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TGA-DSC-MS ANALYSIS OF SILICON CARBIDE AND OF ITS CARBON-SILICA PRECURSOR

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Pure beta silicon carbide of submicron and micron particle size has been synthesized via carbothermal reduction of nanosilica. The resulted powder and its carbon-silica precursor were characterized by means of FTIR spectroscopy, electron microscopy, and X-ray diffraction. The results of TGA-DSC-MS analysis indicate a possibility to estimate by this technique the carbon content in carbon-silica precursor as well as residual carbon in silicon carbide with the sensitivity about 5 ppm.

Keywords*: carbothermal reduction, carbon-silica nanocomposite, silicon carbide, electron microscopy, TGA, DSC*

INTRODUCTION

Silicon carbide is a promising non-oxide ceramic material with various industrial applications. It has unique properties such as high hardness and strength, chemical and thermal stability, high melting point, high oxidation and erosion resistance, *etc.* [1–3]. These properties make SiC a perfect material for high power, high temperature electronic devices [4–8] as well as for abrasion and cutting applications [9, 10].

The most common used methods for SiC synthesis are physical or chemical vapour deposition, sol-gel, liquid phase sintering, and mechanical alloying [11]. Traditional way to produce SiC is the conventional carbothermal reduction method (Acheson process) envisaging solid-state reaction between silica sand and petroleum coke at the temperature of more than 2500 °C [3]. This method has several drawbacks such as high energy consumption and poor quality of the product. Nevertheless, carbothermal reduction of silicon dioxide seems to be one of the most attractive methods for SiC fabrication due to the availability of cheap precursors and possibility to reduce significantly the temperature of the process and to improve the product quality by using sufficiently pure and highly dispersed reagents.

Upon SiC synthesis via the SiO_2 carbothermal reduction route it is important to control the carbon:silica ratio in starting mixture. Besides, among other properties, the crucial parameters to be controlled in dispersed materials based on silicon carbide are temperature of their oxidation and the amount of residual carbon. In this respect, it is very useful to apply various methods of thermal analysis. The aim of this work was to synthesize dispersed silicon carbide and to study thermal behaviour of this material as well as its carbon-silica precursor under air atmosphere.

EXPERIMENTAL

Thermodynamic calculations on the feasibility of SiC synthesis via the silica carbothermal reduction route were performed using the HSC Chemistry v.7 software.

Nanostructured carbon-silica composite was obtained via low-temperature carbonization of a carbohydrate in the presence of nanodispersed silica. Silicon carbide powder then was synthesized from this precursor in a high-temperature reactor under Ar atmosphere at reduced pressure.

Carbon-silica and SiC powders were analyzed by means of FTIR spectroscopy (a Nicolet Nexus spectrometer, Thermo Scientific, with an attachment of frustrated total internal reflection) and electron microscopy (PEM-125K and

REMMA-102 microscopes, Selmi), the crystallinity of SiC particles was studied by X-ray diffraction (a DRON-3 diffractometer).

Thermal analysis of carbon-silica nanocomposite and silicon carbide powder was performed using a coupled DSC-TGA thermal analyzer TA SDT Q600 (TA Instruments) under air atmosphere in an interval of temperatures 20–1100 °C with accuracy of mass detection at the level of 0.1 µg. In order to control the volatile products of thermal oxidation a Thermo ProLab mass spectrometer (Thermo Scientific) has been used.

RESULTS AND DISCUSSION

Theoretical considerations on the optimum conditions of SiC synthesis. In general, the scheme of silicon carbide synthesis via the carbothermal reduction of silica can be represented by the following reaction:

$$SiO_2(s) + 3C(s) \rightarrow SiC(s) + 2CO(g). \qquad (1)$$

Reaction 1 is highly endothermic, ΔH being varied from 589.22 to 558.67 kJ/mol SiC within the temperature range from 1520 (when the reaction starts being thermodynamically feasible) up to 2200 °C. Moreover, it requires the process to be carried out under inert atmosphere to avoid carbon and silicon carbide oxidation.

