INVESTIGATION OF THE PROCESS AND PRODUCTS OF THE MASHS INTERACTION OF SILICON DIOXIDE WITH MAGNESIUM IN THE CARBON-FREE METHOD FOR OBTAINING SILICON

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Abstract
Mechanocomposites SiO₂ / Mg with different component ratios were obtained. It was demonstrated that chemical interaction between the components in these systems starts at lower temperatures. The products of the SHS process with SiO₂ / Mg mechanocomposites as precursors are mainly silicon and magnesium oxide; in addition, magnesium silicate and silicide are formed. After the treatment of the product in three stages with different acids, silicon was obtained in the form of agglomerates about 500-1000 nm in size, composed of smaller particles.

Introduction
The goal of the present work was to study the possibility to obtain silicon through the reduction of silicon dioxide with magnesium by means of MASHS. Oxide reduction by active metals, such as Al, Mg is a known phenomenon. Due to the exothermal character of these reactions, they can be carried out also mechanochemically, for example the reduction of copper oxide by aluminium [1], and by means of self-propagating high-temperature synthesis (SHS) [2]. Preliminary mechanical activation of the components of SHS is known to decrease the temperature of the start of chemical interaction, and also allows one to modify the conditions of chemical reactions and strongly vary the thermal parameters of synthesis providing the possibility to obtain ultrafine and even nanocomposite materials [3]. Previous studies showed
that silicon dioxide is reduced by aluminium by means of MASHS with the formation of nanocomposite Si / α-Al₂O₃ [4].

Methods and materials
We used aerosil (nanometer-sized SiO₂ – d < 10 nm) and magnesium powder (TU 4312). The mixtures of silicon dioxide and magnesium taken in various ratios were treated in AGO- [5], (cylinder volume 250 cm³, ball diameter 5 mm, the total mass of balls 200 g, the weighed portion of the sample 10 g) at different frequencies of cylinder rotation (600 r.p.m. and 1000 r.p.m.) and activation time, in the atmosphere of argon. IR spectra were recorded with TENSOR 27 spectrometer. X-ray studies were carried out using X’TRA diffractometer (Termo ARL, Switzerland) with CuKα (λ = 1.789 Å). Thermal processes were studied by means of differential scanning calorimetry (NETZSCH STA 409 PC/PD). The SHS in the system SiO₂ / Mg and investigation of its technological parameters were carried out in the SHS-8 reactor in the atmosphere of argon. The SHS was initiated with the help of a tungsten coil by passing the electric current. Temperature and combustion rate were estimated using the thermocouple method (chromel-alumel thermocouples with a diameter of ≈ 0.2 mm) with the help of the external 2-channel 24-rate ADC ADSC24-2T. The structure of resulting samples was studied with the help of the high-resolution scanning electron microscope (SEM) MIR@TESCAN with the attachment for micro-X-ray structural analysis (MPCA).

Results and discussion
Magnesium is an active reducing agent, so at the first stage we studied the products of the mechanochemical reduction of well dried SiO₂ by magnesium in the atmosphere of argon. According to the data of IR spectroscopy, during the treatment in a high-energy ball mill with the maximal load of 60 g, as early as after 40 s the product is mainly magnesium silicate Mg₂SiO₄ (Fig. 1 b).

Instead of the characteristic bands of SiO₂ ν₃, ν₁, ν₄, with the maxima at 1095; 805 and 480 cm⁻¹, respectively, the bands at 1200-800 cm⁻¹, 600 cm⁻¹ and in the region of 550-400 cm⁻¹ appear; according to [6], these bands are to be assigned to the vibrations ν₃, ν₁ and (ν₄+ν₂)
SiO$_4^-$ of the tetrahedron of silicate magnesium, respectively. An increase in the number of maxima of bands $v_3$, $v_4$ and the appearance of the vibration band $v_2$ are connected with the low symmetry of SiO$_4^-$ tetrahedron in the structure of magnesium silicate [6]. If the load in the mill is decreased to 20 g, then Mg$_2$SiO$_4$ is not formed after mechanical activation for a short time, as the bands of SiO$_2$ are conserved in the spectrum (Fig. 1 c); chemical interaction with the formation of silicates starts much later ($\tau_a \approx 4$ min - Fig. 1 d).

Fig 1. IR-spectrum mixtures Mg + SiO$_2$ stoihioemetries (2:1) before (a) and after MA 1min, 60g,(b); 40s., 20g (c); 4 min, 20g, (d).
The DSC studies of SiO\(_2\)/Mg mechanocomposites showed that as early as after activation for 40 s the thermal effect of the reaction decreases in comparison with the initial mixture (Fig. 2), correspondingly, the chemical interaction between the components starts at substantially lower temperature.

