Prospects for the activation of hydroaluminosilicates by a microwave electromagnetic field for hydrogen power engineering and ceramic technology

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Abstract. Literature information about the problems in hydrogen power engineering is presented. The data on the effect of the microwave field on aqueous solutions of hydroaluminosilicates, the mechanism of absorption of microwave energy and its use in hydrogen energy are considered. The effect of the microwave field on the structure and properties of the material is shown. The results of firing in a microwave oven of samples made of compositions based on natural aluminosilicate - marl and microsilica. The micrographs of the structures of the obtained materials are presented. For compositions of microsilica and NaCl salt, marl, microsilica and NaCl salt, a porous structure of the material was obtained. The phase compositions of the fired materials have been determined. A phase transition of amorphous silica to quartz was discovered for a composition of microsilica and NaCl salt at a temperature of 957.3 ° C with a weight loss of 1.99% - the temperature range of sintering of aluminosilicates. The pore size for this composition is in the nanoscale range. The composition of marl, silica fume and NaCl has a micron-sized porous structure of high strength. A promising direction for research into the technology of hydrogen synthesis and storage is outlined.

1 Introduction

Hydrogen energy is one of the most promising areas in the search for environmentally efficient renewable energy sources alternative to natural fuels. The creation and use of hydrogen fuel is one of the most promising areas for the development of the future energy industry. The use of hydrogen fuel will reduce carbon dioxide emissions into the atmosphere. It is believed that the efficiency of a hydrogen engine is higher than that of an internal combustion engine. This is an absolute plus in comparison with traditional natural energy sources [1-4]. In this regard, the most promising way of energy development should be based on the use of hydrogen, and the most popular as an energy accumulator is the Power-to-Gas technology [5], as well as the replacement of carbon motor fuels for cars [3].

Hydrogen is considered as a universal type of energy resource. Being a carrier of energy like electricity, it can be saved, but in order to release hydrogen it is necessary to expend energy. Development of new environmentally friendly methods for the production of hydrogen fuel is the subject of research by many scientists around the world, and one of the most popular is the extraction of hydrogen from water by decomposing it using electrolysis technology. It is a simple, easy-to-use, environmentally friendly method of producing hydrogen from renewable or nuclear energy sources. The use of fuel cells and renewable energy sources, which do not have a negative impact on the operation of networks, has a high environmental friendliness [6].

To implement this technology, it is proposed to use the energy of the sun and microwave radiation, with the help of which a beam of microwave radiation can transport solar energy to the surface of the Earth, use it independently and convert it into current energy [7-9].

In addition to the problem of obtaining hydrogen, there is the problem of its storage / accumulation, which at the moment is one of the key problems in the development of power engineering [10-15]. They offer different ways to solve this problem. One option would be to use a material active in the presence of water [12-15]. The most studied are metal hydrides, spongy iron, magnesium and aluminum are considered promising. It is proposed to use microspheres [16, 17] for storing hydrogen and nanostructured porous materials for storing hydrogen in molecular form [18]. The most studied aluminosilicates are zeolites [13, 19].

The experience of using solid oxide fuel cells SOFC (Solid Oxide Fuel Cells) indicated the prospects for using a ceramic material as a solid ion-conducting electrolyte operating at temperatures of about 1000 °C [20].

To implement the technology for producing hydrogen fuel, materials will be required that can be potential sources of hydrogen, and when absorbing any type of energy, release hydrogen due to the splitting of water. In this case, the materials themselves should not lose strength. Such materials include hydroaluminosilicate minerals widespread in nature, the composition of the crystal structure of which includes water. In addition to crystallization water, adsorption water is present in the pore structure of the mineral at different levels of dispersion. Water vapor is present in the bulk of the material in a wide temperature range from 100 to 600 °C, depending on the decomposition temperature of a particular mineral.