Generally accepted reaction mechanism of SiC synthesis envisages [12] that the process occurs through the gaseous silicon monoxide (SiO) formation which then reacts with carbon to produce SiC. So reaction 1 could be divided in two consecutive reactions:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g), \qquad (2)$$

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g). \qquad (3)$$

As indicated in the work [13], reactions 2 and 3 are dominating at the temperature 1400 °C and higher. When the temperature is lower than 1400 °C, silicon carbide formed can react rapidly with silica to produce silicon monoxide. So if one pumps out CO at these temperatures in order to accelerate the process of SiC synthesis, it may result in significant loss of silica in the form of volatilizing SiO, probably via the reaction

$$SiC(s) + 2SiO_2(s) \rightarrow 3SiO(g) + CO(g). \qquad (4)$$

In order to determine the conditions for direct reactions 2, 3 and 4 to occur, we performed thermodynamic calculations of Gibbs energy (ΔG) change upon the temperature growing from 1200 to 2200 °C. As one can see (Fig. 1), under the atmospheric pressure direct reactions are thermodynamically feasible ($\Delta G < 0$) at the following temperatures: reaction 2 – > 1740 °C, reaction 3 – all the temperature range considered, reaction 4 – > 1860 °C.

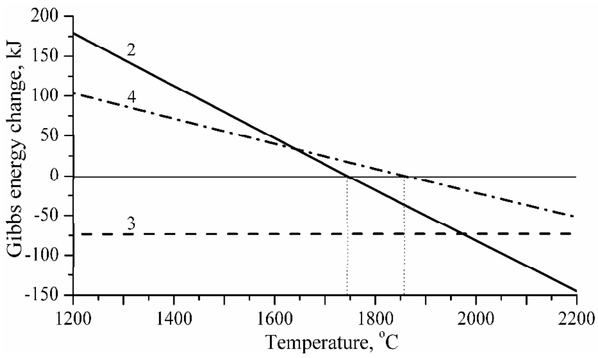


Fig. 1. Gibbs energy change *vs* temperature for reactions 2, 3, and 4

Thus, from the thermodynamic point of view, under 1 bar pressure the optimum temperature range to carry out the process of silicon carbide synthesis is 1740 to 1860 °C. This will enable passing the direct reactions 2 (silica interaction with carbon to produce silicon monoxide) and 3 (silicon monoxide interaction with carbon to produce silicon carbide), whereas reaction 4 (silicon carbide interaction with silica) will be hindered. The temperature interval mentioned is too high in the case when there is a need to obtain nanostructured SiC with high specific surface [13].

To reduce the temperature of SiC synthesis and simultaneously to accelerate this process, one may reduce the pressure in the system by pumping out carbon monoxide. At reduced pressure reaction 3 (interaction of gaseous SiO with solid carbon) will be the limiting stage of the process, moreover, the less is the carbon particle size, the higher will be the rate of reaction of silicon carbide formation [12].

In order to define the conditions (temperature and pressure) which enable proceeding of reaction 2 but prevent undesirable reaction 4, we performed thermodynamic calculations and determined minimum temperature values when the reactions 2 and 4 become thermodynamically feasible within the pressure range (0.0001÷1) bar. In Fig. 2 the dependence of these temperatures upon the pressure is shown in the form of the appropriate curves 2 and 4. As it can be seen, in all the pressure range considered there is a possibility to carry out the process of SiC synthesis at such temperature and pressure when only reaction 2 will take place. In Fig. 2 this crosshatched region is assigned as thermodynamic region to carry out the process of SiC synthesis. Thermodynamic calculations suggest that this region represents optimum conditions for SiC synthesis within the temperature range 1100÷1860 °C and the pressure range 0.0001÷1 bar. When the temperature-pressure point is situated lower than thermodynamic region, there is a risk of not full silica conversion into silicon carbide, while in the case of its higher positioning the SiC yield may be low because of silicon loss in the form of gaseous SiO.

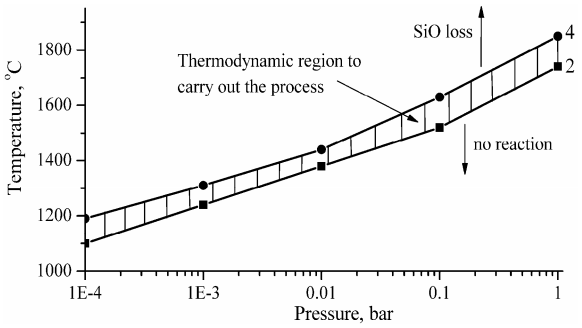


Fig. 2. Initial temperature of thermodynamic feasibility of reactions 2 and 4 *vs* pressure

