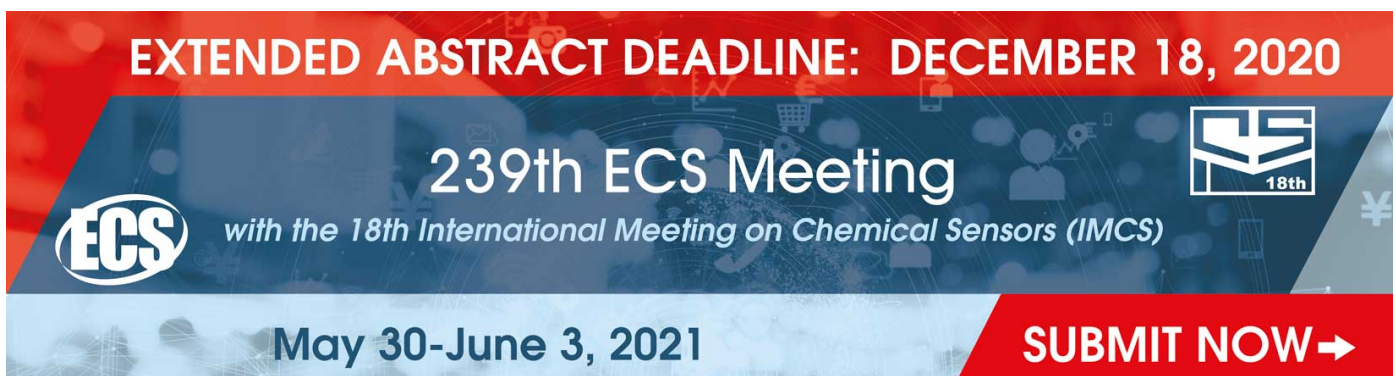


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# Sintering in a microwave field is a promising ecological technology for producing nanostructured ceramic composites from natural raw materials

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**Abstract.** The article provides literature data on sintering inorganic substances in an electromagnetic field, shows the prospects for research in this direction. The results of sintering samples from masses based on natural compositions: marl, low-melting loam and diatomite with carbonate additives in a microwave oven are considered. The possibility of sintering in a microwave field of natural raw materials, which is traditional for the production of many fired ceramic products, has been established. The phase compositions of the fired materials have been determined. The composition of sintered compositions, consisting of nanoscale phases, has been established. The effect on the sintering process of the composition of the raw material composition from the carbonate component, diatomite and the addition of NaCl salt is shown. Samples from a mass based on marl, with the addition of diatomite and NaCl salt show high quality and increased strength of the samples, the presence of a large percentage of the amorphous phase in the fired sample, and a uniform microstructure of the material. Specimens from masses based on clay with the addition of chalk and NaCl salt after firing in the microwave field showed a significant increase in strength.

## 1. Introduction

Compliance with environmental, energy and resource-saving requirements is the priority aspects of any promising material production technology. For fired materials, heat treatment is the most energy-intensive and environmentally problematic process due to the combustion of hydrocarbon fuels. In addition, the duration of the thermal process does not contribute to the formation of a fine-grained structure, on which the strength of the material depends. This is especially important with a simplified scheme for processing raw materials, which does not allow obtaining a high degree of dispersion of the components of the molding mass. The aforementioned problems of traditional firing technology and the need for materials with special, often extreme properties create the need to search for alternative solutions. One of these options is the development of a technology for the synthesis of a material under the action of a microwave electromagnetic field. The study of the sintering process at a high heating rate in an electric field showed the possibility of obtaining a material with an ultrafine, with increased density and strength of a material with a microcrystalline structure, which has increased viscous fracture rates [1-3]. This is especially important for ceramic, traditionally fragile materials. Differences are found in the structure of crystalline materials obtained by heat treatment in an electromagnetic field and in the process of convective heating [4].

For clay compositions, it was found that the microstructure of the samples and its main phases are formed at low firing temperatures and include nanoscale formations [5-6].



