The prospects for hydrothermal processing leucoxene concentrates for the production of synthetic wollastonite

Y V Zablotskaya, G B Sadyhov, K. G Anisonyan and T V Olyunina

A. A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, 119334 Leninskii pr. 49, Moscow, Russia.

E-mail: Nboxclear@gmail.com

Abstract: The paper presents the results of a study of the simultaneously receive β-wollastonite in autoclave beskrainyi leucoxene ore Yarega field. The parameters of thermal treatment of calcium metasilicate hydrate with the production of β-wollastonite were determined by thermogravimetric and x-ray phase analyses. With the help of electron microscopy it was found that the resulting CaSiO₃ has a needle shape. The possibility of using the obtained wollastonite in the production of ceramic composites was studied and the compositions of ceramic masses and the modes of its heat treatment were determined.

1. Introduction

World production of wollastonite (calcium metasilicate CaSiO₃) is about 1 million tons per year [1]. According to the data of the U.S. Geological Survey, natural wollastonite is produced by a relatively small number of mining enterprises located in the following countries: China, India, USA, Mexico, Finland [2]. Synthetic wollastonite is produced mainly in European countries that do not have large reserves of natural wollastonite (UK, Denmark, France, Germany). In Russia, wollastonite is rather an unconventional type of raw material and the volume of its consumption is very small.

The main areas of application of wollastonite are the production of ceramics 30-40%, polymers (plastics and rubber) 30-35 %, paints 10-15%, as well as used in the construction industry, metallurgy. The world market of wollastonite can be divided into two segments – needle wollastonite with a high ratio of grain length (L) to diameter (d) (L/d>3) (high-aspect-ratio – HAR) and powder wollastonite with L/d<3 (low-aspect-ratio – LAR). Grades HAR are mainly used as micro-reinforcing fillers in polymers, elastomers and coatings to provide thermal resistance, corrosion resistance and abrasion resistance. Wollastonite of the grades LAR is used in those areas where the chemical composition is more important than the physical (for example, reinforcing) properties [1].

Small proven reserves of natural wollastonite in the world and its price, as well as the increasing demand for this raw material stimulate interest in the development of methods for producing synthetic wollastonite. The cost of synthetic wollastonite is almost two times lower than the commodity price of natural. The properties and structure of synthetic wollastonite will be determined by the nature of the raw materials, the ratio of calcium and silicon - containing components, as well as the synthesis conditions. Unlike natural wollastonite, synthetic material is characterized by a higher degree of uniformity in composition and low content of impurities, as well as adjustable dispersion.

The main methods of synthesis of wollastonite are: solid-phase synthesis (sintering of calcium and silicon - containing components at 1000-1400 ° C), hydrochemical and hydrothermal synthesis of
calcium hydrosilicates at temperatures from 80 °C to 350 °C and their subsequent dehydration and calcination at temperatures above 800 °C [3]. The hydrothermal method is more promising and manageable for industrial use, since it allows to simultaneously vary many parameters of the process (temperature and duration of synthesis, chemical composition of hydrothermal solutions and the ratio of components) to obtain calcium hydrosilicates of a certain stoichiometric composition. The raw materials for the synthesis of wollastonite are a variety of compounds of calcium and silicon of natural (diatomite, flusk, cristobalite, tridimite, gypsum, chalk, calcite, marble, limestone) or man-made origin (for example, phosphogypsum, borohypse, quartz glass, blast furnace slag).

In Russia, the Republic of Komi is one of the largest titanium deposits - Yareg silicon-titanium sandstones. Main titanium mineral is leucoxene, which is a mineral the structure of thin intergrowths of rutile and quartz (about 40%). Processing of such high-silicon raw materials is associated with significant difficulties. In IMET RAS proposed a new complex approach to the issue of processing ore leucoxene, which provides for the use of silica as raw materials for the simultaneous synthesis of wollastonite. As a result, not only titanium-containing product-artificial rutile, but also synthetic wollastonite is obtained as final products [4].

2. Experimental
Method of desiliconization of a leucoxene concentrate flows in the process of autoclave leaching at a temperature of 200-220°C, pre-reduced in terms of magnetizing roasting, with milk of lime in the presence of NaOH, serving only as the initiator of the process. The result is the dissolution of silica with soluble compounds Na₂SiO₃, followed by its interaction with CaO·H₂O and deposition of the hydrate calcium silicate (HCS). The process is carried out at the stoichiometric ratio CaO/SiO₂, which allows to obtain calcium metasilicate hydrate CaO·SiO₂·nH₂O. With the help of wet magnetic separation, the torsional concentrate is separated from the HSC, which is then dried and calcined at 1050-1100°C.

The phase composition of the material obtained in the process of desiliconization of a leucoxene and further heat treatment, were determined by x-ray diffraction, which was performed on the diffractometer DRON-3M in CuKα-radiation. Transcript of diffraction patterns was carried out using the PDF (POWDER DIFFRACTION FILE).

The specific surface area and porosity of the obtained synthetic wollastonite powders are determined using the Tristar 3000 analyzer. The morphology of the samples of calcium silicate hydrate and wollastonite were investigated using scanning electron microscopy on the microscope LeO – 430i. The determination of the compressive strength was performed on a universal Electromechanical Instron machine 3382.