Another important parameter for the process of SiC synthesis is the time of full silica conversion into silicon carbide. Several groups have performed various kinetic studies on SiC synthesis applying different reaction conditions and carbon/silica precursors (see, for instance, [12, 14–18]). Although the activation energies reported varied from 230 to 550 kJ/mol, there is a general consistency that the reaction rate increases when the temperature is higher, the precursor particle size is finer, and CO is removed. Weimer *et al.* [12] state that the mechanism of SiC synthesis includes rapid formation of gaseous SiO, and its further reduction by carbon to SiC (reaction 3) is overall reaction rate-controlling. Upon this, carbon particle diameter affects substantially not only the reaction rate, but also the size of SiC produced. According to the shrinking core model proposed in [12] the reaction occurs at carbon surface and its rate "decreases as the growing SiC product layer decreases the reaction surface area". The model equation represents the relationship between the reaction temperature (T, K) and time (t, s), particle diameter of carbon precursor (d, m), and silica conversion (X):

$$k = \frac{1-(1-X)^{1/3}}{t} = \frac{k_0}{d}\exp\left(-\frac{E}{RT}\right),$$

where k – reaction rate; $k_0 = 27.4$ m/s; $E = 382 \pm 34$ kJ/mol.

Based on this model, we have plotted a dependence of the reaction time (time of full silica conversion into SiC) on the temperature and carbon particle diameter in carbon-silica precursor under the following conditions: $X = 1$, $d = (10 \div 100)$ nm, T = (1200÷1900) °C. The results are shown in the form of isosurface in Fig. 3.

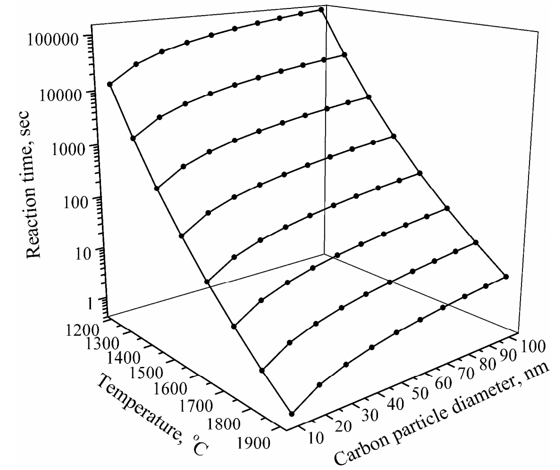
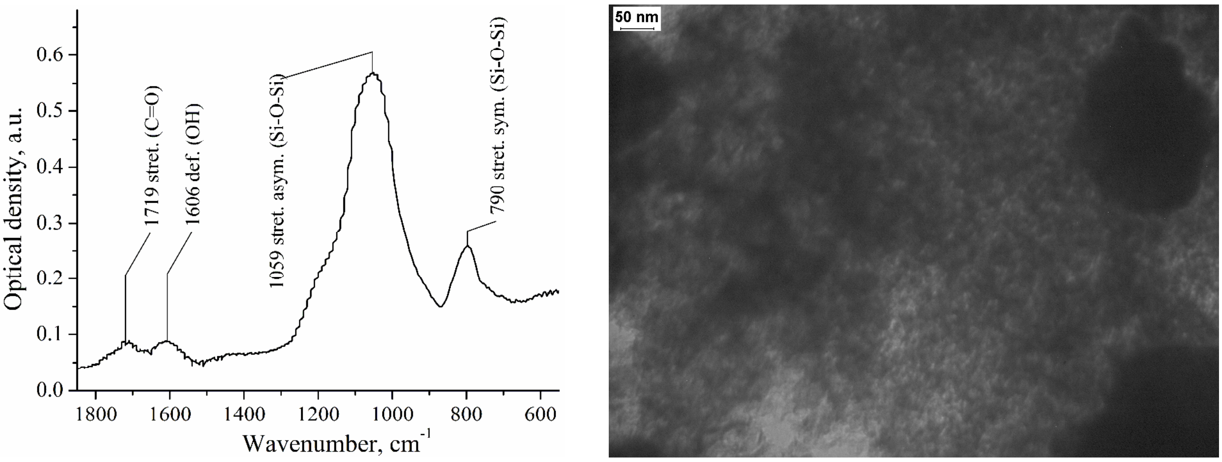


Fig. 3. Relationship between temperature, diameter of carbon particles in carbon-silica precursor, and time of full silica conversion into SiC (the kinetic model for calculations was taken from [12])

The results suggest that full silica conversion would achieve within few seconds when the temperature is high (1800–1900 °C) and carbon particle size is low (10–20 nm). At the same time, the reaction would last for 32–36 h when T is 1200 °C and d is 90–100 nm. The reasonable reaction time (within several hours) for nanostructured carbon-silica precursors (d = 10–100 nm) is achieved when the temperature of the process is from 1350 to 1500 °C. The theoretical time needed for full silica conversion in this case is from 1 min to 2 h.

