



# Solid-phase synthesis of wollastonite in natural and technogenic siliceous stock mixtures with varying levels of calcium carbonate component



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## ABSTRACT

Solid-phase synthesis of wollastonite has been determined to be primarily affected by the structural and mineralogical properties of the siliceous stock – its chemico-mineralogical composition (purity and presence of amorphous component) and granularity, as well as variations in phase change behaviour at high temperatures. Wollastonite synthesis occurs most completely in the mixtures of calcium carbonate with amorphous (microsilica) or semi-crystalline (gaize or diatomite) siliceous stock, yielding 92–96% wollastonite at 1200 °C. For natural quartz-based stock (marshallite), wollastonite yield does not exceed 60–80%. Solid-phase wollastonite synthesis in mixtures of reactive amorphous or semi-crystalline siliceous stock with varying quantities of calciferous stock (10–50 wt% CaO) produces wollastonitic ceramics chemically resistant to molten aluminium with the specific gravity of 1.1–1.7 g/cm<sup>3</sup> and the compressive strength of 28–76 MPa, which exceeds the requirements for ceramics in foundry equipment by a factor of 3–3.5.

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## 1. Introduction

One of the possible ways to enhance the strength characteristics of porous ceramic materials is by utilising additives with reinforcing effect due to non-isometric habit of the particles of their crystalline phase, which form acicular aggregates within the ceramic matrix. Wollastonite rocks are one example of such additives [1–5]. Another way to improve strength of highly porous ceramics is to synthesize such a crystalline phase within the ceramic matrix in situ in the process of firing [6,7].

The use of natural or synthetic wollastonite is highly promising in terms of quality enhancement of ceramic materials used in thermal insulation and aluminium foundry equipment. This is due to a recent tendency to replace carcinogenic asbestos-based refractories with environmentally friendly wollastonite-based ceramic materials. Enhanced performance characteristics of the wollastonite-based refractory lining materials are ensured by the reinforcing effect of acicular crystals of wollastonite, its high thermal stability and chemical resistance to molten aluminium.

The composition, structure and properties of synthetic wollastonite largely depend on the nature of the source materials,

their ratio and the synthesis environment [7,8]. A number of methods are currently known for production of wollastonite from various substances containing calcium and silicon: crystallisation from melt [9], sol-gel method [10–12], hydrothermal (autoclave-based) synthesis of calcium hydrosilicates with their subsequent dehydration [13–17], and synthesis via solid-phase reactions [18–20].

A bulk of scientific and practical experience in the development of intensive processes for wollastonite production using ceramic technologies has been accumulated to date [21–23].

A specific aspect of solid-phase synthesis of wollastonite CaO · SiO<sub>2</sub> is the presence of an intermediate stage – synthesis of dicalcium silicate – in this process. Formation of 2CaO · SiO<sub>2</sub> as the initial product is predicated upon the insular structure of its crystal lattice with separate and isolated SiO<sub>4</sub> tetrahedra [24,25]. The rates of formation of the intermediate product (calcium orthosilicate, 2CaO · SiO<sub>2</sub>) and the final one (wollastonite, CaO · SiO<sub>2</sub>) depend on the particle size of the stock mixture components, their ratio, crystallochemical structure of silica, and process temperature and duration [7,8]. Low yields of the target product, high temperatures (1100–1200 °C) required for synthesis and limited availability of the stock materials provide a rationale for research in activation of solid-phase processes for wollastonite synthesis from natural and technogenic stock using ceramic technologies.

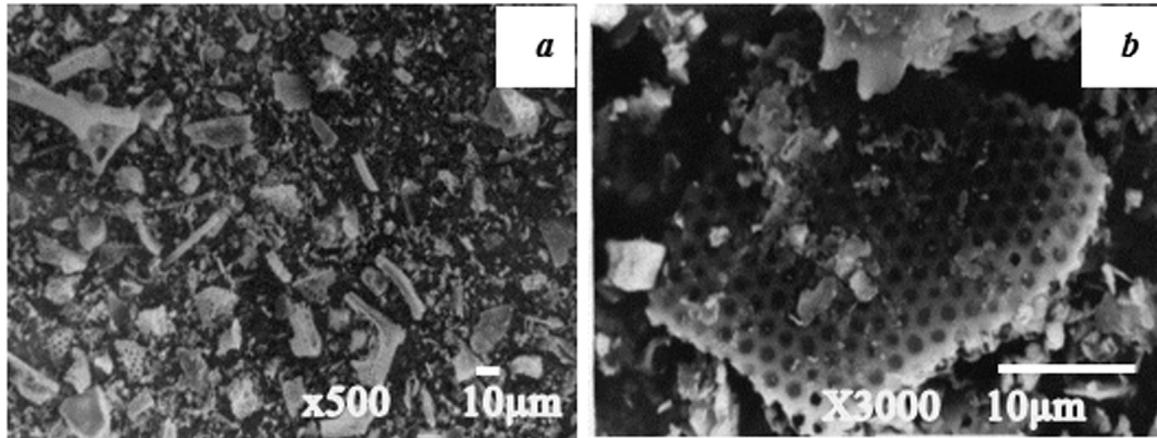
The present paper is dedicated to research issues in solid-phase wollastonite synthesis in high-silica stock mixtures (diatomite,

