

SCIENCE FOR CERAMIC PRODUCTION

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WOLLASTONITE AS A NEW KIND OF NATURAL MATERIAL (A REVIEW)

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An analysis of literature and patent data on the problem of producing and using wollastonite and wollastonite-based materials is carried out; the results of studying the properties of heat-insulating articles produced by the vacuum pumping technology are summarized. The theoretical possibility of using natural wollastonite as a material for the production of heat-insulating articles is demonstrated.

Wollastonite is an extremely interesting but little studied material. Due to its set of valuable, sometimes unique properties, especially the low thermal conductivity, it is indispensable in many instances, for example, in production of heat-insulating ceramics, such as foundry lining and packing in the metallurgy and automobile industry.

Natural wollastonite is encountered in the form of a mineral based on calcium silicate (CaSiO₃).

The largest world producer and consumer of natural wollastonite is the USA [1]. There are a few wollastonite deposits in our country (in Siberia, the Ural Region, and Karelia), but this mineral is not currently mined; therefore, concentrated natural wollastonite has to be imported from Finland, USA, India, or the CIS countries.

Since 1997, the Trans-Resurs JSC is the only supplier of natural wollastonite from the Verkhne-Bodamskoe deposit in Kazakhstan to the Russian mineral market [2]. Wollastonite from the Bosaginskoe deposit in Kazakhstan is known as well and is in demand. As for imported varieties of natural wollastonite, the especially pure wollastonite from India merits a special note, since it surpasses the Bosaginskoe variety in its content of the main components and in several physicochemical properties.

Wollastonite has a fibrous structure in the form of needle-shaped crystals, which makes it possible to use it as a filler in paints [1]. The needle-shaped wollastonite crystals facilitate a better and more homogenous distribution of paints over the surface of an article. It is used as well in the

synthesis of pigments applied as underglaze paints to majolica products [3]. Its use in the production of high-quality glazes for porcelain ensures good spreadability of glaze, luster, and color.

A specific feature of natural wollastonite is the fact that wollastonite articles do not undergo significant volume changes in the course of their manufacture. Wollastonite is added to ceramic mixtures in making facing tiles [1]. Its use contributes to a decrease in the TCLE, linear shrinkage, and water absorption and ensures high thermal resistance and a constant volume in articles.

The quality of wollastonite and wollastonite-based materials improve when its concentration is high.

The demand for wollastonite is currently expanding, in particular, with respect to metallurgy companies working for aircraft, and in the context of the problem of replacing asbestos, which is hazardous to health [4, 5].

The most objective parameter characterizing hazard represented by various chemicals is the value of their maximum permissible concentration (MPC) in air. Below are comparative MPC values for the compounds used in making heat-insulating materials [6, 7].

Material	MPC, mg/m ³
Natural and synthesized asbestos, as well as mixed asbestos-rock dust containing not more than 10% asbestos	2
Glass and mineral fiber (as a typical representative of wollastonite)	4

Comparing the MPC values for dust of asbestos, asbestos-bearing materials, and wollastonite, it can be seen that

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wollastonite is a relatively safe material: its MPC is two times higher than that of asbestos and asbestos-bearing materials.

As for wollastonite, the U.S. National Labor Safety Institute has carried out an epidemiological research of the miners employed at the Wilsborough mine in order to clarify the effect of this material on their health. The investigation established that wollastonite is virtually safe with respect to its effect on health [1].

There is a known method for producing calcium silicate from a suspension containing diatomite, lime, and water by hydrothermal synthesis under heating and elevated pressure (U.S. Patent No. 4647499). The filling agents in making heat-insulating products are inorganic compounds: calcium carbonate; iron and zirconium oxides; silicon nitride or carbide. The resulting product has thermal conductivity $0.054 \text{ W}/(\text{m} \cdot \text{K})$ at temperature 100°C and $0.108 \text{ W}/(\text{m} \cdot \text{K})$ at 600°C . The bending strength at temperature 600°C is 0.5 MPa .

The Osaka Packing Company (Japan) has patented a method for making a lightweight material of calcium silicate (Japan Patent Application No. 63-19468). A suspension is prepared of silicic acid, calcium hydroxide, a compound based on amorphous carbon, and water in a quantity 5 times greater than the solid component. The solid carbon compound comprises 7–50 parts of the solid component. As a consequence of hydrothermal reaction, zirconite crystals and amorphous carbon are synthesized. After molding, drying, and firing, a material based on calcium silicate and amorphous carbon is formed. The company also suggested a method for making articles of CaSiO_3 with a metallic powder additive (Japan Patent No. 63-23148).

