwave oven (fig. 1).

Microphotographs of fractures of the samples, which showed the greatest strength, when sintered in the microwave field are shown in fig. 2. X-ray phase analysis of these samples showed the presence of more than 40% glass phase in their composition (table 1). The fracture structure of these compositions has a glassy matrix that binds the crystalline phase, providing high strength of the samples. The presence in the clay of carbonates (marl) with amorphous silica (diatomite) and fluxing salt (NaCl) provides the highest strength of the material.

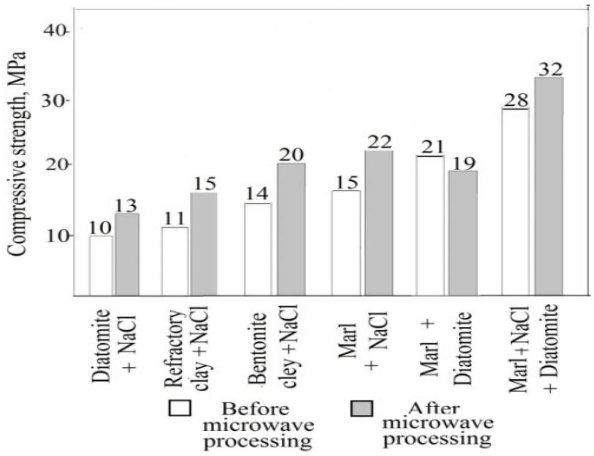

FIGURE 1. Dependence of the strength of the material on the composition of the composition.

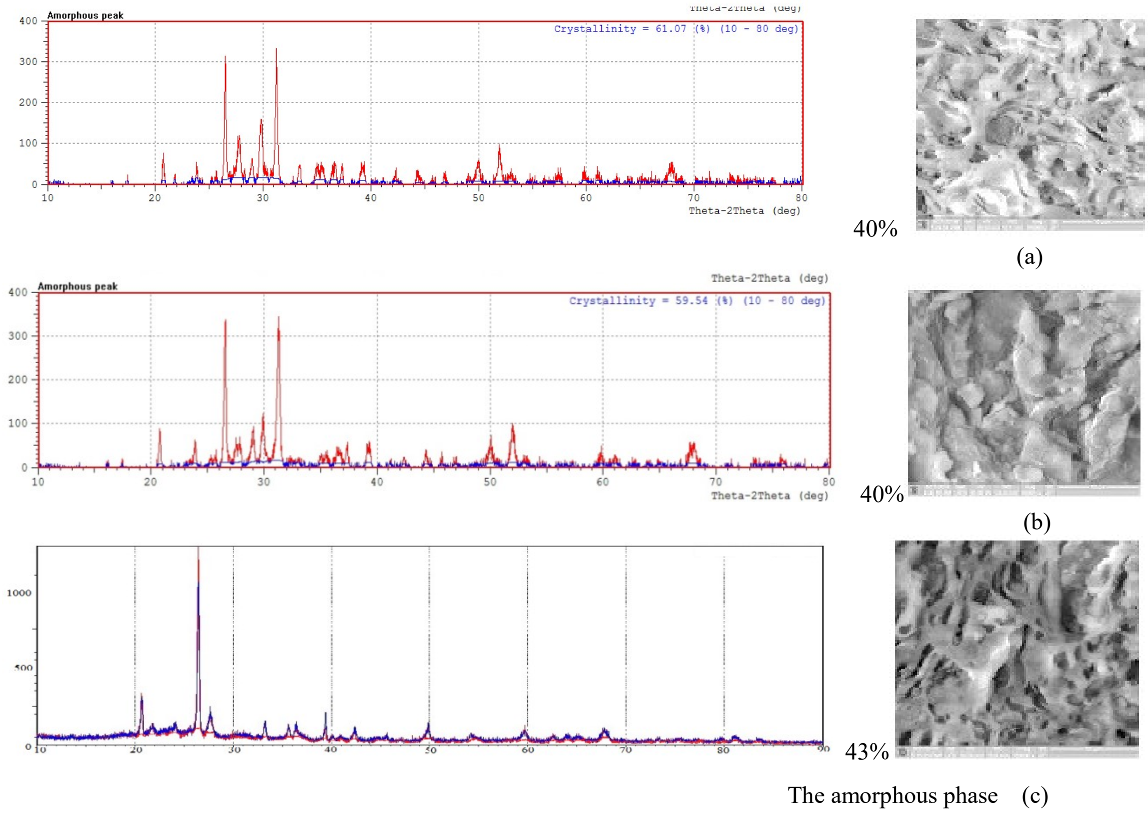

FIGURE 2. X-ray patterns, percentage of amorphous phase and microphotographs of fractures of samples fired in a microwave oven of compositions: (a) - diatomite, marl, NaCl; (b) - marl, NaCl; (c) - diatomite, NaCl.

NaCl salt promotes the formation of glass phase in the temperature range of formation of high-temperature phases of the fired material. This is explained by the fact that the decomposition of clay components and NaCl salt occurs in the same temperature range (600-900 °C). Given the sintering scheme of the composition in the microwave field [32], the presence of the liquid phase between the grains contributes to the formation of high-temperature phases at lower temperatures and with less energy costs [30-33]. The presence in compositions more than 40 % glass phase provides increased strength of samples.

