

Artificial Tobermoryte as Raw Material for Low Temperature Burning

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Abstract – The possibility and condition of wollastonite synthesis by two-stage technology which foresees the receive of intermediate phase in a form of calcium hydrosilicate (tobermorite 11,3 Å) on the stage of hydrothermal treatment with its further burning to β -CaO·SiO₂ were investigated. The influence of forms of SiO₂ and consistency of raw material mixture on the output of synthetic wollastonite was studied. The mineralising effect of boron oxide on the formation of wollastonite was established.

Key words – wollastonite, calcium hydro silicates, tobermorite, hydrothermal treatment, mineralizer.

I. Introduction

Wollastonite as a raw material in ceramic technology is characterized by a number of physical and mechanical properties that largely determine the operating properties of products [1]. Its use in compositions of ceramic masses reduces the fire and air shrinkage. It increases strength, reduces the temperature of sintering and the temperature of formation of glass phase, gives the possibility to produce the ceramics with good dielectric properties and high quality coatings [2].

Mentioned about properties of materials largely depend on the shape and size of wollastonite crystals. Due to the limited resource and purity of natural wollastonite one of the most actual problems is developing the technology of production of artificial wollastonite. In addition it is important to study the influence of conditions of synthesis on the morphology and size of CaO·SiO₂ crystals.

Traditional technology of obtaining of artificial wollastonite involves the solid phase sintering of the mixture of silica and calcium containing components [3]. The regulation of process is carried out by changing the ratio of initial ingredients, their dispersion, condition of pressing and regimes of high-temperature burning. This technology leads to higher power expenses and the high cost of the synthesized product.

It is known that at the hydrothermal treatment (increased pressures and temperatures) in the system of CaO-SiO₂-H₂O an interaction between calcium hydroxide and silica is occurred with formation of calcium hydro silicates [4, 8].

We propose a technology of wollastonite synthesis that involves the use of an intermediate stage of obtaining a hydro calcium silicate during the hydrothermal treatment with parameters which are suitable for a technological realization (temperature is 453-473 K, pressure is 0.8-1.2 MPa) and its further burning at temperatures lower than in traditional ceramic technology.

II. Experimental results

Taking into account the problem of energy saving as an initial component amorphous form of SiO₂ (waste of mechanical processing of natural silica) was used. Chemical composition of natural silica is given in Table 1.

TABLE 1

CHEMICAL COMPOSITION OF NATURAL SILICA

Oxide	Weight fraction, %		
	from	to	average
SiO ₂	91,55	96,96	94,24
Al ₂ O ₃	0,43	0,73	0,58
Fe ₂ O ₃	0,00	0,12	0,06
FeO	0,32	0,43	0,38
CaO	0,38	3,13	1,76
MgO	0,05	0,19	0,12
K ₂ O	0,16	0,21	0,19
Na ₂ O	0,04	0,07	0,06
TiO ₂	0,03	0,06	0,05
SO ₃	0,10	0,33	0,22
B.п.п.	1,15	3,52	2,34

Calcium containing component of the system was presented by quicklime lump which was extinguished directly during the stage of preparing the studied mixture. Chemical composition of lime is given in Table 2.

TABLE 2

CHEMICAL COMPOSITION OF LIME

Oxide	Weight fraction, %
CaO	88
SiO ₂	2
MgO	1,5
Fe ₂ O ₃ + Al ₂ O ₃	1,5
S	0,15
Loss	6,85

The mixture was prepared in the form of viscous-flow mass consistency with the humidity of 50 % from the previously prepared mixture of silica powder and quicklime at a ratio of 1 to 1. After autoclaving during 10 h at pressure of 1.0 MPa the test samples turned into a monolithic stone-like mass.

Valuation of the interaction between Ca(OH)₂ and SiO₂ was carried out by the determination of the amount of unbound calcium hydroxide by the method of complexometric titration. Thus, it was found that amorphous silica is characterized by considerable reactivity. In this case, a consistency of studied mass influenced on the completeness of the reaction (Figure 1). It was found the formation of calcium hydrosilicates passes more completely in samples of viscous-flow consistency than in

pressed samples with humidity of 6-8%. Moreover in order to achieve approximately the same output of hydro calcium silicates for crumbly structure it is required twice less time (5 h) than for dense one (10 h).

