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New manufacturing process for nanometric SiC

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Abstract

Nanometric β-SiC powder was prepared by carbothermal reduction of freeze-dried gel. Initially, the gel was obtained by polycondensation of sol consisting of resorcinol and formaldehyde as a source of C and tetraethoxysilane as a source of silicon. The effect of temperature and time of heat treatment (carbothermal reduction) as well as the effect of C/Si ratio on SiC powder properties was studied. It was possible to obtain nanosized (∼20 nm) β-SiC powder after one-hour heat treatment at relatively low temperature of 1200 °C. The powder was successfully synthesised without the need for excess carbon which is typical for conventional carbothermal reduction using some other sources of graphite. The increase in temperature of heat treatment to 1400 °C caused considerable growth of SiC particles up to 400 nm. It was found that prolonged heat treatment at 1200 °C is an effective way to obtain well crystallized SiC and keep the size of SiC particles below 50 nm at the same time.

Keywords: Sol–gel processes; X-ray methods; SiC

1. Introduction

Unique combination of properties such as high strength and hardness, good oxidation resistance, high thermal conductivity and low thermal expansion coefficient makes silicon carbide (SiC) promising material for various applications at both room and elevated temperatures.[1] However, the wider application of SiC ceramics is limited by the poor fracture toughness and variability of mechanical properties, which is attributed to the presence of defects such as pores, cracks or exaggerated grain growth. Therefore it is essential to manufacture high density SiC ceramics with microstructure consisting of small grains. Because of the strong covalent bonds between Si and C atoms[2] SiC cannot be sintered to a high density without additives, even at temperatures as high as 2200 °C. Although almost fully dense SiC can be obtained using expensive sintering techniques such as hot pressing[3] and hot-isostatic pressing[4] some efforts have been made over the past number of years with the objective of replacing hot-pressing with less expensive techniques such as pressureless sintering.[5] Since external pressure is not applied it is necessary to further improve driving force for sintering using fine starting SiC powder. Besides the increased driving force for sintering, the small particle size of starting powder is also expected to reduce the size of SiC grains in sintered samples which normally leads to improved mechanical properties, especially strength.[6]

On an industrial scale, SiC powder is usually manufactured using the Acheson method.[7] This technique involves mixing of SiO_2 sand and an excess of carbon and heating the mixture with graphite electrodes above 2600 °C. The SiC is obtained in the form of big crystals which require crushing and extensive milling to produce submicron SiC powder. The other way to produce fine and sinterable SiC powder is the vapour phase reaction usually between CH_4 and $SiCl_4$.[8] Since both plasma and laser heating have been used to produce the powder by gas reaction, the production cost is much higher than that for Acheson method. In order to lower production cost an effort has been made to obtain fine SiC powder by sol–gel method which does not require expensive equipment and high temperature. In this method the precursors for Si and C are water soluble organic compounds which after condensation form a gel. The powder obtained after gel drying and subsequent carbothermal reduction at elevated temperature has high surface area which is expected to provide high driving force for sintering. While tetraethyl orthosilicate (TEOS) is usually used as a source of Si the various organic compounds such as urea, phenol resin, polycarbonate, saccharose were used as a source of C.[9–12] Pekala et al. have also reported that carbon aero gels (air-filled foams) can be obtained

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from sol–gel polycondensation of resorcinol with formaldehyde followed by the supercritical drying with carbon dioxide.[13]

In this paper, the mixture of resorcinol and formaldehyde was used as a source of carbon. According to the authors knowledge the use of these precursors in SiC powder synthesis has not been reported yet. Instead of drying a gel with carbon dioxide, the freeze drying under vacuum was used. It appears that sublimation of frozen solvent crystals leaves extremely small pores which suppress the growth of SiC particles during carbothermal reduction and therefore lead to the increased specific surface of the obtained powders. The effects of the carbon/silicon ratio, temperature and duration of carbothermal reduction on properties of the obtained powders were studied.

