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SYNTHESIS OF A SILICON CARBIDE FROM NATURAL RAW MATERIAL IN A SOLAR FURNACE

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In this study, the processes involved in synthesis of silicon carbide (SiC) from a natural mineral raw material (diatomite mixed with coke) were investigated. The initial material mixture was placed in a graphite crucible installed on the focal zone of a large solar furnace. High-temperature heating was carried out using a stream of concentrated high-density solar radiation (200–300 W/cm^2). After irradiating the material sample with the concentrated solar radiation, the crucible was cooled arbitrarily for 30 minutes. The synthesized material contained three phases: β-SiC with a cubic crystalline lattice and lattice parameter of 0.436 nm; α-SiC with a hexagonal crystalline lattice and lattice parameters of a = 0.307 nm and c = 1.511nm; and graphite with a hexagonal crystalline lattice. The SiC material obtained in the solar furnace in a freshly sintered state showed high refractoriness (up to 1650°C), while the material fired at 1550°C showed refractoriness up to 1580°C.

KEY WORDS: *solar furnace, concentrated solar radiation flux, silicon carbide, fireproof material*

1. INTRODUCTION

Silicon carbide (SiC) is an oxygen-free ceramic that has exceptional properties such as high hardness and strength, oxidation resistance, high erosion resistance, etc. All of these properties make SiC an ideal candidate for usage in high-power, high-temperature electronic devices and abrasion and cutting applications. Silicon carbide (moissanite) is very rare in nature, which is why it is produced using different techniques. For example, SiC can be produced by sintering highest purity silicon oxide with carbon in an Acheson graphite electric furnace at temperatures of 1600–2500°C. In this case, a chemical reaction takes place:

$$SiO_2 + 3C = SiC + 2CO.$$

Nitrogen and aluminum are the main impurities found in SiC when obtained in this way. These impurities affect the electrical conductivity of the material (Harris, 1995). Other methods

used to produce SiC are also known. For example, high-quality SiC crystals can be obtained by employing the Lely (1955) process, in which powdered SiC is sublimated in an argon atmosphere at 2500°C and deposited on a colder substrate in the form of single-crystal flakes up to 2 × 2 cm in size. In addition, cubic SiC can be obtained by chemical vapor deposition (Ohtani et al., 2001). Pure SiC can be also synthesized by thermal decomposition of the polymer poly(methylsilane) $(SiCH_3)_n$ in an inert gas atmosphere at low temperatures (Byrappa and Ohachi, 2003). Finely dispersed SiC powders have been produced by processing rice husks in electric (Lee and Cutler, 1975; Krishnarao et al., 1998) and solar heating (Adylov et al., 2003) furnaces. Silicon carbide has been sintered from silica (Abdurakhmanov et al., 2021) and quartzite melted in a solar furnace in a carbon medium (Gulamova et al., 2009). Silicon has also been obtained by employing arc methods (Parmentier et al., 2002; Morancais et al., 2003). The possibility of SiC sintering in a flow of high-energy ion beams was studied by Lee (2004) and Larciprete et al. (2003). The effect of the morphology of raw carbon materials on the properties of the obtained SiC was investigated by Honda and Baek (2003) and Bayazitov et al. (2003).

At the same time, such techniques consume a lot of power, which increases the price of SiC. We have found that ditatomite, which contains silicon dioxide (SiO_2), can be used as a raw material in the production of SiC along with concentrated solar radiation. It was assumed that due to the fine dispersion of diatomite as a mineral of oceanic origin, the resulting product of the carbothermal reduction will also have fine dispersion. It is fine dispersion that determines the special properties of SiC as a semiconductor, fireproof, and abrasive material (Rovin, 2014). Thus, the possibility of SiC sintering from diatomite mixed with coke by heating with a stream of concentrated high-density solar radiation was the aim of this work. The composition of diatomite mineral rocks is presented in Table 1.

Silicon, aluminum, and iron oxides are the predominant components in diatomite rock (see Table 1). Diatomite rocks mixed with clay and siliceous materials are comprised of either loose or cemented siliceous deposits that are white, light gray, or yellow in color. This material has high porosity, low bulk density, good adsorption, and thermal insulation properties. Diatomite has an increased sorption capacity for iron, manganese, and heavy metals. It is *a priori* assumed that the presence of aluminum and iron oxides will play the role of a binding buffer layer at the grain boundaries and favorably contribute to lowering the sintering temperature of the SiC material.

