The method of producing of nano-dimensional silicon carbide by compressing in a cyclic chemical reactor

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Abstract. The method of producing of nano-dimensional silicon carbide and experimental results of pyrolysis of a mixture of a silicon-hydrocarbon composition by compressing in a cyclic chemical reactor has been proposed. New structural design solutions and ceramic coatings obtained by applying the technology of microarc oxidation were used in the compression unit of the chemical compression reactor. This allowed us to forego the traditional schemes, to achieve a high compression ratio, and to obtain the pressure and temperature required in the reaction zone for silicon-hydrocarbon composition pyrolysis. The flow-through pyrolysis method in chemical compression reactor is convenient, technological and efficient to be used in the production of high purity silicon carbide nanopowders.

1. Introduction
A great interest of researchers is caused by a number of unique physical properties of SiC. Electronic components made of silicon carbide have significant advantages over the electronic components based on silicon and gallium arsenide:
- band gap is several times wider;
- electrical strength is 10 times greater;
- high permissible operating temperatures (up to 600°C);
- thermal conductivity is 3 times greater than that of silicon, and almost 10 times greater than that of gallium arsenide;
- resistance to radiation;
- withstands high current densities;
- stability of electrical characteristics with temperature changes and absence of parameter drift in the course of time [1].

Silicon carbide is widely used in power electronics – superfast high voltage Schottky diodes, n-MOS transistors and high-temperature thyristors. In addition, silicon carbide is promising for use in non-silicon electronics as a substrate material – in heterostructures based on GaN and graphene, microwave devices with a frequency of up to 100 GHz and light-emitting diodes resistant to radiation [2-4].

Silicon carbide has been widely used for the manufacture of an abrasive tool since the 19th century. The technology of synthesis of SiC from elementary Si and C under the influence of high temperature,
developed by The Carborundum Company for abrasives, is relevant up to now. The technologies for obtaining high-purity SiC of semiconductor quality for the single crystals growing are still being developed. Preliminary patent search showed that the main works are conducted by US companies - Cree (372 patents of SiC for LED), Northrop and Grumman SiC (closed patents, more than 200 for microwave devices). Among the remaining companies, there should be mentioned Dalian Institute of Chemical Physics, Chinese Academy of Sciences (China); LG Innotec (Korea); Sumitomo Metal Industries, Bridgestone, Shin-etsu (Japan). In total, there are about 900 patents concerning the synthesis of SiC (PatScape.ru search system’s data).

The use of silicon carbide in a nanoscale form makes it possible to obtain new functional materials with predefined physical properties that are necessary for the design of instruments with high performance characteristics. Despite the large number of works, the problem of obtaining a nanoscale silicon carbide powder of the required parameters for purity, dispersion, productivity and other characteristics remains relevant.

There are a number of methods of obtaining a nanoscale silicon carbide powder, such as sol-gel [5], laser pyrolysis from organic precursors [6], self-propagating high-temperature synthesis [7], and the plasma-chemical method [8]. The common drawbacks of these methods are their low productivity, the difficulty of scaling technological installations, need to use expensive unique equipment (due to which the cost of powders becomes high), considerable dispersion of nanoparticles in size (from one to hundreds of nanometers) and high impurity level of the product. In [9] it was suggested to obtain nanoscale powders of silicon carbide by adiabatic compression. The proposed method is not continuous and flowing, therefore its use is not possible for industrial production of nanopowders.

2. Method description

This paper describes a cyclic method of compressing starting material in the gas phase in the chemical reactor. Starting materials pyrolysis and then synthesis take place in the reactor in the compression-rarefaction cycles in the piston-cylinder assembly. The method ensures homogeneity of the reaction conditions in the reactor, which leads to the high nanopowder monodispersity. When the working cycle of compression-rarefaction finished, we get a product which does not require further technological processing.

The compression reactor is well-described in [10]. Reagents are compressed inside the cylinder by a piston, the surfaces of which are covered with the protective ceramic layer made of aluminium oxide by thermo-electrochemical oxidation [11]. The coating withstands repeated thermal cycling while ensuring high sliding. The surface friction coefficient is close to 0.01. Therefore, no lubrication is required to run the piston-cylinder assembly, i.e. the reagents are not contaminated by additional chemical substances.

The mixture of monosilane, argon and one of the light hydrocarbons was used as a chemical reagent in the experiment. The gases were fed into the cylinder through two pipelines. A mixture of monosilane and argon (10% – SiH₄, 90% – Ar) was fed into the cylinder of the first pipeline, and some light hydrocarbon (acetylene, ethylene, propane, butane or their mixture) - through another pipeline. The mixture was compressed at the frequency close to 10 Hz. The product came from the reaction volume and accumulated in an additional capacity of the collection system. Then it was examined by high-resolution transmission electron microscopy (HRTEM) and X-ray diffractometry. The experimental results of using propane and acetylene in the reactor mixture are stated below.