The Tokiyama Soda Company (Japan) has developed a material under the brand Florit, which is intended for producing porous ceramics [8]. The pore formation in ceramics is determined by the high fire shrinkage of calcium silicate. The material absorbs oil and water well and is easily moldable. The specific surface area of the powders is up to $450 \text{ m}^2/\text{g}$, the apparent density $0.08 - 0.22 \text{ g}/\text{cm}^3$, the calcination loss up to 10%, and they contain up to 90% SiO_2 and up to 27% CaO . There also exists a method for making asbestos-free heat-resistant material based on calcium silicate (Gr. Britain Patent No. 2085044). The material contains wollastonite as the filling agent, and a lime-siliceous compound serves as the binding agent. The material after molding is subjected to autoclave treatment under a pressure of over 0.6 MPa and drying at a temperature above 1000°C .

It is known that wollastonite ceramics can be synthesized on the basis of wollastonite material from mica deposits [9]. The mixture also contains clay and quartz sand. It is determined that the samples sinter at $1140 - 1190^\circ\text{C}$. The bending strength of the resulting ceramics is $160 - 180 \text{ MPa}$.

Another research considered the sintering and crystallization of wollastonite synthesized from natural Taiwanese materials [10]. Calcium oxide was introduced using marble

CaCO_3 , vein quartz SiO_2 , rice husk ash, and diatomite. The mixture contained 20% calcium or sodium plagioclase and some other components, as well as mineralizing agents (3% CaF_2 or AlPO_4). The materials were crushed to a particle size less than $10 \mu\text{m}$, the samples were compressed at a pressure of 100 MPa , and the sintering temperature was determined. The largest yield of $\beta\text{-CaSiO}_3$ was obtained in using mineralizing additives.

Wollastonite is known as an additive affecting the mechanical properties of high-temperature ceramics [11]. Introduction of up to 14% wollastonite to zircon mixtures made it possible to lower their sintering temperature to 1280°C (whereas pure zircon sintered at 1600°C). Furthermore, the additive improved the mechanical properties of the material.

The effect of synthesized wollastonite on the microstructure and properties of porcelain has been investigated [12]. It is established that synthesized wollastonite has a high degree of crystallization. An increase in the wollastonite content in porcelain mixture intensifies the sintering process, since it is an intense flux that stimulates porcelain formation, thus lowering the firing temperature by $50 - 80^\circ\text{C}$ and reducing the firing duration.

The study in [13] considers the Kalotermeks refractories (A, B, XP) based on CaSiO_3 , which were produced in Czechoslovakia. Their average density is $230 - 260 \text{ kg}/\text{m}^3$, bending strength $0.2 - 0.5 \text{ MPa}$, and thermal conductivity $0.087 - 0.2 \text{ W}/(\text{m} \cdot \text{K})$. The Kalotermeks refractories were used in the Czech Republic and Slovakia as lining for electric furnaces and high-temperature heaters in melting and thermal furnaces.

Wollastonite is also used in foaming compositions, which contain water-soluble silicate of an alkaline metal, a foaming agent, monticellite, halenite, dolomite, and mervinite powders, and water (Japan Patent Application No. 63-24954). The Japanese researchers proposed a method for producing articles by hydrothermal synthesis of wollastonite from silicic acid, lime, and water with resin and latex additives in the amount of 20–35 parts (Japan Patent Application No. 46137).

Introduction of up to 15% wollastonite in a mixture of plastic and nonplastic clays improves the thermomechanical properties of articles made of this mixture: it decreases the fire shrinkage and the TCLE and increases the mechanical strength and thermal resistance [14].

It is known [15] that the introduction of up to 10% ZrO_2 and CaO additive in the composite material based on $\text{ZrO}_2 - \text{CaO}$ prevents the volume variations in ZrO_2 , which contributes to the strengthening of the material.

Japanese researchers have established that addition of aluminum powder to a lime-siliceous mixture containing Portland cement makes it possible by autoclave treatment to produce a relatively strong lightweight material capable of withstanding temperatures about 750°C for a long time (Japan Patent Application Nos. 2755447, 2755449, 2757877, and 2757878).