There are many ways to decompose water to produce hydrogen. Of interest is the high-temperature electrolysis of water vapor, which is carried out in cells with a solid electrolyte based on oxides. Such an electrolyte has conductivity due to the transfer of oxygen ions formed during the dissociation of water with the release of hydrogen at the cathode [20, 21].

Hydroaluminosilicates are the main constituent of natural clays and, in terms of their structural parameters, are natural nanomaterials. Most hydrated aluminosilicates are layered minerals of two types. The atomic structure of most minerals consists of a layer of silicon-oxygen tetrahedra and a layer of hexahedra, in which the atoms of aluminum, iron, or magnesium are at equal distances from six oxygen and hydroxyls. In the kaolinite group, the mineral is characterized by a two-storied lattice. This grid does not expand depending on the changing water content. This group includes halloysite minerals, the highly hydrated form of which consists of kaolinite layers of different polarity, between which there is a molecular layer of water molecules. Complete dehydration occurs at a temperature of 400 °C, the tubular structure remains up to 1200 °C [22, 23].

Another group of clay minerals is characterized by a three-story lattice, in which an octahedral aluminum layer is located between silicon-oxygen tetrahedral layers. Minerals of the montmorillonite group tend to swell in the presence of water, and when heated, they gradually release adsorbed water.

By keeping water up to high temperatures, hydrated aluminosilicates become potentially interesting materials for the technology of high-temperature electrolysis of water vapor and hydrogen power engineering.

In the process of studying the properties of aluminum nanopowder obtained in the process of an electric explosion, it was found that it actively reacts with water and completely with the formation of hydrogen [2]. When heated and in the presence of salts, acids and alkalis, the reaction rate increases. The effect of self-heating of nanoparticles to temperatures exceeding the temperature of the surrounding water by hundreds of degrees was discovered with the formation of hollow spheres not exceeding 100 ... 200 nm from aluminum hydroxyls [2].

Features of the structure of water show that it reacts to electromagnetic radiation [23]. Excitation from electromagnetic waves of resonant structures is transmitted to neighboring structures. The absorption of microwave radiation by water is due to the orientational polarization of the molecules. The action of microwave radiation on liquid water leads to the formation of metastable clusters (H_2O) n, which gives it the properties of a solid [23].

Storage in capillary structures made of glass, quartz, basalt, etc. is considered a promising option for storing hydrogen in a gaseous form under pressure [19, 24]. Such materials include ceramics sintered in a microwave field [25].

In the process of absorbing the energy of the microwave field, heterogeneous catalytic reactions occur in the space between the phases of the polymineral composition [26-28]. A feature of the layered structure of clay minerals is the presence of metal cations in the space between the layers of water. In the space between the layers, all heterogeneous reactions take place, which form the structure of sintered ceramics [27, 28], and reactions to produce hydrogen are possible during the interaction of active metals Al, Mg with water [2]. This probability is justified by studies on the extraction of metals from polymineral compositions by microwave radiation [29].

The temperature range of such a reaction coincides with the onset of phase formation and the strength of the sintered ceramic. The hydrogen storage technology requires the formation of a porous structure of during sintering [10]. This technology is facilitated by the reaction of water to microwave irradiation [23] and the processes that are possible in the space between the layers of clay minerals during microwave irradiation, which are identical in SOFC.

The study of the sintering process of aluminosilicate compositions showed that already at the stage of activation of the raw material composition, a finely dispersed structure of the material is formed, and after sintering in the microwave field, the nanoscale structure of the material of increased strength [26].

This process is catalyzed by the presence of the salt NaCl [26-28]. Taking into account the presence of active metal ions in the interlayer space of hydrated aluminosilicates, the presence of a salt can catalyze the formation of hydrogen [2].

Previous tests showed that compositions based on refractory clay and marl in the presence of NaCl salt after sintering had a dense vitrified shard and high strength. It was previously found that with such a composition of the composition, many glass phases are formed [25, 31].