In the technology of firing materials, sintering is the main stage of heat treatment, during which the final structure of the material is formed. In recent years, the possibility of obtaining materials with special properties is associated with the formation of a nanoscale structure in them - this is the level of passage of the main interfacial processes during sintering. This level of interaction is possible in compositions with nanosized dispersion of components and is achieved at a high degree of grinding, for example, during slip preparation of the molding mass. According to the traditional firing technology, with prolonged heating and holding of the material at a final temperature, the developing recrystallization processes prevent the formation of its nanoscale structure.

The intense development of nanotechnology in recent years is associated with the discovery of new materials with extraordinary mechanical and physical properties. The study of the structural features of such materials showed that the appearance of special properties in them is caused by the achievement of a certain size of the structure elements of the material in each case [7-12]. A decrease in the grain size below the critical level and structural defects causes a significant increase in strength, and the fracture toughness of traditionally brittle ceramics increases. This fact was recorded in a number of works [13-18]. The effect of the structure, dispersion of raw materials, and the conditions for forming the product on the final properties of the material was shown [19-23]. Most of the studies were carried out on simple compounds or mixtures with a small amount of components. Natural polymineral compositions are multicomponent mixtures of minerals of various chemical and grain composition. This complicates the technological process of obtaining the material.

Sintering of natural mineral compositions, mostly consisting of hydroaluminosilicates of various chemical compositions, occurs after their decomposition and begins between the grains in the interfacial region. The study of heating in the electromagnetic field of dielectrics, which include the components of most natural minerals, indicates the beginning of the process in the interphase region, continuing throughout the entire volume due to diffusion [24].

The results of studies of the behavior of compositions from charges of various polymineral composition showed a significant difference in the sintering mechanism in the microwave field and in a muffle furnace. Qualitatively, without cracks and ruptures, samples made from a charge, the main clay-forming mineral of which decomposes upon heating with a slight energy effect (polymineral mixtures based on montmorillonite - bentonite clay) and samples modified with NaCl salt, were sintered in the microwave field. Specimens from compositions on refractory clay cracked during firing in a microwave field [18-19].

The results of testing a large number of compositions showed an increased strength of the samples, the charge of which was activated or the samples were fired in the microwave field, in comparison with the samples fired by the convective method in a muffle furnace [18-19].

The study of the features of microwave sintering of polymineral composites is of great importance for the development of the fundamental principles of the technology for obtaining materials with special properties and the technology for producing ceramic composites.

The aim of the work was to study the features of heat treatment in the microwave field of compositions from natural polymineral raw materials with impurities of carbonate rocks.

## 2. Materials and methods

Investigations of the effect of the microwave field on natural aluminosilicates containing Ca and Mg carbonates have been carried out. The final structure of the fired material in the microwave field and the structure after convective firing in a muffle furnace is compared.

Natural polymineral raw materials were investigated: Maksimkovsky marl composition in mass %: 33.2% SiO<sub>2</sub>, 11.4% Al<sub>2</sub>O<sub>3</sub>, 26.1% CaCO<sub>3</sub> + MgCO<sub>3</sub>, 3.6% Fe<sub>2</sub>O<sub>3</sub>, 3.6% Na<sub>2</sub>O + K<sub>2</sub>O; Kalininsky loam (42% montmorillonite, 5% mica) with the content of basic oxides (wt%): 68.1% SiO<sub>2</sub>, 12.6% Al<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>, 6.4% Fe<sub>2</sub>O<sub>3</sub>, 3.3% CaO + MgO, 3, 2% Na<sub>2</sub>O + K<sub>2</sub>O; Inza diatomite (98.7% SiO<sub>2</sub>). As a carbonate additive, chalk was used with the composition: CaCO<sub>3</sub> and MgCO<sub>3</sub> 98.2 - 98.4, R<sub>2</sub>O<sub>3</sub> 0.001, Fe<sub>2</sub>O<sub>3</sub> 0.15. As a mineralizer salt NaCl (extra following Russian Federation State Standard GOST 51574-20000) due to its ability to form fusible mixtures with silicates.

Molding mixtures were prepared from raw materials, ground and sieved through a sieve with a hole diameter of 1 mm. The charge components were mixed in a ball mill for an hour. The mass was moistened until a plastic dough was obtained, and specimens with a size of  $20 \times 20 \times 20$  mm were molded. Samples without preliminary drying were fired in a microwave oven at  $1000^\circ\text{C}$  with holding at a maximum temperature of 5 min.