2. EXPERIMENTAL PROCEDURE

A mixture of diatomite with carbonaceous material (coke, coal, and graphite) was used to obtain silicon carbide. It should be mentioned that carbonaceous materials used in SiC smelting must have high reactivity, sufficient mechanical strength, high electrical resistance, and a minimum amount of ash. These properties are possessed by charcoal, petroleum coke, some varieties of low-ash coal, etc. However, it should be noted that none of these materials fully satisfies all of the requirements for a reducing agent.

In the experiments, coke was chosen as the carbonaceous material since it was the most accessible and cheap. A mixture of diatomite with coke was used in the corresponding stoichiometry SiO_2:C = 1:1.67 to obtain silicon carbide. The mixture was dry mixed in a ball mill for 10 hours and then placed in a cylindrical graphite crucible with a diameter of 250 mm and height of

TABLE 1: Composition of diatomite

Parameter	Oxide								
	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	ZrO_2	Other
Mass (%)	1.87	7.72	78.36	2.28	1.66	0.42	4,26	0.21	3.22

300 mm. The crucible was heated in the focal zone of a large solar furnace (Paizullakhanov et al., 2021) in a stream of concentrated solar radiation of 200–300 W/cm^2. The process of heating the material in the crucible during irradiation was monitored using a FLIR thermal imager monitor installed in a pyrometric room, which was located at the opposite height of the focal zone of the solar furnace. After holding the crucible under solar radiation for 20–40 minutes, the flow to the crucible was stopped by closing the shutters. The crucible was cooled randomly on the surface of a water-cooled substrate. Then, the obtained powder material was poured out of the cooled crucible and ground in a ball mill using a dry method.

X-ray phase analysis was carried out on an Empyrean panalytical diffractometer using Bragg–Brentano reflection geometry and CuKα radiation (where λ = 1.5418 Å). The mechanical properties of the obtained materials were studied by determining the hardness and compressive strength using a TBM-1000 hardness meter and TP-1-1500 installation, respectively. The temperature coefficient of thermal expansion (TCTE) was measured on a dilatometer DKT-30 in the temperature range of 25–400°C. The synthesized material was ground in a ball mill to test its possible application as an abrasive powder. Grinding was carried out in using a wet method (material:water:grinding media = 1:1:1) for 10 hours. A SALD 7500 particle analyzer was employed to analyze the produced powder.

3. RESULTS AND DISCUSSION

Figure 1 shows an X-ray diffraction pattern of a sample obtained in a solar furnace using a graphite crucible at 200 W/cm^2. The analysis showed the presence of three main phases in the synthesized material: β-SiC with a cubic crystalline lattice and lattice parameter of 0.436 nm; α-SiC with a hexagonal crystalline lattice and lattice parameters of a = 0.307 nm and c = 1.511 nm; and graphite with a hexagonal crystalline lattice. According to previously published findings (Stein et al., 1992; Stein and Lanig, 1993), the main polymorphic modifications of SiC belong to cubic, hexagonal, and rhombohedral syngonies. In the cubic structure of zinc blends, designated as 3C–SiC or β-SiC, Si and C atoms occupy ordered positions in the diamond framework. In hex-

