

Fabrication of SiC by carbothermal-reduction reactions of diatomaceous earth

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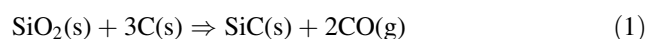
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Abstract In this paper the possibility of using diatomaceous earth as Si precursor for low temperature synthesis of silicon carbide (SiC) by carbothermal-reduction reactions was studied. A diatomaceous earth of Serbian origin and carbon black as reducing agent were used. The green bodies with constant C/SiO₂ ratio (C/Si = 4) were heated at temperatures between 1,250 °C and 1,550 °C with controlled Ar flow atmosphere. Phase evolution was followed as a function of annealing time and sintering temperature. It was found that reaction proceeded via many intermediate phases. The comparatively low reaction temperature is attributed to the nano-porous nature of the raw material. By means of XRD and SEM investigations powders have been characterized. The results show that diatomaceous earth can be very effective source for obtaining of silicon carbide powders.

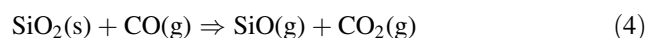
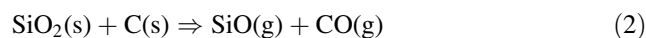
Introduction

Silicon carbide is an important structural material because of its unique combination of properties, such as high temperature strength, thermal shock resistance and resistance to wear and corrosion [1]. Due to this properties SiC has been a major candidate material for widespread use in engineering applications. The synthesis of pure SiC powder is one of the most important factors for obtaining dense SiC

ceramics [2]. Although the quality and performance are important, the cost of mass production should be the key factor in the commercialization of SiC ceramics [3]. The most promising method for obtaining a large variety of non-oxides products with important technical uses is carbothermal-reduction reaction (CRR) [4]. This reaction involves reduction of oxygenated materials, such as silica (SiO₂), usually by mixing it with a reducing agent (carbon) in excess at the temperature higher than 1,600 °C for several hours under an inert protective atmosphere. This treatment liberates Si or SiO in gaseous form, which further reacts with excess carbon to form SiC following the general reaction:



Formation of final product is more complex than above equation shows, since the formation of SiC requires a series of solid–solid, solid–gas and gas–gas reactions [5–7]:



Anyhow, this procedure offers the possibility of an economically attractive production route from natural occurring materials. Many authors have studied the formation of SiC powders from the raw materials, such as high purity quartz sand [8, 9] or aluminosilicates [10, 11].

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Among the raw materials that may be used for SiC powder production, diatomaceous earth has some advantages such as high specific surface area, high silica content and low price [11].

Diatomaceous earth is a natural occurring mineral compound from microscopic skeletal remains of unicellular algae-like plants called diatoms. Diatom particles have pitted surface area that it is several times greater than any other natural compound with the same particle size. The surfaces of diatom frustules possess fine pores with dimensions ranging from the micro scale to the nanometer scale. Such high surface area and siliceous composition can be used as Si precursor for the synthesis of SiC powder by carbothermal-reduction reaction (CRR) by mixing with one of reducing agents. However, no work has yet been done on syntheses of SiC by using diatomaceous earth as Si source. Therefore, in the present investigation, carbothermic method has been used to produce SiC powder from the cheap commercial raw material, i.e., diatomaceous earth and carbon black as a reducing agent.

Experimental

The raw materials used were a diatomaceous earth from the Serbia and the carbon black with a specific surface area $BET = 46 \text{ m}^2 \text{ g}^{-1}$ and 99% purity, as a reducing agent. The diatomaceous earth was previously acid treated with HCl solution of 1 mol/dm^3 concentration in order to remove iron oxide from material. The chemical composition of chemically treated sample is given in Table 1. Mixture with C/SiO₂ ratio four was homogenized by vibro milling in the presence of distilled water. Although the stoichiometric ratio C/SiO₂ in Eq. 1 is 3:1, it has been observed experimentally [12] that that increasing the C/SiO₂ ratio results in faster rates of reactions and larger extents of conversion to β -SiC. Since, increased amount of carbon serves to improve the contact between the reactants, the ratio of 4:1 is chosen for the complete conversion. This starting material was formed into specimens with 10 mm diameter and 10 mm thickness by the cold uniaxially pressing at the applied pressure of 100 MPa. The green bodies were heated at temperatures between 1,250 °C and 1,500 °C in the controlled argon flow atmosphere. The heating of the alumina reactor was carried out in a furnace with SiC heating element. Temperature was measured with

Pt-(Pt-10 wt%Rh) thermocouple ($\pm 5 \text{ }^\circ\text{C}$). The argon flow was kept during cooling until 200 °C. The reaction products were analyzed by X-ray diffraction (XRD) using CuK α radiation (Siemens D5000). XRD was also used to evaluate the crystalline size of the SiC phase. The average crystalline size, D , was calculated from Scherrer formula:

$$D = 0.9 - \lambda / (\beta - \cos\theta) \quad (6)$$

where λ is the wavelength of the X-rays, θ is the diffraction angle, $\beta = (\beta_m^2 - \beta_s^2)$ [13] is the corrected half-width of the observed half width, β_m , and β_s is the halsilicon sample. The microstructural observation was performed by scanning electron microscopy (SEM). Image Pro Plus program was used for particle size measurement.