Synthesis and analysis of carbon-silica precursor. The above mentioned considerations might be valid in the case when silica and carbon particles are uniformly distributed and available for reaction. This can be achieved by special preparation of precursor mixture – from high energy milling of solid carbon and silica to molecular mixing of precursors (for example, mixing the solutions of silicon and carbon-containing precursors or using organosilicon compounds).

In our case to produce carbon-silica nanocomposite solid nanosilica was mixed with carbohydrate solution, then the mixture was dried and subjected to low-temperature carbonization in air. The carbonization temperature was not more than 300 °C to avoid oxidation of carbon nanoparticles formed. FTIR spectrum of carbon-silica nanocomposite (Fig. 4 *a*) indicates the presence of residual oxygen in carbon in the form of carbonyl groups (not fully carbonized and/or partially oxidized carbon) as well as silica (the bands attributed to silicon-oxygen backbone) and water (the band related to hydroxyl groups). The fact that carbon-silica composite obtained is indeed nanostructured is confirmed by the results of its analysis by transmission electron microscopy (Fig. 4 *b*) revealing the mean particle size around 10 nm. The composite also contained some agglomerates with the mean size about 200 nm.



a *b*

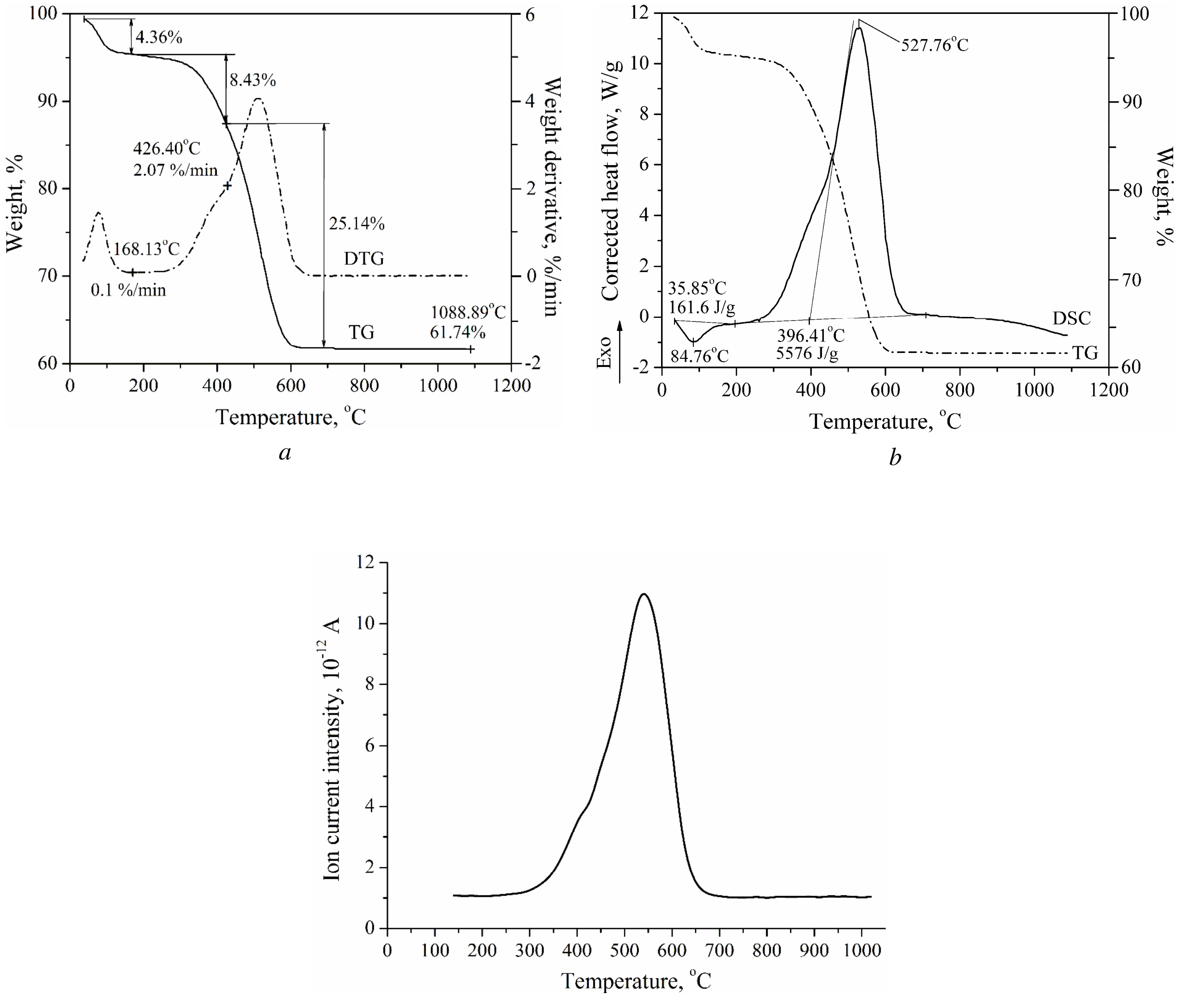
Fig. 4. FTIR spectrum (*a*) and TEM image (*b*) of carbon-silica nanocomposite