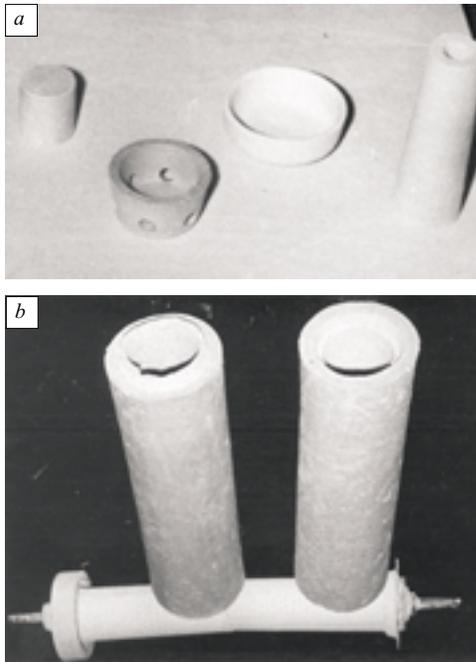


Fig. 1. A set of casting equipment based on wollastonite: sieves, a bush (a) and runner lining elements for casting aluminum-lithium aggregate melt (b).

The metallurgical industry in addition to various molding methods (casting, manual ramming, vibration compression, pressing, etc.) uses the most common and effective vacuum pumping method based on the hydropress technology [16, 17].

We tested natural wollastonite from India in making heat-insulating ceramics in accordance with the technology described in [16, 17].

Natural wollastonite and an inorganic binder were used to mold articles in the form of plates, pipes, and small-size equipment: sieves, bushes (Fig. 1) [17].

The microstructure of the initial sample based on wollastonite (Fig. 2) exhibited interweavings of chaotically distributed needle-shaped fibers of calcium silicate 1 – 6 μm in diameter and 50 – 75 μm long, and the presence of spheroid particles (beads) of diameter 3 – 5 μm . The CaSiO_3 fibers are fixed by fibril beams of calcium hydrosilicate 0.1 μm in diameter.

The wettability of wollastonite-based materials was studied using the lying drop method. A molten aluminum drop was placed on a plate made of the considered material. The drop was then photographed and the contact wetting angle was measured [17]. The resistance of the material was studied by the crucible method in aluminum melt at temperature 730°C in air.

The performed studies demonstrated that the considered material exhibited no visible structure modifications after service in aluminum-lithium alloy grade 1450 (Fig. 2). The fibrous structure persisted, and the beads were clearly visible.

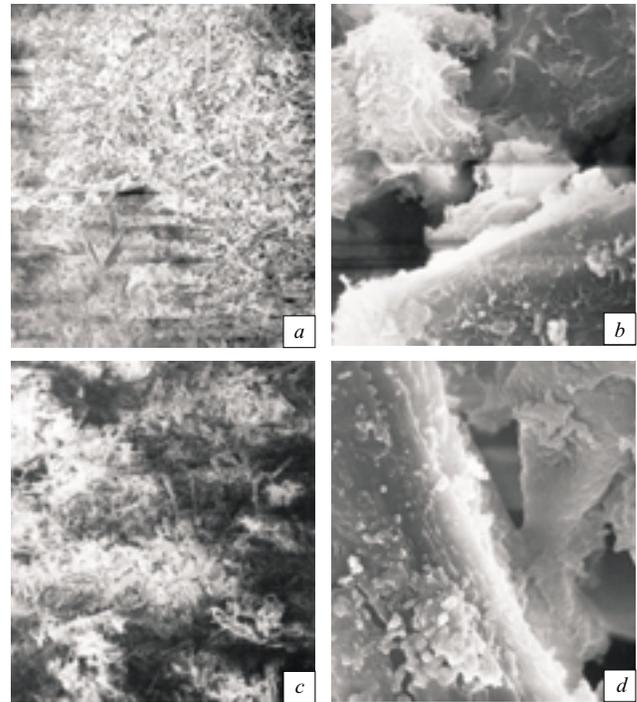


Fig. 2. Microstructure of a wollastonite sample before (a, b) and after (c, d) service in aluminum-lithium melt grade 1450: a, c) $\times 200$; b, d) $\times 10,000$.

The material was not wetted with aluminum melts, which was corroborated by the contact wetting angle values equal to 100 – 150°. A possible reason for nonwettability of wollastonite in aluminum consists in the formation of Al_2O_3 oxide film on the surface of the aluminum melt due to the physical moisture, which is released from the wollastonite sample in heating and reacts with aluminum.

The durability of the obtained materials was 144 h (6 heats), which exceeded several times the resistance of the known asbestos-bearing materials [16].

All this corroborates the principal possibility of using natural wollastonite in making heat-insulating ceramics. Articles based on this material can be recommended for the lining of casting and pouring equipment in melting aluminum melts, which provides for savings in power and metal consumption in transportation and casting of aluminum melts and ensures high quality of the cast metal.

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