In the process of studying the activation of clays and quartz sand in the microwave field, the formation of associates and dispersed structures was established, which, upon further heat treatment in the microwave field, led to the formation of a dense structure of the material with inclusions of nanosized phases [27].

It was noted that silica reacts especially actively to the electromagnetic field by deformation vibrations of interatomic bonds [27].

Thus, the study of the technological features of microwave sintering of aluminosilicate polymineral compositions can be of great importance for the development of the fundamental principles of the technology for producing hydrogen from natural raw materials and materials with special properties for its storage.

The aim of the work was to obtain a porous structure of a high-strength material from an aluminosilicate composition under microwave heating, to study the features of the sintering process, to determine the phase composition, structure and strength of samples.

2 Materials and methods

To achieve the goal of obtaining a microporous structure of the material, the following were selected in the work: marl - clay from the Maksimkovskoe deposit of composition (wt %): 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. Amorphous silica - condensed microsilica produced by Joint Stock Company Kuznetsk Ferroalloys, Novokuznetsk, was chosen as the active form of silica. It is a gray powder with an average particle size of 0.005-0.015 microns, which have a developed system of pores at the nanometer level [30]. NaCl salt (Russian Federation State Standart GOST 51574-2000) was used as a sintering activator. This salt has the ability to form low-melting mixtures with silicates and improve the sintering of polymineral natural mixtures.

It is known that in the process of sample preparation, structures are created and accumulated, the energy of which will be used in the subsequent stages of heat treatment and influence the formation of the material structure. Natural aluminosilicates are clay-silica compositions of varying moisture content - suspensions of dispersed particles in water. The composition and structure of the aluminosilicate component determines the main technological properties of the molding mix and the final properties of the product. It is possible to regulate these properties due to the use of various additives, the influence of which is based on ion-exchange processes occurring on the surface of the mineral particles of the mixture components. In this case, the entire composition passes from a dispersed to a structured system [27].

To prepare the molding mixture, the marl was ground and sieved through a sieve with a hole diameter of 1 mm. The powder with the additives was mixed in a ball mill for an hour. The mass was moistened with distilled water with dissolved salt until a plastic dough was obtained, and specimens with a size of 20 × 20 × 20 mm were molded. The samples were fired in a microwave oven. In the microwave oven, the maximum temperature rise rate was maintained - 30 min. Heat treatment was carried out up to a temperature of 1000 °C with holding at a maximum temperature for 5 min.

A microwave oven (Samsung m 1711 NR) was used for sintering with an output radiation power of 800 W at an operating frequency of 2.45 GHz. The magnetic field is created by a 50 Hz power frequency current that flows in the furnace power supply system. For sintering, a muffle made of mullite-silica slabs is installed inside the microwave oven. The temperature was controlled by a thermocouple with a radiation-protected junction coating installed near the sample.

X-ray phase analysis of fired samples 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 surveyed on a system with an electron and focused ion beam (Quanta 200 3D) in the Tomsk Regional center of collective use.

3 Results

Previous tests showed that compositions based on refractory clay, marl, amorphous silica (diatomite) in the presence of NaCl salt after sintering had a dense vitrified shard and high strength. It was previously found that with such a composition of the composition, many glass phases are formed [25, 31].

When studying the activation of clays and quartz sand in the microwave field, the formation of associates and dispersed structures was established. During further heat treatment in the microwave field, a dense structure of the material with inclusions of nanosized phases is formed [27]. It was noted that silica reacts especially actively to the electromagnetic field with deformation vibrations of interatomic bonds [27].

Micrographs of samples, in which a porous structure was obtained during heat treatment in a microwave field, are shown in Figure 1.