TGA-DSC curves for the carbon-silica nanocomposite (Fig. 5) demonstrate two main regions of the weight loss. The first region is at 30–170 °C (extremum at 85 °C), the weight loss is accompanied by endo-effect indicating water removal from the sample. The total weight loss at this stage was 4.36 %. The second region is at 300–650 °C (maximum at 527 °C), the weight loss is accompanied by exo-effect indicating carbon oxidation and removal in the form of CO and CO_2. The total weight loss at this stage was 33.57 %. The dependence of weight loss upon the temperature has inflection at 430 °C attributed to CO removal in the low-temperature area while at higher temperature CO_2 is formed which has been confirmed by MS analysis of 44 *m/z* ion formation.

Synthesis and analysis of silicon carbide. TEM analysis of carbon-silica precursor revealed that mean carbon nanoparticle size in the composite is about 10 nm. This indicates that theoretically the temperature 1400 °C and the reaction time of 1 h would be enough to fully convert silica into silicon carbide. The pressure in the high-temperature reactor, according to Fig. 2, should be around 0.015 bars to ensure carrying out the process in thermodynamically optimum region. By the data of TGA-DSC analysis, carbon-silica nanocomposite contained not more than 33.57 wt. % of carbon. The silica content was around 61.74 wt. % (residual weight after heating up to 1090 °C, Fig. 5 *a*). These values are equivalent to molar ratio SiO_2:C=1:2.72. So silica is in slight excess, since theoretical silica-to-carbon molar ratio to produce SiC (according to reaction 1) is 1:3. To avoid the presence of excess silica in the produced silicon carbide, it is necessary either to increase the temperature or to reduce the pressure at the end stage of the process. This will enable residual silica to react with silicon carbide and leave the reactor in the form of gaseous SiO (reaction 4). In our case at the end of the process the temperature was increased up to 1550 °C.

The resulted yellow-greenish powder was β-SiC with primarily monocrystalline particles of submicron to micron size. This was confirmed by the data of FTIR spectroscopy, electron microscopy, and X-ray diffraction (Fig. 6).

FTIR spectroscopy and XRD data demonstrate no residual silica in SiC (or at least trace amounts of silica are beyond the sensitivity of these methods). In the middle IR range one may distinguish longitudinal optical (LO) and transverse optical (TO) absorption bands (Fig. 6 *a*) which are the characteristics of silicon carbide [19]. Narrow XRD peaks (Fig. 6 *d*) indicate that synthesized β-SiC powder is of high crystallinity. TEM analysis (Fig. 6 *b*) reveals that the size of spheroidal SiC particles is 485–615 nm, the mean particle size being 590 nm. Larger particles with size of several and even tens of microns are also present as confirmed by SEM analysis (Fig. 6 *c*). Possible explanation of this could be as follows [20]. At the first stage non-agglomerated and agglomerated carbon particles directly chemically transform into β-SiC crystallites without significant change in size. Then individual β-SiC crystallites coalesce into polycrystalline aggregates and agglomerates by surface diffusion which results in changes of particle size and morphology. When the temperature is higher than 1500 °C, large monocrystalline β-SiC particles (> 1 μm) are formed via bulk diffusion.

