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Investigation of the Process and Products of the MASHS Interaction of Silicon Dioxide with Magnesium Reparation in the Carbon-Free Method for Obtaining Silicon

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Mechanocomposites SiO_2 / 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 SiO_2 / 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, compoused of smaller particles about 50-80 nm.

Keywords: Mechanocomposites, Mechanochemical activation, Self-propagating High-temperature Synthesis, Nanoparticles silicon, Leach.

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1. 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-Al_2O_3 [4].

2. METHODS AND MATERIALS

We used aerosil (nanometer-sized SiO_2 – d < 10 nm) and magnesium powder (TU 4312). The mixtures of silicon dioxide and magnesium taken in various ratios were treated in AGO-2, (cylinder volume 250 cm^3, 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 CuK_α (λ = 1.789 Å). Thermal processes were studied by means of differential scanning calorimetry (NETZSCH STA 409 PC/PG). The SHS in the system SiO_2 / 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-chanel 24-rate ADC ADSC24-2T. The structure of resulting samples was studied with the help of the high-resolution scanning electron microscope (SEM) MIRA\TESCAN with the attachment for mciro-X-ray structural analysis A template is a tool for enforcing a standard layout and look and feel across multiple pages or within content regions. It provides stricter standardization controls of the documents. In other words, a template is a form, or pattern used as a guide to making something. Due to it you do not need every time set the margins, spacing, page layout, fonts, format options, etc. (MPCA).

3. 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 Mg_2SiO_4. Instead of the characteristic bands of SiO_2 ν_3, ν_1, ν_4, 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 [5], these bands are to be assigned to the vibrations ν_3, ν_1 and (ν_4 + ν_2) SiO_4^- of the tetrahedron of silicate magnesium, respectively. An increase in the number of maxima of bands ν_3, ν_4 and the appearance of the vibration band ν_2 are connected with the low symmetry of SiO_4^- tetrahedron in the structure of magnesium silicate [5]. If the load in the mill is decreased to 20 g, then Mg_2SiO_4 is not formed after mechanical activation for a short time, as the bands of SiO2 are conserved in the spectrum; chemical interaction with the formation

of silicates starts much later ($\tau_a \cong 4$ min). The DSC studies of SiO_2 / Mg mechanocomposites showed that as early as after activation fro 40 s the thermal effect of the reaction decreases in comparison with the initial mixture, correspondingly, the chemical interaction between the components starts at substantially lower temperature. The conditions for mechanical activation (40s. with the acceleration of 20 g) 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 1).

Table 1 – The stoichiometric composition SiO_2 / Mg produce the required amounts of precursors Mg / SiO_2 with different stoichioemtries for SHS processes

№	**Mg (g)**	**SiO_2**	**Molar ratio of Mg/SiO_2**
1	4.8	6.0	2.0 : 1
2	6.0	6.0	2.5 : 1
3	7.3	6.0	3.0 : 1
4	9.7	6.0	4.0 : 1

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, because SiO_2 used in this work is X-ray amorphous. Thermograms of SHS processes for different compositions of the reaction mixture (Mg + SiO_2) show that for the precursors of the stoichiometric composition 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. 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. The amount of Mg_2Si increases substantially with an increase in magnesium excess; the amount of magnesium silicate decreases because reduced silicon immediately interacts at high temperature with magnesium to form Mg_2Si. 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 silicon was to a substantial extent purified from the impurities, such as MgO, Mg_2Si, Mg_2SiO_4, SiO_2. 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. 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 (see Fig. 1**)**.

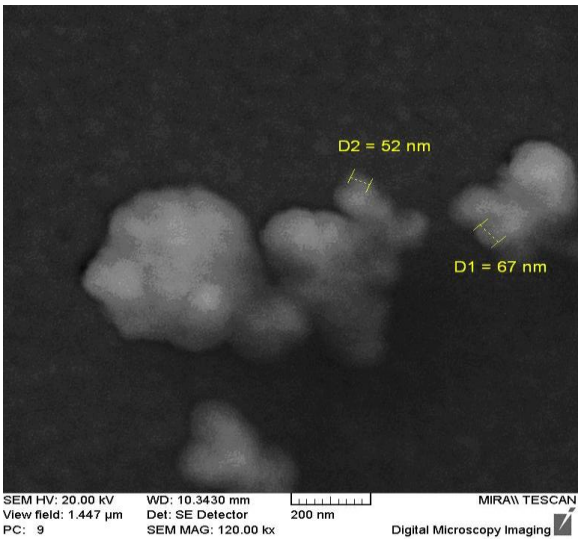

Fig. 1 – Powder Si after purification

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. 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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