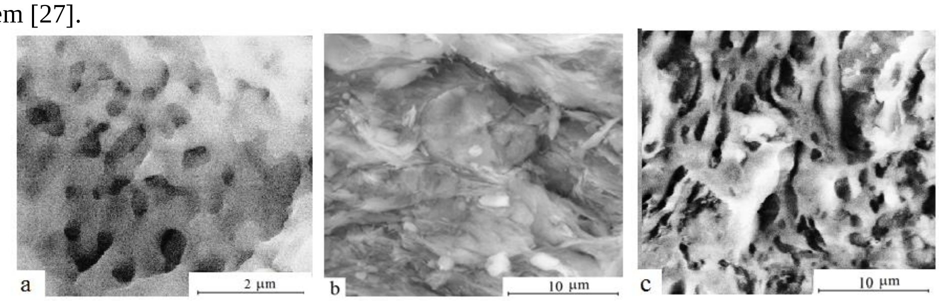

Fig.1. Microstructure of compositions sintered in the microwave field of compositions: a - silica fume + NaCl, b - marl + silica fume, c - marl + silica fume + NaCl.

These are compositions based on marl, silica fume and NaCl salt. The samples were sintered without destruction and have a uniform porous structure.

For comparison, a composition based on marl and silica fume is shown. The structure of the sample is dense and has no visible pores. This composition showed the greatest strength of the sample (Figure 2).

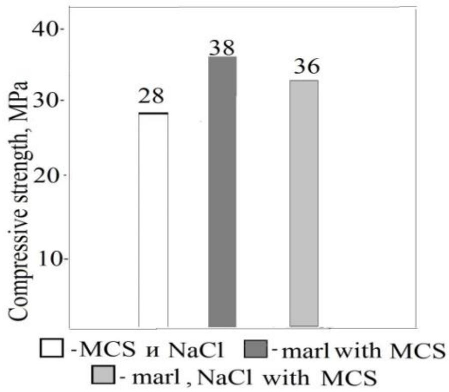

Fig. 2. Dependence of the strength of the material on the composition of the composition

The composition based on silica fume and salt has a uniform microporous structure. The results of differential thermal analysis of this composition are shown in Figure 3. A clear exotrmic peak is seen at 957.3 °C with a weight loss of 1.99%.

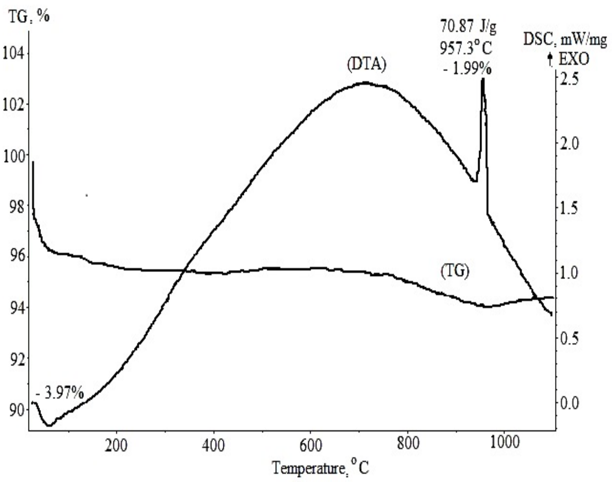

Fig.3. Thermal analysis results for DTA (1), TG (2) of the silica fume + NaCl composition

The data of X-ray phase analysis of the samples are presented in Table 1. The phase composition of the sample from silica fume and salt consists of quartz of various polymorphic modifications. From the results of the analysis, it can be concluded that amorphous silica passed into a crystalline phase of two types (quartz, cristobalite) with a weight loss and the formation of a glass phase in the amount of 26%. The structure is uniform and porous. The pore size is in the nanometer range.