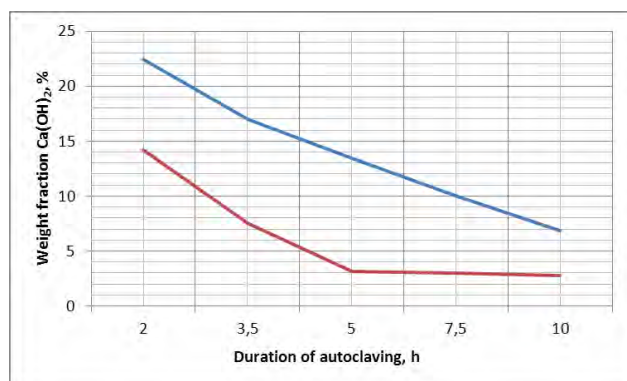


Fig. 1. Dependence of content of unreacted Ca(OH)₂ on the duration of autoclaving of pressed samples (1) and samples in viscous-flow state (2)

A character of diffractograms of samples indicates the formation of calcium hydro silicates of tobermoryte composition during the autoclaving (Figure 2). Their presence is confirmed by diffraction peaks with $d/n = 1,130; 0,560; 0,307; 0,305; 0,297; 0,280; 0,270; 0,252; 0,228; 0,215; 0,200; 0,183; 0,167; 0,161; 0,159; 0,153$ nm.

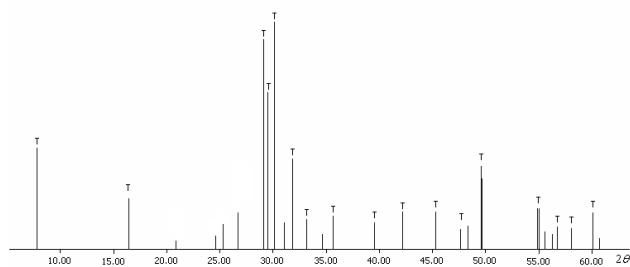


Fig. 2. Diffraction of sample after autoclaving:
T – tobermorite phase

Besides, electronic microscopy data of material structure is characterized by significant structural and morphological inhomogeneity (Fig. 3). A typical feature of the microstructure of these samples is the presence of tightly bound and chaotically oriented in different directions fibrous and plate structures. Formation of that structure is mainly evident in the cavities, while the total mass matrix is characterized by gel monolithic structure in certain areas. The sample surface is characterized by areas presented a complex of needle and flake-plate structures that form separate conglomerates in the pores.

In order to intensify the process of phase formation of calcium hydrosilicates of more perfect forms the hydrothermal treatment of samples masses with the addition of previously synthesized tobermoryte (up to 5 %) was carried out.

X-ray diffraction analysis of samples with addition of synthesized calcium hydro silicates characterizes the presence of peaks with $d/n = 1,130; 0,560; 0,307; 0,305; 0,297; 0,280; 0,270; 0,252; 0,228; 0,215; 0,200; 0,183; 0,167; 0,161; 0,159; 0,153$ nm of tobermoryte. In this case

the electro-microscopic study of the microstructure of the samples shows the presence of clusters of chaotically directed, elongated petal-like crystal structures existing throughout the volume structure (Fig. 4). The size of elongated crystals reaches 5 and more microns. The diameters of linked and turned clusters are near 40 microns. The structure of the material is also characterized by the existing of single inclusions of amorphous mass, located mainly in cavities of linked clusters of crystalline formations. Besides, compared to the previous samples the total mass matrix have got more perfect and developed crystalline structure.