In order to study the prospects of using the obtained synthetic wollastonite in the production of ceramics, the performance properties of ceramic samples based on it were studied, the compositions of ceramic masses and the modes of its heat treatment were determined. Based on the analysis of literature data, two variants of mixtures were chosen: wollastonite and kaolin clay; on the basis of wollastonite with the addition of oxalic acid [5, 6]. Silicate mixtures (ceramic masses) were prepared from the resulting material CaSiO₃, then composite billets of cylindrical shape were formed, which were fired at temperatures of 1100-1300°C with an isothermal exposure of 1 hour in the Nabertherm GMBH HTCT 03/16 furnace.

3. Results and discussion
In the process of desiliconization of a leucoxene concentrate was obtained, the calcium metasilicate, which is a white finely dispersed substance with a specific surface equal to 11.2 m²/g and the volume of the inner pores is 1.1 m³/g. The dried material has the following composition: 50.2% of SiO₂, 46.9% of CaO, up to 0.9% of TiO₂ and 1.6% Na₂O. Using scanning electron microscopy established that in conditions of autoclave leaching the formation of calcium metasilicate, consisting of needle-like crystals to form separate agglomerates with sizes from 4 up to 20-30 μm (Figure 1 a, b).
Figure 1. Photomicrographs of wollastonite, obtained by autoclave leaching of leucoxene concentrate with milk of lime: a, b – dried at 105°C; c, d – calcined at 1050°C.

As shown in figure 1, the morphology of the material dried at 105°C (a, b) or calcined at 1050°C (c, d) does not change. This suggests that the formation of "needles" occurs in the autoclave at the stage of hydrothermal treatment of silicon-titanium concentrate. It should be emphasized that the associated production of wollastonite needle modification in the processing of leucoxene concentrates Yarega field is one of the advantages of the proposed method.

The method of dry pressing at a pressure of 10 MPa formed ceramic samples of variable composition of wollastonite (W.) and kaolin clay (C.). In the process of firing clay forms a glass phase, which contributes to the sintering of the material. Samples after heat treatment, carried out to 1150°C, have a low degree of hardening, due to the insufficient amount of binder formed under these conditions. Samples of composition 50%W+50C%, 70%W+30%C, and 87.5%W+12.5C%, annealed at a temperature above 1200°C, characterized by an optimal compressive strength of 6.4 ÷14.1 MPA, the linear shrinkage of the material is 6.9 to 17.6 per cent. The average density is 2.4 g/cm³. It should be noted that the samples prepared from pure wollastonite without additional additives are characterized by a decrease in strength characteristics from 16 MPA to 5 MPa with an increase in temperature from 1250°C to 1300°C.

In the course of the study, comparative tests of ceramic samples based on wollastonite, additionally containing oxalic acid and water at the following ratio of components (wt. %): wollastonite 36-50, oxalic acid 4-5, H₂O – the rest. Preparation of the ceramic mass was carried out by the method of molding the mixture in a mold with pre-drying at room temperature and at 105°C. Further, the samples were fired at temperatures of 1200-1300°C with an isothermal exposure of 1 hour. In this version of the ceramic mass oxalic acid creates an acidic environment in which the dissolution of the wollastonite and its transformation into silica gel. During the subsequent high-temperature firing of the samples, the silica gel turns into a wollastonite bond, leading to the regeneration of the dissolved wollastonite.
As a result, it was determined that the optimal composition of the ceramic mass is a composition containing wollastonite 40%, oxalic acid 4%, at a firing temperature of 1250-1300°C. Figure 2 shows the ratio of strain to compression stress applied to this sample after high-temperature firing at 1300°C.

![Deformation diagram of a ceramic sample based on wollastonite (40%) with the addition of oxalic acid.](image)

**Figure 2.** Deformation diagram of a ceramic sample based on wollastonite (40%) with the addition of oxalic acid.

4. **Conclusion**

The strength characteristics and density of the obtained calcined ceramic composites, consisting of a mixture of calcium metasilicate and clay, based on wollastonite with oxalic acid, correspond to the performance characteristics of high-temperature ceramics, can be recommended for use in industry, for example, as a lining and refractory material in the metallurgy of aluminum alloys. It should also be noted that according to the latest literature data, wollastonite with a needle structure is a promising and high-quality filler in cement, acts as a reinforcing component that increases the strength of cement stone.

**Acknowledgements**

The work was carried out according to the state task № 007-00129-18-00.

**References**

[1] Review of the wound of wollastonite in the CIS (6) 07.04.2017 Access mode: [http://www.infomine.ru/files/catalog/58/file_58.pdf](http://www.infomine.ru/files/catalog/58/file_58.pdf)

[2] Wollastonite. Prepared by Daniel M. Flanagan U.S. Geological Survey, Mineral Commodity Summaries January 2017 Access mode: [https://minerals.usgs.gov/minerals/pubs/mcs/2017/mcs2017.pdf](https://minerals.usgs.gov/minerals/pubs/mcs/2017/mcs2017.pdf)

[3] Gladun V D, Akatyeva L V, Andreyeva N N and Kholkin A I (2004) Obtaining and application of synthetic wollastonite from natural and industrial row. *Chemical technology* 9 pp. 4 – 11.

[4] Sadykhov G B, Zablotskaya Yu V, Anisonyan K G, Kopyev D Yu, Olyunina T V and Goncharenko T V (2015) Obtaining of needle wollastonite under catalytic pressure leaching of leucoxene concentrate by lime milk *Journal of Advanced Materials* 1 pp 65-72.

[5] Suzdalytsev E, Vikulin V and Rusin M The method for producing ceramic products based on wollastonite *Patent RF*, no. 2298537 publ. 10.05.2007.

[6] Simonova N, Samoylo A and Veresthagin V Ceramic mass on the basis of wollastonite *Patent RF*, no. 2422402 publ. 27.06.2003.