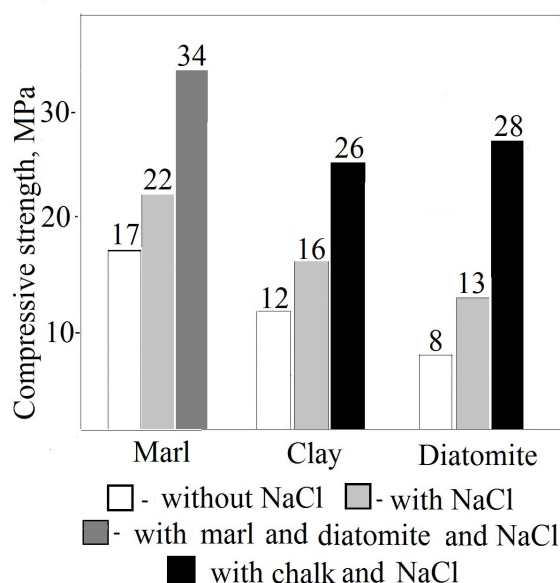
Microwave treatment was carried out in a microwave oven (Samsung m 1711 NR) with an output radiation power of 800 W at an operating frequency of 2.45 GHz. The magnetic field is created by current of the industrial frequency of 50 Hz, which proceeds in a furnace power supply system. For sintering, a muffle made of mullite-silica plates is installed inside the furnace. The temperature was monitored by a thermocouple with a radiation-protected junction coating installed near the sample.

X-ray phase analysis of the fired samples was carried out on a Shimadzu XRD 6000 diffractometer in  $\text{CuK}\alpha$ -radiation (PDF 4+ base, POWDERCELL 2.4 full-profile analysis program), sampling of sample breaks - on a system with an electron and focused ion beam (Quanta 200 3D) in the Tomsk Regional center of collective use of NU TSU.

### 3. Results

All the samples under study, which included a carbonate additive and NaCl salt, sintered without destruction and showed a significant increase in strength.

The greatest increase in strength was obtained from the composition based on marl with the addition of diatomite and mineralizing salt NaCl (figure 1). Samples without defects with increased strength were obtained from diatomite and clay with the addition of chalk and NaCl salt.



**Figure 1.** Durability on compression of the samples burned at  $1000^\circ\text{C}$  from: marl, clay and diatomite with additives.

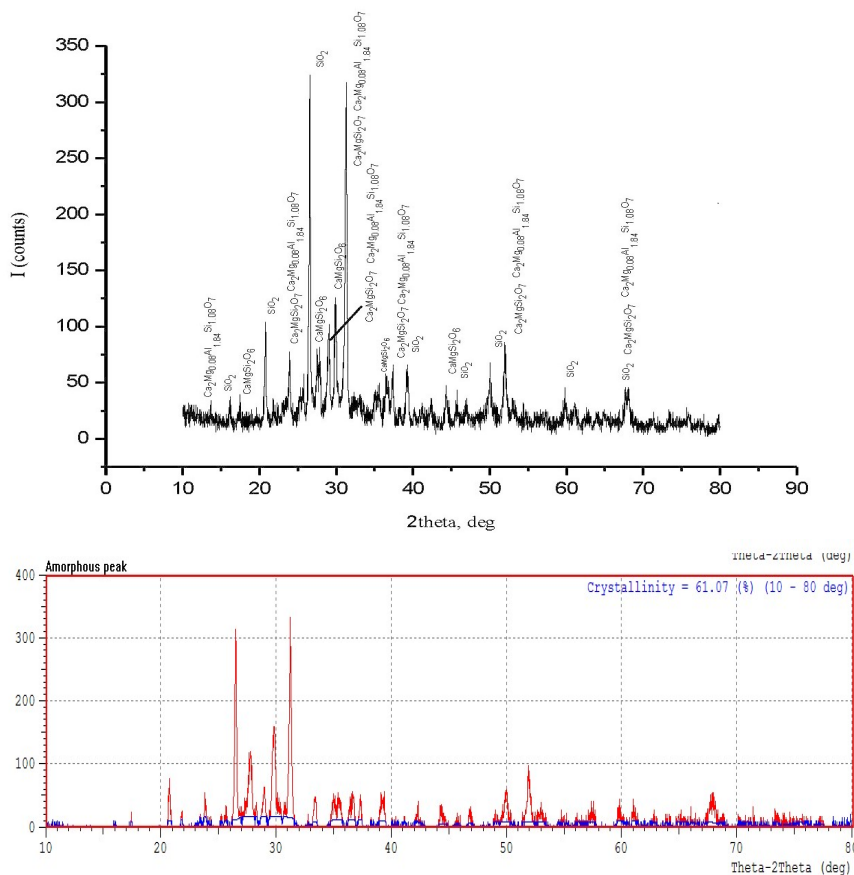
The decomposition of the constituent components of the charge for all investigated compositions occurs in the same temperature range ( $600\text{--}900^\circ\text{C}$ ). Salt NaCl contributes to the formation in this temperature range of the liquid phase and the formation of high-temperature phases, which, in the presence of a liquid phase, are formed in the low-temperature range and with lower energy costs [5, 6]. Samples from all structures were received free of defects.