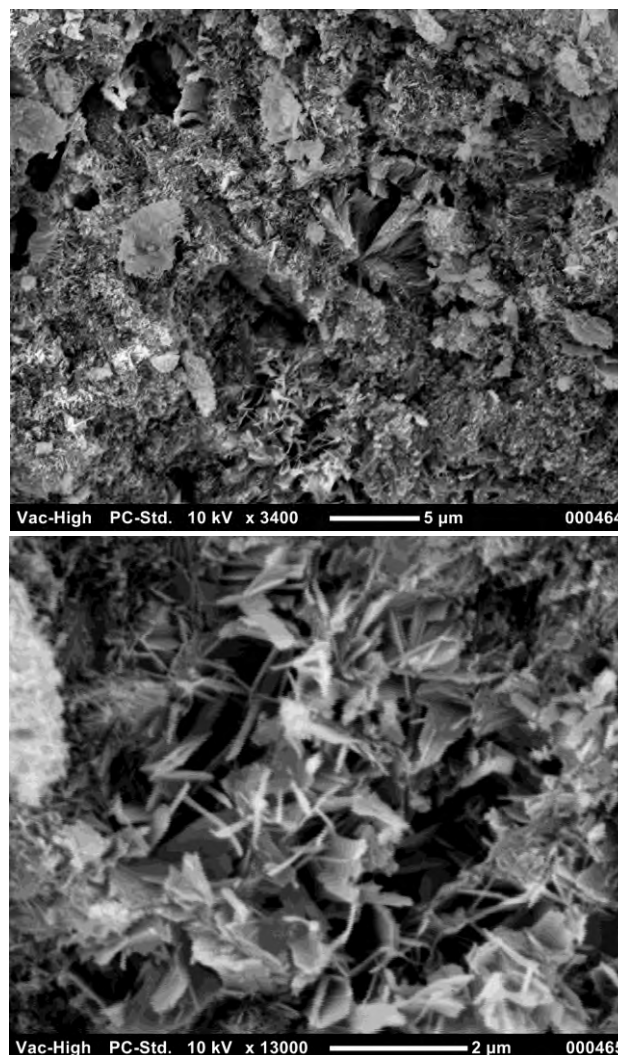


Fig 3. Electronic photomicrographs of autoclaved samples of amorphous SiO₂

According to DTA the regeneration of tobermorite into β -CaO·SiO₂ starts at temperatures above 1113 K (Fig. 5).

To provide the highest degree of regeneration of hydrosilicates into wollastonite and creating the conditions for crystal growth of wollastonite phase autoclaved sample were burned at a temperature of 1173 K with an holding for 5 h.

According to the X-ray diffraction analysis crystalline phase of burned material regardless of the specific of sample formation for burning is monophasic and represented in a form of β -CaO·SiO₂ (Fig. 6). ($d/n = 0,330; 0,309; 0,298;$

0,280; 0,255; 0,218; 0,201; 0,198; 0,191; 0,188; 0,175; 0,160; 0,153; 0,151; 0,138; 0,135; 0,133 nm).