2. Experimental

2.1. Preparation of silicon carbide nanopowder

In the present work, the source of silicon was TEOS (tetraethyl orthosilicate, $Si(OC_2H_5)_4$) whereas the source of carbon was carbon cryogel. The carbon cryogel, was synthesized by polycondensation of resorcinol, R, $C_6H_4(OH)_2$ with formaldehyde, F, HCHO according to the method proposed by Pekala et al.[13] Sodium carbonate, S, Na_2CO_3 was used as a basic catalyst. RF solutions with different amounts of TEOS (99% purity, Prolabo) were prepared by mixing resorcinol, (99% purity E. Merck), formaldehyde, (36% methanol stabilized, Fluka Chemie), sodium carbonate, (p.a. quality, E. Merck) and deionized water. The starting compositions were designed in order to yield different carbon/silicon ratios: 1–4. In all samples the concentration of the RF starting solution was 20 mass% and R/S ratio was 100. RF sols, with different amounts of TEOS were decanted in glass tubes (inner diameter = 10 mm), sealed and placed 2 days at 25 °C, 1 day at 50 °C and 4 days at 85 °C. The gels obtained after polymerization were immersed in a 10-times volume of t-butanol, p.a. quality (Centrohem-Beograd), for more than one day and rinsed to displace the liquid contained in the gels with t-butanol. The rinsing with t-butanol was repeated twice. The samples were afterwards subjected to freeze drying according to the procedure of Tamon et al.[14–17] Modulyo Freeze Dryer System Edwards, England, consisting of freeze dryer unit at High Vacuum Pump E 2 M 8 Edwards was used. The gels were pre-frozen in deep-freeze refrigerator at −30 °C for 24 h. After that, they were freeze-dried in the acrylic chambers with shelves arrangements mounted directly on the top of the condenser of freeze dryer. The vacuum during 20 h of freeze-drying was around 4 mbar.

Mixtures of carbon and silica were prepared by carbonization of the cryogels in a conventional horizontal tube furnace, in nitrogen flow. After the pyrolysis at 800 °C, the furnace was cooled to the room temperature. In order to obtain SiC, the prepared mixtures of carbon and silica were compacted and subjected to carbothermal reduction at temperature ranging from 1100 °C to 1500 °C. The powders (∼0.7 g) were compacted by cold uniaxial pressing at a pressure of 100 MPa into pastiles with diameter of 10 mm and height of 10 mm. The samples were isothermally heat treated for 1–8 h in graphite resistance furnace under argon atmosphere.

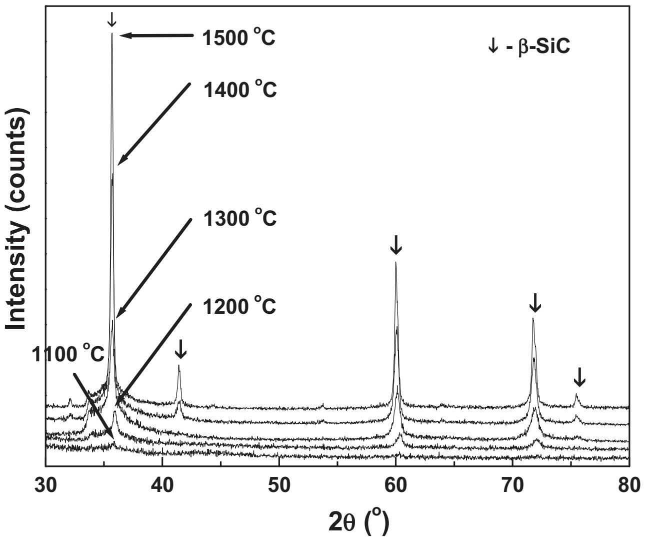

Fig. 1. X-ray diffraction patterns of samples heat-treated for 1 h at different temperatures.

2.2. Characterization of SiC nanopowders

SiC powders were characterized by recording their X-ray diffraction (XRD) patterns on a Siemens D500 X-ray diffractometer using Cu Kα radiation with a Ni filter. The 2θ angular regions between 5° and 80° were explored at a scan rate of 1°/s with the angular resolution of 0.02° for all XRD tests. Crystallite size was calculated using Scherrer equation.

Raman scattering measurements were performed at room temperature on micro-Raman system using Jobin-Yvon T64000 triple spectrometer. The Raman spectra were excited with the 514.5 nm of the Ar^+/Kr^+ laser operating at low incident power in order to avoid sample heating.