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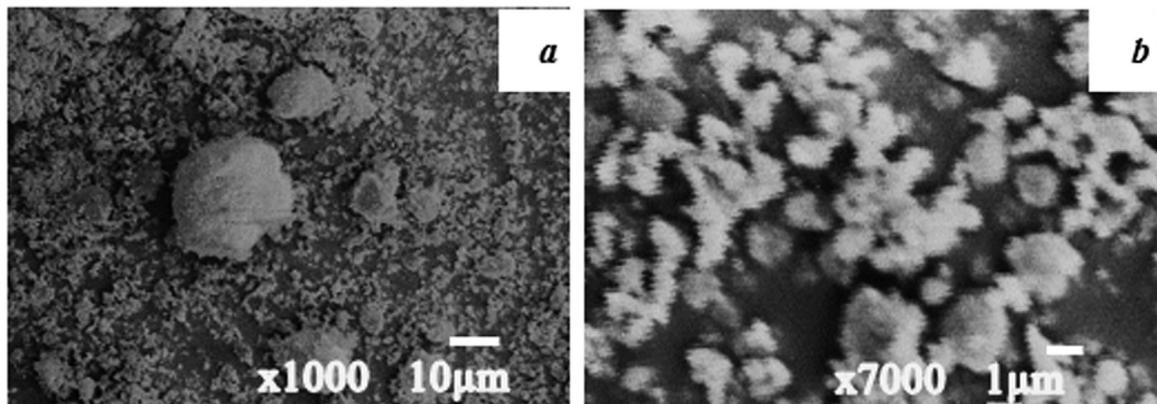
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**Table 1**  
Chemical composition of feedstock components in the study.

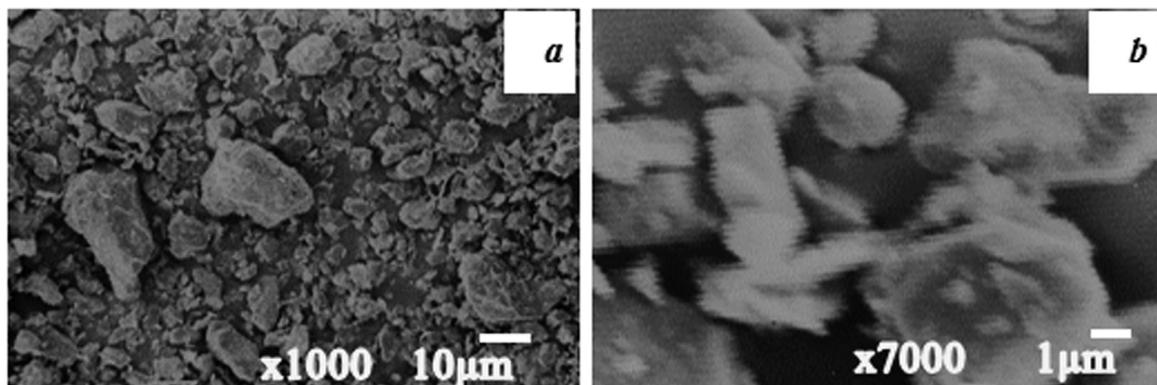
Feedstock	Oxide content (wt%)									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	C	Δm <sub>imp</sub>
<i>Siliceous feedstock</i>										
Marshallite (Aleksandrovskoe)	97.11	1.51	0.32	0.13	0.01	0.22	0.02	0.02	–	0.66
Marshallite (Elbashinskoe)	95.70	2.10	0.27	0.80	0.60	–	–	–	–	0.53
Microsilica	88.00	0.40	0.70	2.70	2.70	2.62	1.50	–	1.40	3.00
Diatomite	86.44	5.30	1.60	0.74	0.53	–	–	–	–	5.39
Gaize	83.00	5.25	2.72	2.05	1.47	–	–	–	–	5.51
<i>Calcium carbonate feedstock</i>										
Chalk (Inzenskoe)	1.64	0.60	0.17	54.40	0.12	–	–	–	–	42.30



**Fig. 1.** Electron microscope images of diatomite: a –  $\times 500 \times$  b –  $\times 3000 \times$ .



**Fig. 2.** Electron microscope images of gaize: a –  $\times 1000 \times$  b –  $\times 7000 \times$ .



**Fig. 3.** Electron microscope images of marshallite: a –  $\times 1000 \times$  b –  $\times 7000 \times$ .

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