Table 1. Phase composition of samples after microwave sintering

Composi-tion	Weight percent	Mainte-nance of phases, mass %	Crystallite size, nm
Micro-silica + NaCl	SiO_2_ 154	97.2	80.4
	SiO_2_ 92	3.1	83.2
	Amorphous phase	26	-
Marl + micro-silica	SiO_2	6.9	48.3
	$Al_2Si_2O_5$	9.6	12.8
	Fe_2O_3	0.4	-
	AlSiO-mullite	5.9	43.1
	$CaCO_3$	1.2	43.7
	Amorphous phase	76	-
Marl + micro-silica + NaCl	$Ca_2MgSi_2O_7$	21.6	12.4
	$Ca_2Mg_{0,08}Al_{1,84}Si_{1,08}O_7$	36.2	>100
	SiO_2	17.6	51.8
	$CaMgSi_2O_6$	24.6	15.2
	Amorphous phase	40	-

The composition fired in the microwave field based on marl, silica fume and salt has a less uniform microporous structure, a wide composition of crystalline phases and a glass phase in an amount of 40%. The pore size is larger and lies in the micron range. In terms of strength, the material of this composition is superior to the material of the composition based on silica fume and salt, most likely due to the composition of the crystalline phase and a larger amount of glass phase. The phase composition of the alloy has the components of the cement clinker.

4. Discussion

The paper analyzes the literature data on problems in hydrogen energy.

The economic growth of modern society and the associated growing needs of mankind for energy resources are forcing the search for alternative solutions to the modern fuel and energy complex. In this regard, the creation and use of hydrogen fuel is one of the most promising directions for the development of the future energy industry. The environmental and operational advantages of hydrogen fuels have led to increased research into the production and storage of hydrogen fuels.

The development of new environmentally friendly methods for the production of hydrogen fuel is the subject of research by many scientists. Particular attention is paid to the method of separating hydrogen from water. Electrolysis is considered one of the most promising technologies. There is a search for natural materials that can become potential sources of hydrogen.

In parallel to this direction in energy, in recent years, much attention has been paid to research on the use of renewable energy sources and microwave radiation.

The study of sintering processes in high-frequency electromagnetic fields of natural aluminosilicate raw materials will allow replacing traditional roasting technologies that use fuel combustion with an environmentally friendly and energy-efficient technology. In addition, the study of high-speed sintering of hydrated aluminosilicates in electromagnetic fields may make it possible to develop a technology for producing hydrogen fuel that is sufficiently universal in terms of raw materials using an environmentally friendly technology.

The most important directions of searching for ways of not only obtaining, but also storing hydrogen are analyzed. The prospects of using compositions with a highly dispersed structure and high strength for hydrogen storage are noted. Traditionally brittle ceramics and composite materials based on it are of particular interest in this area. The need for such materials is increasing due to a wide range of areas of their use, the development of nuclear energy and space.

Analysis of the results of studies of sintering in the microwave field of compositions based on microsilica and marl indicated the direction for further research on the technology of synthesis and storage of hydrogen. Materials of microporous structure and high strength have been obtained.

In addition to power engineering, research in this direction is important in materials science and is important for the development of the fundamental foundations of the technology for obtaining materials with special properties, especially from natural and technogenic polymineral raw materials.

The presented work is devoted to the study of sintering in a microwave field of an aluminosilicate and silica composition - marl and microsilica, the effect of a salt activator of sintering on this process.

5. Conclusion

The result of the study was the process of sintering samples from natural carbonate-clay raw materials with amorphous silica and a salt activator in a microwave electromagnetic field.

As a result of the research, it was established:

- the fundamental possibility of sintering a polymineral composition from natural raw materials with carbonate inclusions, amorphous silica in a microwave oven;

- dependence of the process on the additive and the type of sintering activator;

- the presence of a sintering activator in the composition of the activator contributes to the production of defect-free samples of increased strength;

- the formation during sintering of a composition of marl-microsilica-salt in an electromagnetic field of microwave microwave of a nanosized and glass phase;

- during sintering of compositions: marl-microsilica-salt in the microwave electromagnetic field forms a uniform porous and high strength microstructure of the material.

The results of the study on sintering in the microwave field of an aluminosilicate composition showed prospects for hydrogen energy and 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.

It was possible to obtain in the process of firing samples without defects from a polymineral carbonate-clay composition due to the addition of a sintering activator, among which the most effective was silica fume and NaCl salt as an activator of glass formation.

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