Scanning electron microscopy (SEM) analysis of SiC samples was carried out using a Tescan VEGA TS 5130MM instrument.

Adsorption and desorption isotherms of N_2 were measured on SiC samples at −196 °C using the gravimetric McBain method. The specific surface area, S_{BET}, for the samples was calculated from the isotherms.

3. Results and discussion

The powders obtained after pyrolysis at 800 °C were amorphous and consisted of SiO_2 network with dispersed graphite. Subsequent heat treatment (carbothermal reduction) at higher temperature was necessary to initiate the formation of crystalline SiC through the following reaction:

$$SiO_2 + 3C \rightarrow SiC + 2CO \uparrow \qquad (1)$$

The effect of temperature of heat treatment on SiC crystallization is presented in Fig. 1. As expected, the amount of β-SiC increases with an increase in temperature of heat treatment.

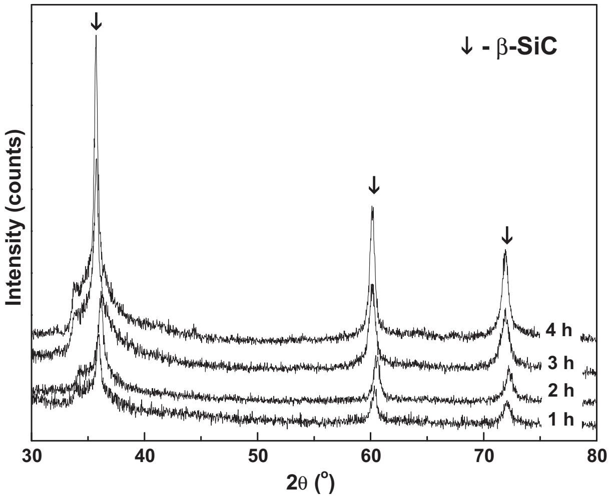

Fig. 2. X-ray diffraction patterns of samples heat-treated at 1200 °C for different time periods.

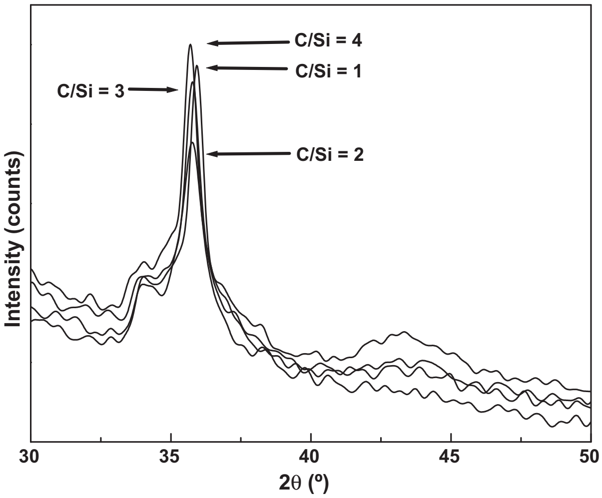

Fig. 3. X-ray diffraction patterns of samples heat-treated at 1200 °C for 1 h with different C/Si ratios.

Although the powder obtained after heat treatment at 1100 °C is completely amorphous the considerable amount of crystalline β-SiC was obtained even at temperature of 1200 °C, which is significantly lower than that for Acheson method. It is believed that the relatively low temperature of SiC crystallization is the result of intimate (atomic) mixing of SiO_2 and C obtained through the sol–gel procedure. This way diffusion path is much shorter than that for solid state reaction in which Si and C atoms have to diffuse throw the SiC layer created at the surface of SiO_2 and C particles. It also appears that the temperature necessary for crystallization of SiC depends on the origin of Si and C. For example, it was reported that somewhat higher temperature of 1400 °C is required for intensive crystallization of SiC when silica sol and saccharose were used as a source of Si and C, respectively.[18] This points out that the mixture of resorcinol and formaldehyde might be a promising candidate for graphite source in sol–gel synthesis. Besides lower production cost, another advantage of low temperature of carbothermal reduction is SiC powder consisting of low-temperature, β modification. Transformation of β-SiC to high-temperature modification, α-SiC, during liquid phase sintering normally leads to formation of elongated SiC grains with improved fracture toughness.[19] Also, the additional diffraction peak was detected at $2\theta = 33.6$, which represents stacking faults on the $\langle 1\,1\,1 \rangle$ planes in cubic SiC whiskers.[20]

Fig. 2 shows that the amount of crystallized SiC increases with prolonged duration of heat treatment. After 8 h long heat treatment at 1200 °C the powder completely crystallized with no traces of α-SiC. Based on Figs. 1 and 2 it can be concluded that 1 h heat treatment is sufficiently long to induce crystallization of β-SiC at temperature as low as 1200 °C.