Results and discussion

SEM image of the frustules of as received raw material is shown in Fig. 1. The frustules have capsule-shaped form with middle circular opening. Regularly spaced rows of fine pores run along the cylindrical walls. They possess pitted surface area with fine pores with dimensions ranging from the micro scale to the nanometer scale. According to the shape and morphology, diatoms belong to Aulacoseira type [14]. XRD pattern of diatomaceous earth reveals only one mineralogical phase, crysballite (SiO₂), which is accompanied by amorphous phase [15]. Chemical composition shows that diatomaceous earth is mainly composed of SiO₂ and of Al₂O₃. Also the impurities such

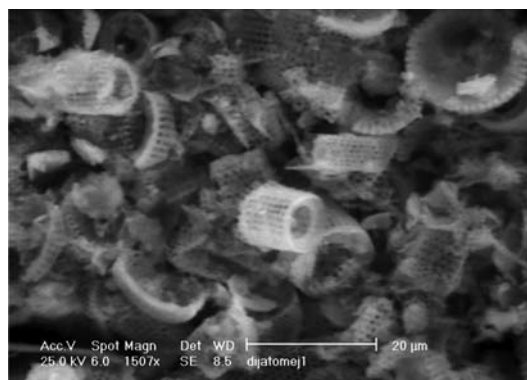


Fig. 1 SEM image of diatomaceous earth

Table 1 Chemical composition of as-received diatomaceous earth and chemically treated diatomite

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	L.O.I. (1,000 °C)	Sample
73.68	12.28	3.29	0.72	0.44	1.01	0.12	8.26	As-received
76.58	11.34	1.72	1.22	0.44	0.9	0.11	7.13	Chem. treated

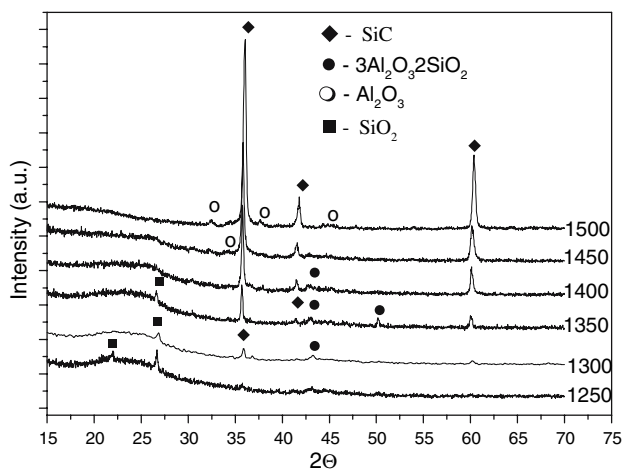


Fig. 2 XRD Patterns of synthesized powder with C/SiO₂ ratio four at 1,250–1,500 °C and soaking time 1 h

as Na₂O, K₂O, Fe₂O₃ are present. However, it is known that the MgO, Na₂O and K₂O are largely lost at the carbothermal reduction stage [16]. On the other side, it would be expected that the Fe₂O₃ would be reduced to Fe or to iron silicides (FeSi), but small quantities of iron has been shown to help initialize carbide formation due to catalytic behavior [17].

Figure 2 shows the evolution of the crystalline phases formed as a function of the reaction temperature. At low temperature (1,250 °C), a small amount of cristobalite (SiO₂) phase is still present. However, cristobalite tends to decrease with increasing of temperature. This behavior results from the mullite formation. Mullite is formed by recrystallization of starting diatomaceous earth through direct reaction between SiO₂ and Al₂O₃:

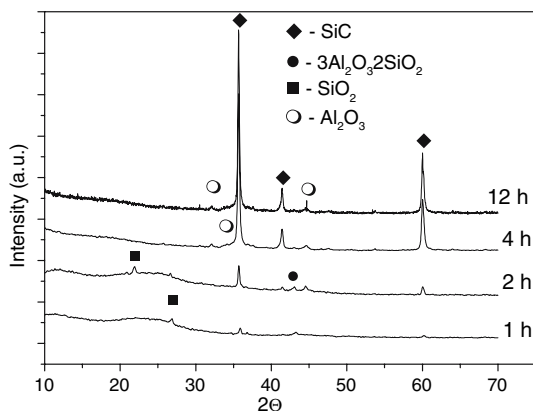
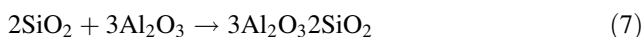
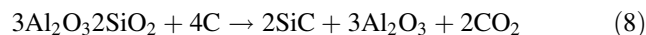


Fig. 3 SiC evolution during isothermal heating versus annealing time at 1,300 °C for mixtures with C/SiO₂ ratio equal to four

The reaction (7) explains the appearance of mullite, which increases at 1,300 °C and 1,400 °C and then disappeared at 1,500 °C. Since mullite is coming from diatomaceous earth recrystallization, it is highly reactive in the formation of β -SiC phase:



The XRD pattern shows small broadening of the diffraction lines in the regions around 35–37° of 2 θ , which is associated with the presence of β -SiC phase. This indicates that nucleation and crystallization of β -SiC takes place at

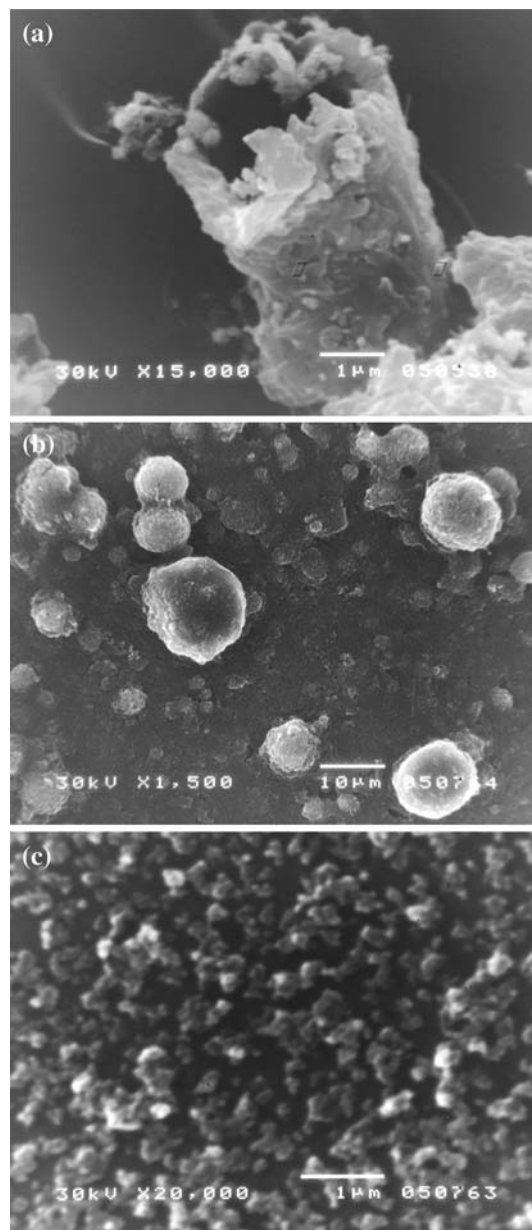


Fig. 4 SEM micrograph of powders obtained at lower temperature, 1,250 °C (a), 1,300 °C (b) and at higher temperature, 1,550 °C (c)

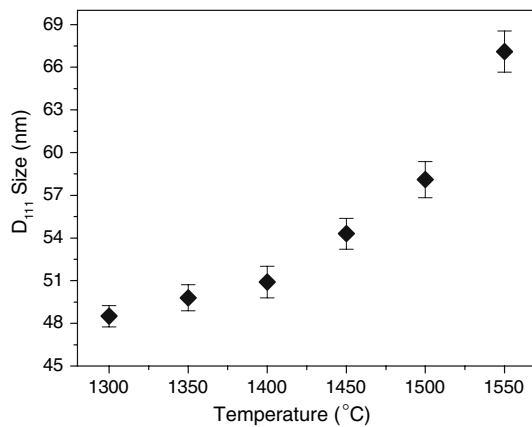


Fig. 5 Crystallites size versus temperature annealing. The error bars indicate the range of crystallite size calculated for each sintering time

1,250 °C after 1 h of annealing. Figure 3 illustrates the effect of annealing time on β -SiC formation at 1,300 °C. The progress of the intensity of X-ray diffractometry profile of synthesized samples is associated with increased amount of β -SiC. The reaction products at 1,500 °C are β -SiC as a dominant phase and minor Al_2O_3 phase. Having in mind that Al_2O_3 in combination with Y_2O_3 is the most useful additive for densification of silicon carbide ceramics [18, 19], thus the phase composition formed (SiC and low amount of Al_2O_3) is suitable as raw material for high performance ceramics.

The morphology of powder obtained at low temperature (1,300 °C) shows that these products retain characteristic of some fragments of original diatomite (Fig. 4a). The β -SiC crystals are cemented by residual SiO_2 in the form of agglomerated lumps. However, at higher temperatures the micrograph of the powder is completely different (Fig. 4b). All agglomerates are broken and exhibit individual grains with grain size less than 100 nm.

The nano size of synthesized powders is also confirmed by crystallites size measurement and it is illustrated in Fig. 5. At low temperature (1,300 °C) the average crystalline size is less than 50 nm. With increasing temperature the crystalline sizes increase to near 70 nm for the 1,550 °C. Thus, for all processing temperatures it was found that the particle size lies in the nanometric range (≈ 50 –70 nm).

Conclusions

Formation of β -SiC was confirmed by the reaction of carbon black with gaseous SiO generated from the carbothermal reduction of diatomaceous earth. It was found that X-ray intensity and yield of β -SiC increased with increase of temperature and retention time. The crystalline size and particle morphology indicate that nano size particles of synthesized powders were obtained. The results suggest that diatomaceous earth is a very effective source for obtaining of silicon carbide powders.

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