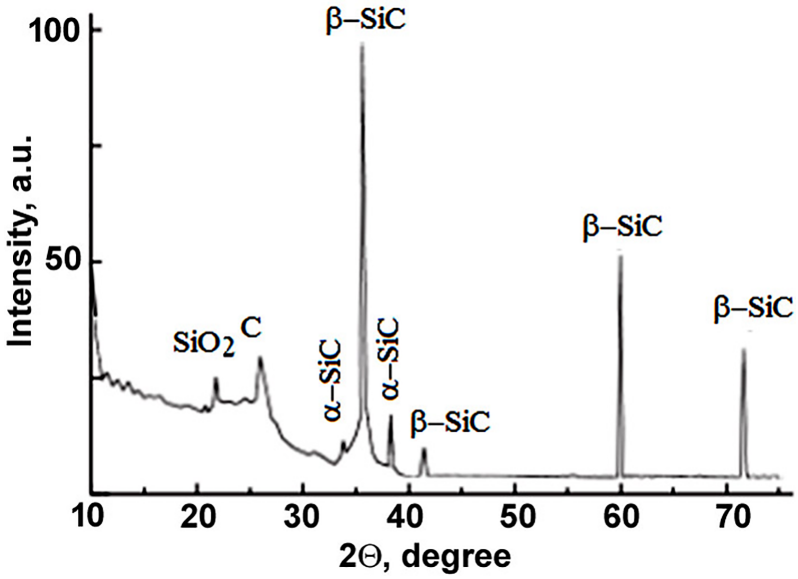

FIG. 1: X-ray diffraction pattern of material synthesized after heat treatment in a graphite crucible

agonal *n*H–SiC and rhombohedral *n*R–SiC polytypes (commonly referred to as α-SiC and *n*Si-C, respectively), bilayers consisting of C and Si layers fold into a primitive unit cell (Muranaka et al., 2008). In the experiment, the same diffraction pattern was obtained after processing the mixture in a solar furnace in a corundum crucible.

The average microhardness value and compressive strength limit of the material synthesized at 200 W/cm^2 were 2900 kg/mm^2 and 2200 MPa, respectively. These values were close to those given in reference books. Figure 2 shows the particle size distributions in the powder produced by ball milling, where it can be seen that the size of the maximum number of particles is 0.9 μm. Therefore, the synthesized material can be used to produce finely dispersed abrasive particles. In the experiments conducted at flux densities of 300 W/cm^2, the predominant formation of hexagonal α-SiC was observed. Consequently, under certain heat treatment conditions, different polymorphic modifications of SiC can be synthesized from diatomite, a material necessary for the production of both refractory and abrasive products. Figure 3 shows the temperature dependence of the TCTE of material sintered at 200 W/cm^2. The material also showed fairly high resistance to high temperatures. The TCTE value in the temperature range of 300–400°C changed insignificantly.

As is known, refractoriness (or fire resistance) is the property of a material to withstand, without melting, exposure to high temperatures. Thermal deformation of a sample (pyroscope) of a special shape (truncated pyramid) and size (30 mm high with base sides of 8 and 2 mm) was investigated to determine the fire resistance of a material. To determine the fire resistance of a material, thermal deformation of a sample of a special shape (truncated pyramid) and size (30 mm high with base sides of 8 and 2 mm) - a pyroscope is investigated. When the sample was heated, the liquid phase accumulated in it and at a certain temperature the sample became deformed. The temperature at which the sample touched the upper part of the surface of the support as a result of softening was determined. This temperature determined the refractoriness of the material.

Thus, at the second stage of experiments, pyroscopes were made from the synthesized material. Pyroscopes were used to test the refractoriness of the material up to 2000°C according to