For compositions based on bentonite and refractory clay, Table 1 shows the effect of sintering method on the phase composition of the material. The phase composition of the composition fired in the microwave field differs from that of the composition fired traditionally in a muffle furnace. We can see the formation of nanoscale phase structure of the material fired in the microwave field. The composition based on marl, diatomite and NaCl salt sintered in the microwave field contains nanoscale phases. This explains the high strength of microwave-fired samples.

TABLE 1. Phasecompositionofthesamplesafterfiring.

Composition	Phases Identified	Weight Percent	Crystallite Size, nm
Bentoniteclay +NaCl	SiO_2	44.73	99.4
	Al_2SiO_5	10.59	-
	γ-Fe_2O_3	4.87	-
	$(Na_{0.7}K_{0.3})(Al_{1.02}Si_{2.98}O_8)$	36.89	23.5
	CaO	2.91	-
Bentoniteclay +NaCl + MWP	SiO_2	1.6	>100
	$NaAlSi_3O_8$	22.6	35.53
	$Na_{7.5}(Al_{7.2}Si_{8.8}O_{32})$	37.4	30.33
	Al_2SiO_5	38.5	22.40
	Trace levels of $NaAlO_2$, $MgSiO_3$, and Na_2SiO_3		
Refractory clay+NaCl	SiO_2	57.18	-
	Al_2SiO_5	16.13	-
	Fe_2O_3-HEMATIT	0.76	-
	$(Na_{0,7}K_{0,3})(Al_{1,02}Si_{2,98}O_8)$	25.94	-
Refractory clay+NaCl + MWP	SiO_2	63.4	63.28
	Al_2O_3	19.5	6.39
	Al_2SiO_5	17.1	3.63
Marl, diatomite,NaCl	SiO_2	17.6	51.84
	$Ca_2MgSi_2O_7$	21.6	12.36
	$CaMgSi_2O_6$	24.6	15.15
	Amorphous phase $Ca_2Mg0,08Al,84Si1,08O_7$	40	

DISCUSSION

The paper provides information on new technologies in power engineering and roasting technologies in materials science. The economic problems associated with the combustion of carbon fuels have become a priority problem for any technological solutions and have stimulated the search for alternative solutions.

The solution to the problem was found in technologies that use high-frequency electromagnetic field microwave energy.

Wireless energy transfer by means of microwave rays, peculiarities of structure, properties of materials during high-speed sintering in the microwave field showed the prospects for development in this direction of technology for energy and environmental firing technology in materials science. The need for such development is associated with the possibility of obtaining materials with enhanced performance characteristics. Studies have shown that the special properties of materials obtained by sintering in the microwave field are associated with the formation of nanoscale material structure [1-14].

Rapid heating of the material in the microwave field causes acceleration of ion diffusion, an increase in the reaction rate in the interfacial region and the formation of a microcrystalline structure.

Studies in the field of hydrogen energy and technology associated with the use of solid oxide fuel cells have shown the prospect of using ceramic ion-conducting electrolytes operating in the temperature range of sintering clay ceramics [26]. Clay minerals decompose at energy absorption with the release of water in a wide temperature range, coinciding with the decomposition of water vapor and the release of hydrogen. This process can be catalyzed by active metals present in the interlayer space of clay minerals [22-25] and microwave electromagnetic field activating water [27].

Given the different response of each component of the clay blend to the microwave field, research in clay ceramic sintering technology is promising not only for the development of energy and cost-effective firing technology of ceramics, but also for hydrogen energy, to study materials capable of accumulating hydrogen in its honeycomb structure [28-30].

There are developments of ceramic microwave energy absorbers [31], which include metal oxides that form the basis of clay ceramics. Of particular interest are clay compositions with a high content of carbonates - marls, which in the process of sintering decompose with the formation of a porous structure. This occurs in the temperature range of hydrogen formation during electrolysis of water and the release of CO_2 can catalyze this process [26-27].

Studies conducted in the direction of using the microwave electromagnetic field for sintering polymineral compositions, primarily on aluminosilicate basis, will allow to develop an environmentally friendly technology for obtaining roasting materials, to obtain information for developing the technology of synthesis and accumulation of hydrogen. These studies are useful for the development of technology in the energy sector as a whole and to obtain data for the development of the fundamentals of efficient technology in materials science.

The presented work is devoted to the study of sintering in the microwave field of polymineral clay compositions with sintering activating salt NaCl.

CONCLUSION

The result of the study was sintering in the microwave field of polymineral compositions with sintering-activating salt NaCl.

As a result of the studies it was established:

- The fundamental possibility of sintering a polymineral composition from natural raw materials with sintering activator salt NaCl;
- The dependence of the process on the addition of sintering activator;
- The presence of NaCl in the aluminosilicate composition helps to obtain defect-free samples with high
- The composition of marl, diatomite, salt of NaCl has the greatest efficiency at sintering;
- Formation of a nanoscale structure during sintering of the composition clay - NaCl in the microwave electromagnetic field;
- At sintering the composition of marl, diatomite and NaCl in the microwave electromagnetic field formation of a dense microstructure of the material with inclusions of 40% or more of the amorphous phase.

Conducted research on sintering in the field of microwave sintering compositions of natural clay raw materials showed promise for the creation of ecological technology for the production of firing materials.

The results obtained during the study of firing in the microwave field confirmed the conclusions drawn earlier on the sintering of individual compounds. The increase in the strength of the material was associated with the formation of a material structure containing nanoscale phases.

It was possible to obtain samples without defects from all compositions due to the addition of a sintering activator - NaCl salt, which promotes the formation of a liquid phase in the aluminosilicate composition.

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