Another important parameter of sol–gel synthesis is the C/Si ratio. An excess of carbon is normally used in SiC synthesis especially when it comes to solid state reaction. The excess of carbon was found to be effective in increasing the contact area between SiO_2 and C particles and therefore accelerating the SiC synthesis (Eq. (1)). The introduction of excess C is also essential in increasing the crystallinity of SiC powder obtained by sol–gel procedure. It was reported that the optimum C/Si ratio was 4 when silica sol and saccharose were used as a source of Si and C, respectively.[19] The unreacted C is usually removed by heat treatment at 600 °C in oxygen, which additionally increases the production cost and duration of SiC synthesis. However, our study shows that the C/Si ratio does not affect the formation of SiC in any significant way. As can be seen in Fig. 3, the intensities of β-SiC peaks and therefore the amounts of created β-SiC in samples with C/Si ratios 1 and 4 are almost the same. It appears that good homogenisation of SiO_2 and C achieved by using mixture of resorcinol and formaldehyde as carbon source plays an important role not only in decreasing the temperature of carbothermal reduction but also in decreasing the amount of excess graphite. Again, an intimate contact between SiO_2 and C on an atomic level allowed us to obtain SiC without the addition of excess graphite. Therefore the following discussion will be focused on samples with C/Si = 1.

The X-ray diffraction patterns given in Figs. 1 and 2 were also used to calculate the crystallite size of obtained SiC powders. The effect of temperature of heat treatment on crystallite size is presented in Table 1. As expected, the increase in temperature causes a continuous increase in crystallite size. It is worth noting that the crystallite size is below 40 nm even at temperature of 1500 °C. Furthermore, Table 2 shows that the prolonged heat treatment at 1200 °C promotes the growth of SiC crystallites but still the crystallite size in samples treated for 8 h is smaller than 30 nm. Based on this modest increase in crystallite size (Table 2) and considerable increase in peak intensity with treatment time (Fig. 2) one can conclude that prolonged heat

Table 1
Crystallite size of samples heat treated at different temperatures for 1 h.

	Temperature of heat treatment (°C)			
	1200	1300	1400	1500
SiC crystallite size (nm)	19	21	28	36

Table 2
Crystallite size of samples heat treated at 1200 °C for different time.

	Heat treatment time (h)			
	1	2	4	8
SiC crystallite size (nm)	19	20	22	24

treatment at 1200 °C promotes crystallization of SiC rather than intensive crystal growth.

Microstructure of the obtained powders was observed under SEM. Fig. 4 presents the change of size and shape of SiC particles with temperature of heat treatment. As can be seen in Fig. 4a, the SiC powder obtained at 1200 °C consists of agglomerates estimated to be 300–400 nm in diameter. Although it is quite difficult to estimate the actual size of the agglomerated SiC particles it is evident that the particle size is below 50 nm. Fig. 4b reveals that an increase in temperature of heat treatment to 1300 °C does not change considerably the size and the shape of powder agglomerates. However, an increase in temperature of heat treatment to 1400 and 1500 °C significantly changes the morphology of SiC powders as shown in Fig. 4c and d. These powders consist of particles with relatively smooth surface, which are quite different than the agglomerates with rough surface observed at lower temperature (Fig. 4a and b). It is interesting to note that the average size of these particles is close to the average size of agglomerates observed at lower temperatures (space ~400 nm). It is believed that the heat treatment at temperature as high as 1400 °C promotes coalescence of fine, agglomerated, SiC particles into much bigger particles. The support to the above conclusion was also found in Table 1 which shows that crystallite size of samples heat treated at 1500 °C is about 10 times smaller than the average particle size observed under SEM. A simple calculation, assuming spherical shape