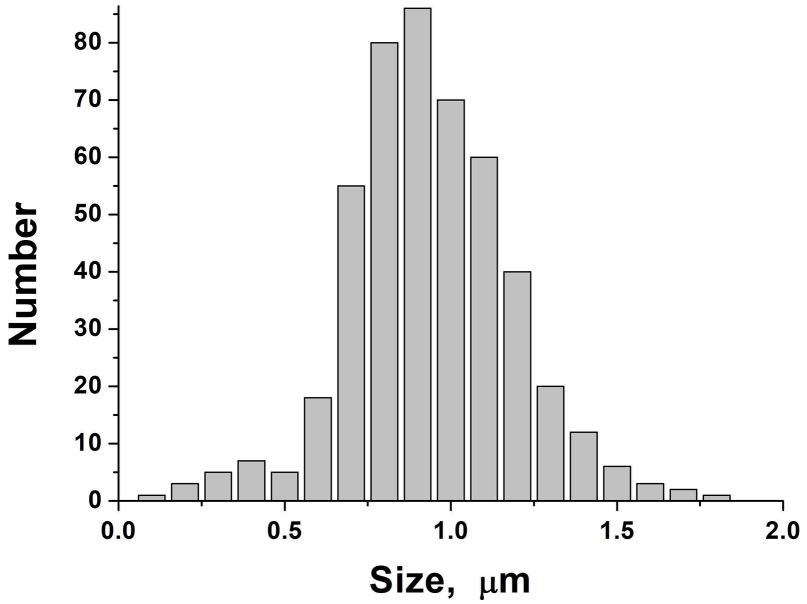

FIG. 2: Particle size distributions

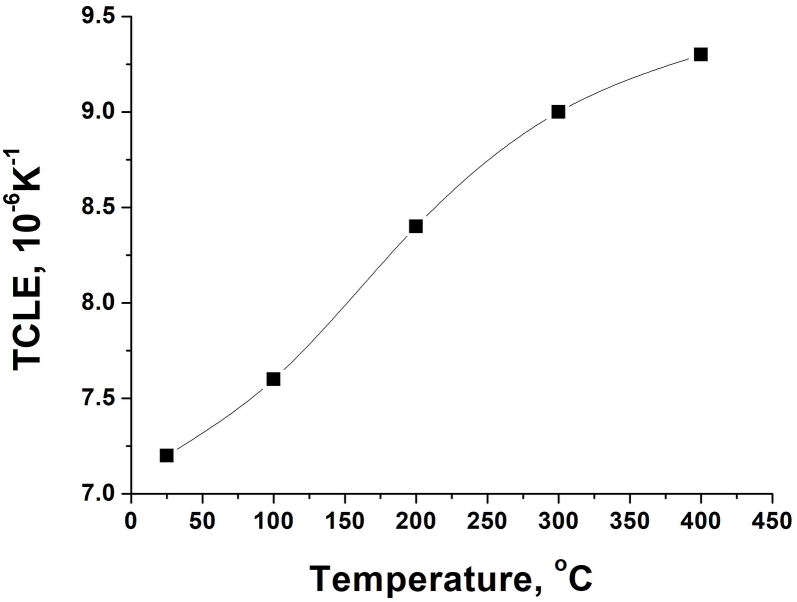

FIG. 3: Temperature dependence of the linear thermal expansion coefficient

TABLE 2: Fire resistance of samples obtained using rice husks

Number	Sample type	Fire resistance
1	Freshly sintered	Up to 1650°C
2	Fired	Up to 1580°C

Standard GOST 4069-69 (USSR) in a furnace with SiC heaters. Table 2 shows the results of the refractoriness tests for two types of samples: those freshly sintered in a solar furnace and those fired at 1550°C. As can be seen from Table 2, the freshly sintered sample had higher fire resistance. Analysis of the X-ray diffraction pattern of the sample after firing at 1550°C showed that this material contained SiC, SiO_2 in the cristabolite form, and mullite ($3Al_2O_3{\cdot}2SiO_2$). The cristabolite phase formed due to oxidation of some part of SiC according to the following reaction:

$$SiC + O_2 \rightarrow SiO_2 + CO_2.$$

A mullite phase formed from the kaolinite that was added as a binder by the following reaction:

$$3(Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O) \rightarrow 3Al_2O_3{\cdot}2SiO_2 + 6H_2O.$$

The ratio of the intensities of the diffraction lines belonging to different phases of $SiC:(3Al_2O_3{\cdot}2SiO_2):SiO_2$ was 1:1:3.

The observed deterioration in the refractoriness of the samples after firing can be explained by the presence of cristabolite and mullite in its composition. As the temperature increased, the

individual phases in the material gradually melted. The liquid states of these phases had different viscosities. As a result, the pyroscope sample began to deform at lower temperatures, thus reducing the refractoriness. In this case, an interfacial boundary of complex shape and character played a peculiar role in the formation of the refractory and abrasive characteristics of the massive material, i.e., the product. Therefore, the choice of kaolin as a binder was not entirely justified.

4. SUMMARY

Using a mixture of diatomite with coke, silicon carbide was obtained under heat treatment in a solar furnace. The synthesized material contained β-SiC, α-SiC, and graphite. At low flux density (200 W/cm^2), cubic β-SiC was the main phase of the synthesized polycrystalline material, while at a flux density of 300 W/cm^2, a hexagonal α-SiC phase mainly formed. The average microhardness value and compressive strength limit were 2900 kg/mm^2 and 2200 MPa, respectively.

The SiC material obtained in the solar furnace in a freshly sintered state showed high refractoriness (up to 1650°C), while the raw material fired at 1550°C showed refractoriness up to 1580°C. The observed deterioration in the refractoriness of the material after firing can be explained by the usage of kaolinite as a binder.

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