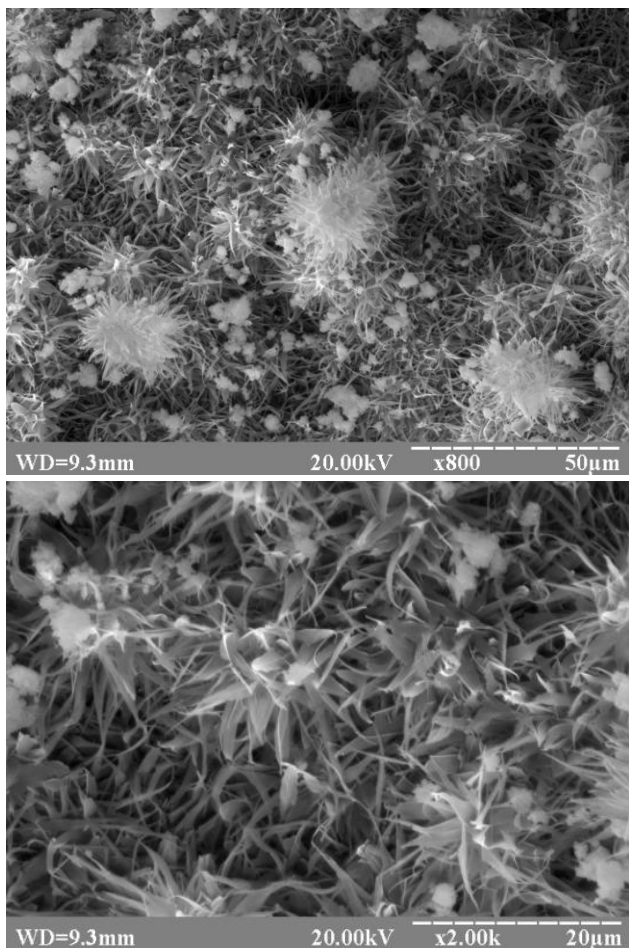


Fig 4. Electronic photomicrographs of autoclaved samples of amorphous SiO_2 with addition of presynthesized tobermorite

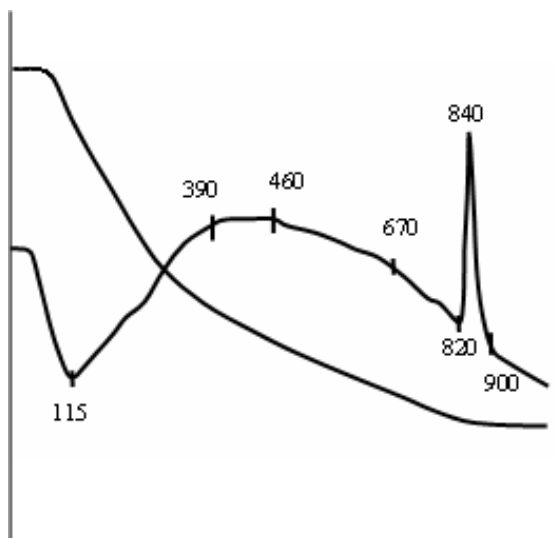


Fig. 5. Results of graphic studies of samples based on amorphous SiO_2

After burning the structure of the matrix phase of the hydro calcium silicate undergoes the significant changes. During the heating of a sample due to the dehydration of tobermorite and the release of chemically bound water

with the change of the density from 2.44 g/cm^3 to 2.92 g/cm^3 , the formation of the spongy structure represented by massive (up to 50 μm) conglomerate of separate structures with sizes ranging from 2 to 7 μm is observed (Fig. 7).

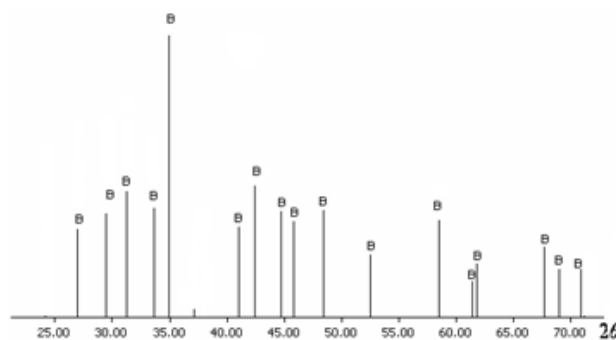


Fig. 6. DTA of autoclaved sample of tobermorite composition after burning: B – $\beta\text{-CS}$