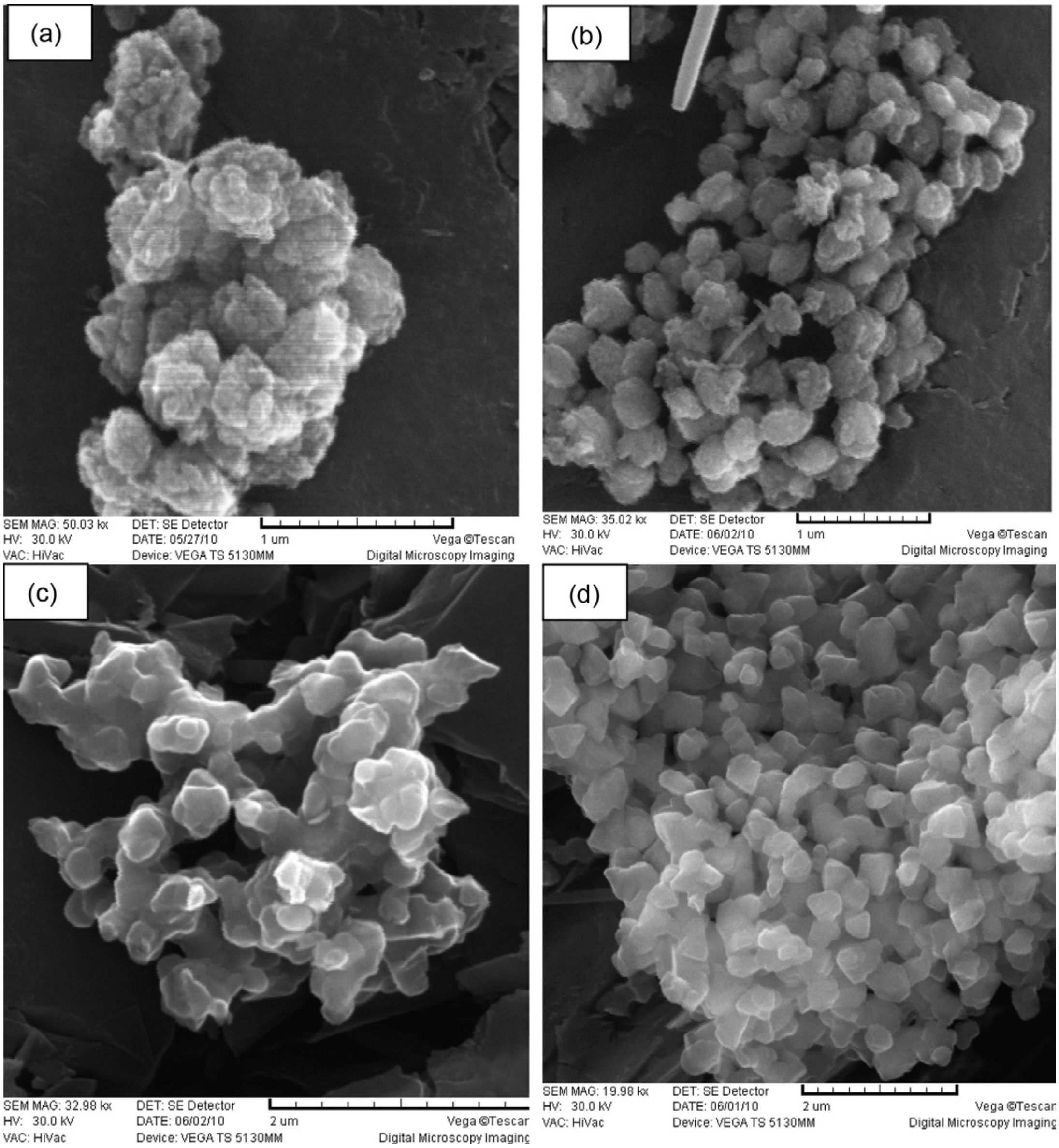

Fig. 4. SEM micrographs of samples with C/Si = 1 heat-treated for 1 h at temperature (a) 1200 °C, (b) 1300 °C, (c) 1400 °C and (d) 1500 °C.