The results of X-ray phase analysis of the fired samples, which showed the highest strength, are shown in table 1.

**Table 1.** Phase composition of the samples after firing.

Composition	Weight percent	Maintenance of phases, mass%	Crystallite size, nm
Marl, diatomite, NaCl	$\text{Ca}_2\text{MgSi}_2\text{O}_7$	21,6	12,36
	$\text{SiO}_2$	17,6	51,84
	$\text{CaMgSi}_2\text{O}_6$	24,6	15,15
	Amorphous phase	< 40	
	$\text{Ca}_2\text{Mg}_{0,08}\text{Al}_{1,84}\text{Si}_{1,08}\text{O}_7$		
Diatomite, chalk, NaCl	$\text{SiO}_2$	36,7	92
	$\text{Al}_2\text{Si}_2\text{O}_5$	8,7	24,9
	$\text{Fe}_2\text{O}_3$	1,1	40,8
	$\text{Na}_{0,7}\text{K}_{0,3}\text{Al}_{1,02}\text{Si}_{2,98}\text{O}_8$	5,5	16,9
	Amorphous phase, phase	43	
Clay, chalk, NaCl	traces $\text{CaCO}_3$		
	$\text{SiO}_2$	48,9	139
	$\text{Al}_2\text{SiO}_5$	12,2	29,6
	$\gamma\text{-Fe}_2\text{O}_3$	3,4	>100
	$(\text{Na}_{0,7}\text{K}_{0,3})(\text{Al}_{1,02}\text{Si}_{2,98}\text{O}_8)$	35,4	34

The X-ray diffraction pattern of the composition of the marl sample with the addition of diatomite and salt is shown in figure 2.