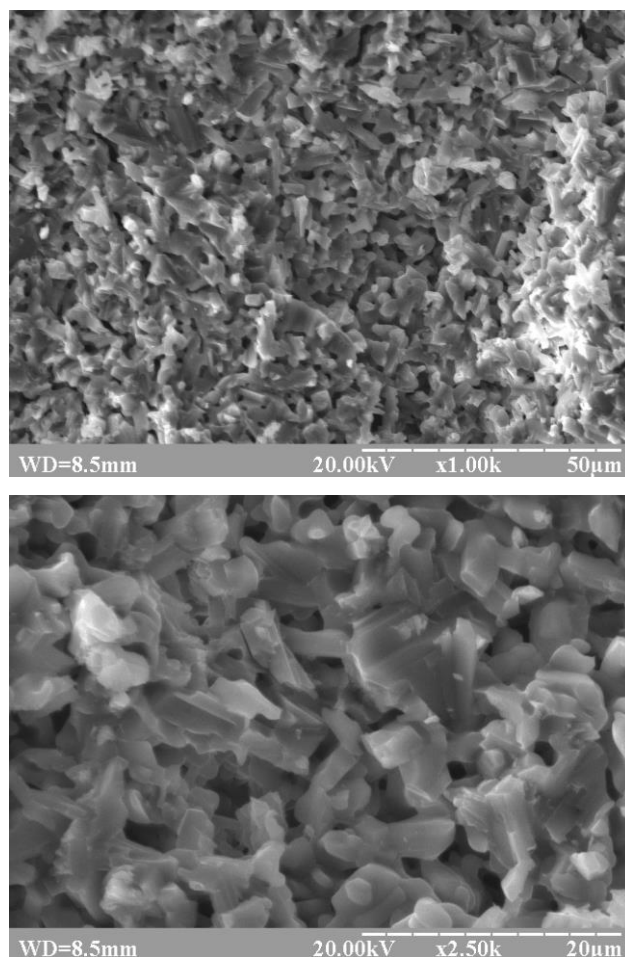


Fig. 7. Electronic photomicrographs of the surface of the burned samples

In order to intensify the process of crystal formation of wollastonite of more perfect form the burning of samples of powder tobermorite masses with the addition of 0,5-1 % mineralizer (B_2O_3) was carried out. According to the electromicroscopic results, addition of mineralizers intensify the crystallization processes and during the

burning promote the formation the more perfect crystals of wollastonite by size up to 70 μm with formation of typical parallel and columnar structure of material (Fig. 8).

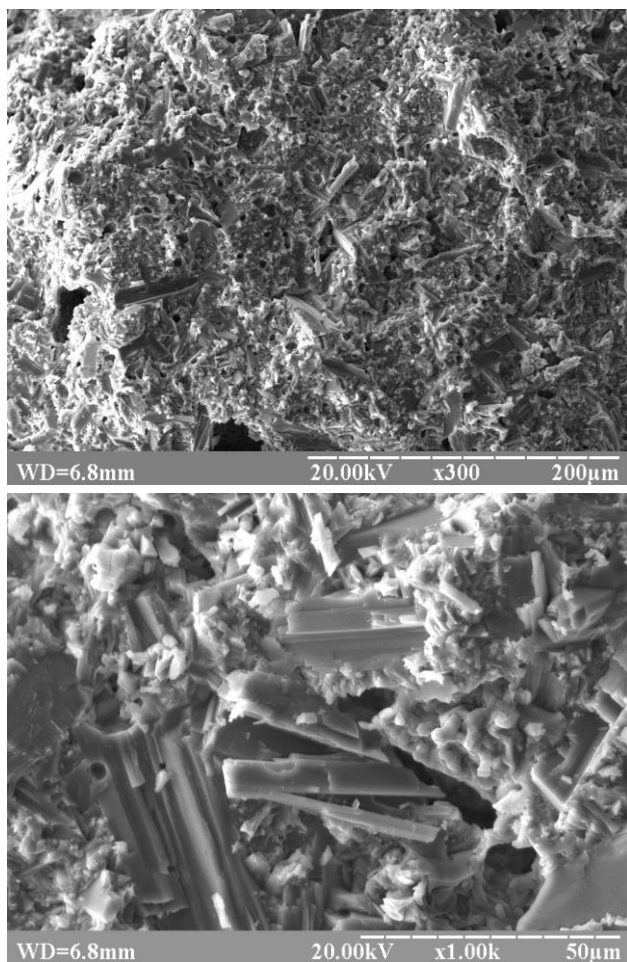


Fig. 8. Electronic photomicrograps of surface of burned sample as a powder with addition of 1 % of mineralizer (B_2O_3)

The accretion of column crystals leads to the formation of monolithic areas that after an impact split into the prismatic crystals of different sizes. The length of these areas is up to 70 μm , the width is 20 μm .

Conclusion

The conditions of synthesis of wollastonite by the technology, which includes the stage of hydrothermal treatment with obtaining calcium hydrosilicates of tobermorite group with its further burning of intermediate product to calcium metasilicate were investigated. According to the microscopic studies the presence of mineralizing ions significantly intensifies the processes of structure formation. The proposed technology allows to reduce the maximum temperature of burning by 200-300 K.

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