**Fig 2.** DSC-curves mixtures 4.8g Mg +6.0g SiO\(_2\): a – before, b – after 40s. activation

The conditions for mechanical activation (40s. with the acceleration of 20g) was adjusted with the stoichiometric composition SiO\(_2\) / Mg = 1: 2 and applied to produce the required amounts of precursors Mg / SiO\(_2\) with different stoichioemtries for SHS processes (table).

**Table**
Composition SiO\(_2\)/Mg with different stoichioemtries for SHS processes

<table>
<thead>
<tr>
<th>No</th>
<th>Mg (g)</th>
<th>SiO(_2) (g)</th>
<th>molar ratio of Mg/SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.8</td>
<td>6.0</td>
<td>2 : 1</td>
</tr>
<tr>
<td>2</td>
<td>6.0</td>
<td>6.0</td>
<td>2.5 : 1</td>
</tr>
<tr>
<td>3</td>
<td>7.3</td>
<td>6.0</td>
<td>3 : 1</td>
</tr>
<tr>
<td>4</td>
<td>9.7</td>
<td>6.0</td>
<td>4 : 1</td>
</tr>
</tbody>
</table>
The excess amount of magnesium was introduced in order to accelerate the heat sink during the SHS process and thus reduce combustion temperature.

XRD data of mechanochemically obtained precursors showed that no phase transformations occur during mechanical activation within this time interval; only the intensity of the diffraction reflections of magnesium changes (Fig. 3), because SiO₂ used in this work is X-ray amorphous.

![Diffractograms mechanocomposites Mg / SiO₂. Number of curve according in table](image)

Fig. 3. Diffractograms mechanocomposites Mg / SiO₂. Number of curve according in table

Thermograms of SHS processes for different compositions of the reaction mixture (Mg + SiO₂) are presented in Fig. 4. One can see that for the precursors of the stoichiometric composition (Fig. 4a) sharp temperature disturbance occurs at the stage of initiation, followed by multi-stage combustion with the isothermal plateau at a temperature about 600°C, and subsequent comparatively slow cooling. At that stage, the maximal combustion temperature (~1283°C) is achieved. In the
samples with the excess magnesium content, a very rapid (almost momentary) temperature rise and its very rapid drop are observed. The maximal combustion temperature of these samples reaches 1050° C.

Fig 4. Thermograms of SHS processes for compositions (table): a – 1; b – 4

The IR spectra of the SHS products provide evidence of the formation of magnesium silicates in all the mixtures under investigation. According to the data of X-ray phase analysis, the major products of SHS are silicon and magnesium oxide; the formation of definite amounts of magnesium silicate and silicide is also confirmed.

Fig 5. Diffractograms for products MA SHS for compositions (table): 1, 2, 4
The amount of Mg$_2$Si increases substantially with an increase in magnesium excess; the amount of magnesium silicate decreases (Fig. 5) because silicon immediately interacts at high temperature with magnesium to form Mg$_2$Si. It should be noted that it is easier to separate chemically silicon from magnesium silicide than from silicate.

XRD data results show that after a thorough three-stage acid treatment of the SHS product (Fig. 6) silicon was to a substantial extent purified from the impurities, such as MgO, Mg$_2$Si, Mg$_2$SiO$_4$, SiO$_2$.

Fig 6. Diffractograms for products MA SHS for compositions after a thorough acid treatment of the SHS product composition (table) 3 after SHS (a) и after a thorough acid treatment (b)

The average size of agglomerates of silicon particles after purification is ~500 nm, though some larger agglomerates with a size up to 2-3 µm occur. One can see in Fig. 7 that the agglomerates consist of nano-dispersed particles with narrow size distribution (the average particle size is 50-80 nm), and the shape of the particles is almost spherical. It should be noted that the powder samples, obtained from initial mixtures with magnesium in excess, in addition to the particles of round shape contain also somewhat larger particles (with a size up to 1 µm) having typical faceting; the higher is magnesium excess, the less is the relative content of smaller rounded particles. The presence of the
particles with typical faceting is likely to be due to the realization of some other mechanism of the formation of silicon particles.

Fig 7. Powder Si after purification (precursor composition No 1)

Investigation showed that it is possible to obtain rather pure silicon from silicon dioxide using magnesium as the reducing agent according to the MA SHS procedure.

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References