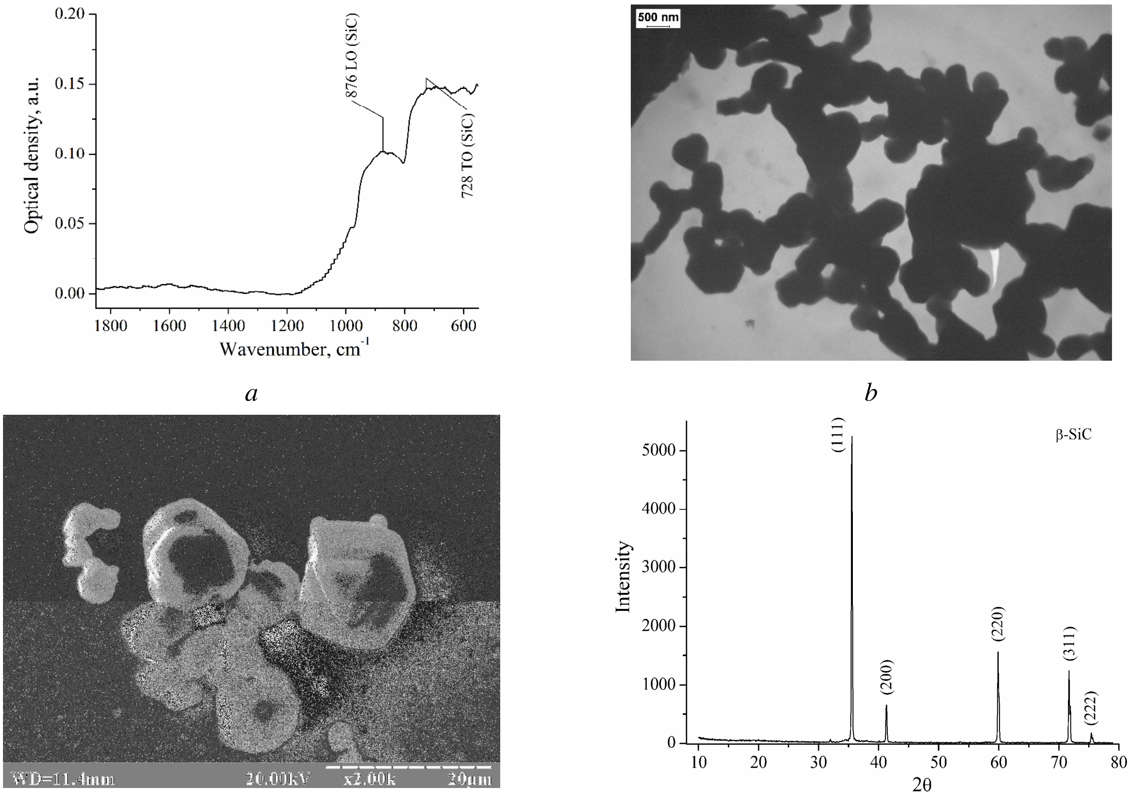


a

b

c

Fig. 5. TGA-DSC-MS analysis of carbon-silica nanocomposite: (*a*) TG-DTG curves; (*b*) TG-DSC curves; (*c*) dependence of ion current intensity on temperature for *m/z* 44 (related to CO_2 formation)