The experiments were carried out both for the concentrations necessary for the performance of the stoichiometric ratio for a mixture of monosilane with acetylene and monosilane with propane and for the concentrations in the gas mixture with an excess or lack of carbon according to stoichiometric ratios:

\[
3\text{SiH}_4 + \text{C}_2\text{H}_8 \rightarrow 3\text{SiC} + 10\text{H}_2, \quad (1)
\]
\[
2\text{SiH}_4 + \text{C}_2\text{H}_2 \rightarrow 2\text{SiC} + 5\text{H}_2, \quad (2)
\]
The further analysis showed that in the case of compression of "poor" carbon mixtures together with SiC crystallites, in the final product Si crystallites are observed. In contrast, the "rich" carbon mixtures compression results in formation of SiC crystallites, covered with several layers of graphene – so-called Core-shell structures.

The reaction of SiC synthesis was monitored online using a UGA-200 universal gas analyzer. The greater amount of hydrogen indicated a synthesis reaction and disappearance or a small amount of initial reagents (SiH$_4$) showed that the raw materials were fully processed.

A D8 Advance powder X-ray diffractometer (vertical goniometer with 0/20-geometry) manufactured by Bruker (Germany) was applied for X-ray diffraction analysis. The device is equipped with a Lynx-Eye linear semiconductor energy-dispersive detector. The X-ray tube with a copper anode was the radiation source. The average radiation wavelength was CuK$_\alpha$=0.154184 nm (CuK$_{\alpha_1}$=0.15406 nm, CuK$_{\alpha_2}$=0.154439 nm), the generator current was 35 mA, and the voltage was 35 kV. The scanning range was 8-75° to 2θ with the 0.075° step; the time per point was 1.5 sec.

The obtained samples were studied by HRTEM using a JEM-2010 electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and a resolution capacity of 0.14 nm. Digital processing of the obtained electron microscopic images with calculated interplanar spacings by Fourier analysis was carried out in GatanDigitalMicrograph software.

Figure 1 shows typical electron-microscopic images of the morphology and structure of the silicon carbide samples obtained for the mixture (1). The sample is represented by two morphologically different types of particles: rounded well-crystallized silicon carbide particles (more contrasting in the image) and less contrasting nano-sized particles forming extended dendritic aggregates. Dimensions of silicon carbide particles vary in the range of 10-40 nm. The observed interplanar spacing of 2.52 and 2.53 Å correspond to a spacing of 2.52 Å of the (111) plane for silicon carbide from the database of Powder Diffraction File (PDF) No. 00-029-1129. The composition of the initial gas mixture was close to the stoichiometric ratio (1).

![Figure 1. Electron-microscopic images of the nanodispersed silicon carbide sample’s particles.](image)

The figure 2a shows crystalline silicon particles (interplanar spacing 3.1355Å corresponds to (111) plane of PDF card 00-027-1402) with a size of 20-30 nm with an amorphous near-surface layer obtained from a reaction mixture that is poor in carbon content. The figure 2b shows a picture of the Core-shell structure. The nucleus is formed by the SiC crystallites sized 3-7 nm, covered with several layers of graphene (acetylene, ratio (2) was used).

The figure 3 shows the diffractogram of a powder sample obtained by using the concentrations of the reactor mixture (2) with a lack of carbon. The diffraction analysis data confirm the presence of Si.
(PDF 00-027-1402) and SiC (PDF 00-029-1129) phases. The broadening of the SiC 111 peak corresponds to a crystallite size of about 4 nm.

Figure 2. Nano-dimensional Si (a) and SiC (b) crystallites covered with 2-5 layers of graphene.

Figure 3. Diffraction pattern for the mixture (1). Bar-charts: dashed – Si (PDF 00-027-1402) and solid – SiC (PDF 00-029-1129).

3. Conclusion
The optimal modes needed for nano-dimensional SiC synthesis were determined. A high repeatability in composition and physical properties (crystallites, amorphous condition) of the synthesized product was achieved, depending on the main input parameters – chemical composition of the mixture, the pressure in the reactor zone etc. It has been shown that the proposed method provides a high (reaching almost complete) degree of the starting reagents processing.

The resulting product of the synthesis in cyclic compression reactor is chemically pure and is determined only by the degree of purification of the initial reagents. Technological processes do not add additional contaminants to the product. The resulting product does not require further
technological processing, as proposed by most methods, such as chemical etching, etc. It is ready to be applied in technologies and tasks of materials science with the purpose to obtain materials with predefined functional characteristics, including modification of the metals and alloys’ structure and characteristics [2, 12].

The proposed method for obtaining nano-dimensional silicon carbide is suitable for the industrial production. The process is cyclic and requires the gaseous reagent feeding and resulting products collecting for the continuous production of nano-dimensional silicon carbide. The process can be fully automated. Time for continuous operation of the reactor depends on the reliability of its mechanisms, the amount of starting materials and need for the product – nano-dimensional silicon carbide crystallites.

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