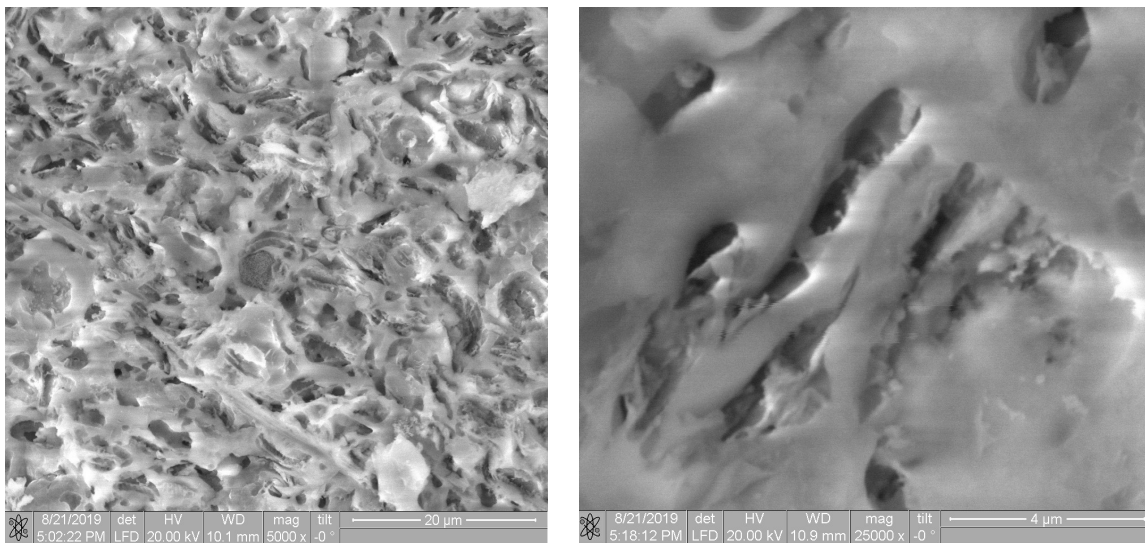


**Figure 2.** Results of the X-ray phase analysis of a sample from composition: marl-diatomite-NaCl with interpretation on phases (a) and allocation of an amorphous phase (b).

X-ray phase analysis of the samples showed the presence of nanoscale phases in all compositions, and in the compositions with marl, diatomite, and salt, a significant amount of an amorphous phase. The presence of an amorphous phase in fired samples can be associated with the formation of a large amount of a liquid phase during sintering and the formation of a material structure, which is responsible for the high strength of the sample.

In the composition of the sample based on marl, diatomite, and salt, during sintering, phases were formed that are the basis of clinker and cement binder. This feature creates a prospect for studying the possibility of obtaining cement clinker by sintering in a microwave field and is important for further research.

The microstructure of an alloy based on marl, diatomite and salt is shown in figure 3.



**Figure 3.** An alloy microstructure from marl with an additive of diatomite and NaCl salt.

The dense lattice structure of the composition with vitrified ribs is visible. Such a uniform structure must have high strength, which is confirmed by test results.

#### 4. Discussion

The paper presents an analysis of the literature data on a possible solution to the ecological problem of traditional firing technologies. Listed are studies on the synthesis of materials in an electromagnetic field, which are distinguished by special, often extreme properties. The study of the sintering process at a high heating rate in an electric field has shown the possibility of obtaining a material with an ultrafine, with increased density and strength of a material with a microcrystalline structure, which has increased viscous fracture rates, which is especially important for strengthening traditionally brittle ceramics.

The research results showed the differences in the structure. formed under the conditions of traditional convective firing and high-speed sintering under the influence of the microwave electromagnetic field. It was noted that under the conditions of sintering the composition in a microwave field, a microstructure with inclusions of nanosized phases is formed. A number of studies have shown the influence of characteristics, primarily the fineness of raw materials, molding conditions on the final properties of the material, the role of interfacial processes during sintering in an electromagnetic field is noted.

Materials with extraordinary mechanical and physical properties have been obtained, primarily based on low-component mixtures. The prospects of research in this direction in materials science and the importance of research for the development of the fundamental principles of the technology for obtaining materials with special properties from polymineral raw materials are shown.

The presented work is devoted to the study of the possibility of using polymineral, containing carbonates of natural raw materials to obtain materials with high strength indicators under conditions of firing in an electromagnetic field of microwave frequency, to the study of the features of the sintering process.

## 5. Conclusion

The result of the study was the process of sintering samples from natural polymineral raw materials with carbonate inclusions in the microwave electromagnetic field.

As a result of the research it was found:

- The fundamental possibility of sintering a polymineral composition from natural raw materials with carbonate inclusions in a microwave oven;
- The dependence of the sintering process on the composition of the carbonate-silica component of the composition;
- The presence of a fluxing additive (NaCl) in the composition of the carbonate-silica polymineral composition contributes to the production of defect-free samples of increased strength;
- Formation of a nanoscale phase during sintering in a microwave electromagnetic field, the composition of which depends on the composition of the raw material composition;
- In compositions with a carbonate-diatomite component and NaCl salt, a glass phase is formed during sintering in a microwave field and a uniform microstructure of the material is formed.

The results of the study on sintering in the microwave field of polymineral compositions with carbonate inclusions showed the prospects for the technology of obtaining many firing materials.

The results obtained confirmed some of the conclusions made earlier on the sintering of low-component mixtures and compositions based on carbonate and silica raw materials. An increase in the strength of the material is associated with the formation of a special structure of the material, the presence of nanoscale phases.

The firing of samples without defects from the polymineral composition was possible due to the introduction of the NaCl salt into the composition, which forms low-melting compositions.

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