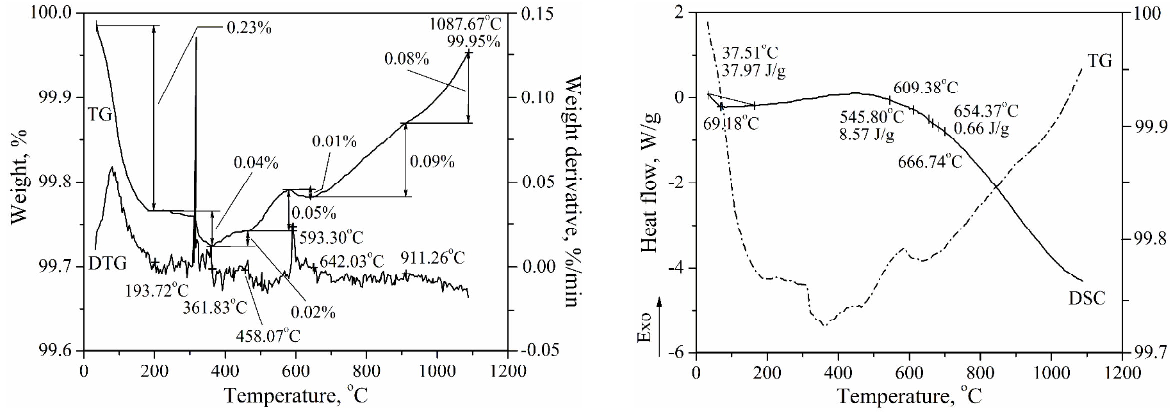


a *b*

c *d*

Fig. 6. FTIR spectrum (*a*), TEM image (*b*), SEM image (*c*), and X-ray diffraction pattern (*d*) of silicon carbide

TGA-DSC curves for silicon carbide (Fig. 7) demonstrate several regions of the weight loss. The first region is at 30–194 °C (extremum at 69 °C), the weight loss is accompanied by endo-effect indicating water removal from the sample. The total weight loss at this stage was 0.23 %. The weight loss corresponding to carbon oxidation was observed at 325–360 °C, afterwards the sample weight started to grow indicating the beginning of SiC oxidation. The total weight loss at 325–360 °C was 0.04 % which means that the amount of residual carbon in SiC was not less than that value. The total weight growth during heating at 360–1100 °C was 0.23 % which could be an evidence that mainly the surface of SiC particles is oxidized at these temperatures.



a *b*

Fig. 7. TGA-DSC analysis of silicon carbide: (*a*) TG-DTG curves, (*b*) TG-DSC curves

The weight loss of SiC sample corresponding to carbon oxidation and removal was approximately 8 μg. Taking into account that SDT Q600 measures the mass with the accuracy of 0.1 μg, it is possible to estimate with this instrument the quantity of residual carbon in silicon carbide at a level of 5 ppm.

CONCLUSION

Thermodynamic and kinetic considerations performed allowed us to determine theoretical optimum conditions for silicon carbide synthesis via the silica carbothermal reduction route.

Carbon-silica nanocomposite has been synthesized and based on the results of its analysis and theoretical considerations, the conditions for SiC synthesis (temperature, pressure, time) were defined.

Pure dispersed beta silicon carbide has been synthesized from carbon-silica nanocomposite, the analysis has shown that this powder is comprised of mainly monocrystalline particles with submicron and micron size. Thermal analysis revealed low free carbon content – around 0.04 wt. %.

The TGA-DSC analysis using the commercially available instruments such as TA SDT Q600 allows determining the amount of residual carbon in silicon carbide at 5 ppm level.

Аналіз карбіду кремнію та кремнезем-вуглецевої шихти методом ТГА-ДСК-МС

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Шляхом карботермічного відновлення нанокремнезему було синтезовано бета карбід кремнію високої чистоти з субмікронним та мікронним розміром частинок. Одержаний порошок та кремнезем-вуглецеву шихту охарактеризовано методами інфрачервоної спектроскопії з Фур'є перетворенням, електронної мікроскопії та рентгенівської дифракції. Результати аналізу методом ТГА-ДСК-МС вказують на можливість кількісного визначення цим методом вуглецю в шихті та залишкового вуглецю в карбіді кремнію з чутливістю на рівні 5 ppm.

***Ключові слова**: карботермічне відновлення, кремнезем-вуглецевий нанокомпозит, карбід кремнію, електронна мікроскопія, ТГА, ДСК*

Анализ карбида кремния и кремнезем-углеродной шихты методом ТГА-ДСК-МС

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Путем карботермического восстановления нанокремнезема был синтезирован бета карбид кремния высокой чистоты с субмикронным и микронным размером частиц. Полученный порошок и кремнезем-углеродная шихта были охарактеризованы методами инфракрасной спектроскопии с

Фурье преобразованием, электронной микроскопии и рентгеновской дифракции. Результаты анализа методом ТГА-ДСК-МС указывают на возможность количественного определения этим методом углерода в шихте и остаточного углерода в карбиде кремния с чувствительностью на уровне 5 ppm.

***Ключевые слова**: карботермическое восстановление, кремнезем-углеродный нанокомпозит, карбид кремния, электронная микроскопия, ТГА, ДСК*

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