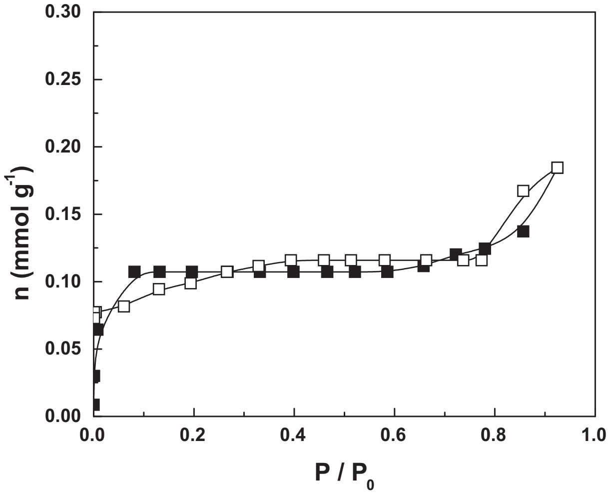

Fig. 5. Adsorption and desorption isotherms of N_2 on SiC powder obtained after 1 h heat treatment at 1200 °C given as amount of adsorbed N_2 as a function of relative pressure at −196 °C. Solid markers denote adsorption.

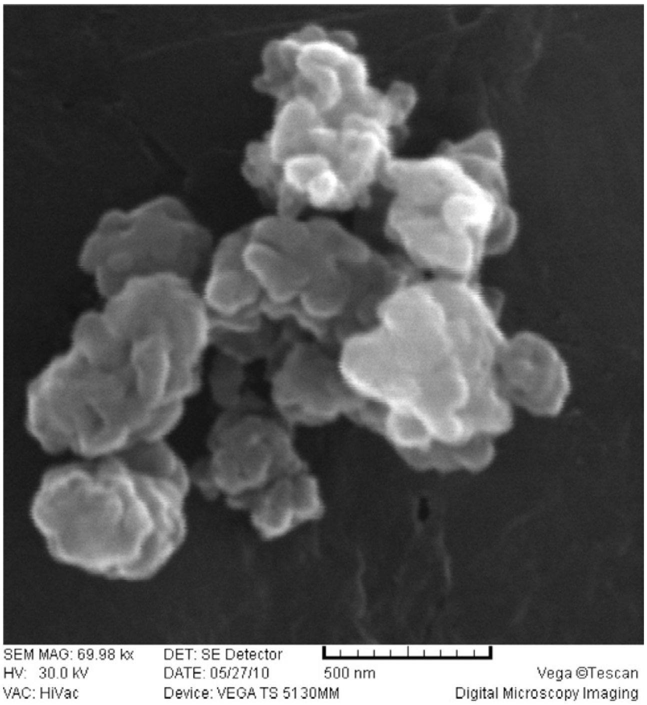

Fig. 6. SEM micrograph of sample heat-treated at 1200 °C for 8 h.

of both crystallites and particles seen under SEM, shows that approximately 1000 crystallites participate in formation of one SiC particle. It is also important to stress that the size distribution of these particles is uniform which is normally beneficial in avoiding exaggerated grain growth during sintering.

The coalescence of fine crystallites is followed by a decrease in specific surface. While specific surface of samples heat treated at 1200 and 1300 °C is about 10 m^2/g, the specific surface of samples heat treated at 1400 and 1500 °C is way below 10 m^2/g. The specific surfaces were calculated from adsorption isotherms of N_2 on obtained powders using BET equation. Adsorption and desorption isotherms of N_2 on SiC powder obtained after 1 h heat treatment at 1200 °C are presented in Fig. 5.

The effect of prolonged heat treatment at 1200 °C on microstructure of SiC powder was presented in Fig. 6. When compared to sample treated for 1 h (Fig. 4a) it can be noted that prolonged heat treatment slightly increases the size of agglomerates (up to ∼600 nm) whereas the shape of agglomerates does not change. Particles smaller than 50 nm, observed in Fig. 6, provide an additional support to the previously made conclusion that prolong heat treatment at low temperature such as 1200 °C promotes crystallization of SiC but does not cause intensive growth of SiC particles.

Raman spectroscopy was used to determine the polytype of SiC. The results presented in Fig. 7 confirm that the obtained

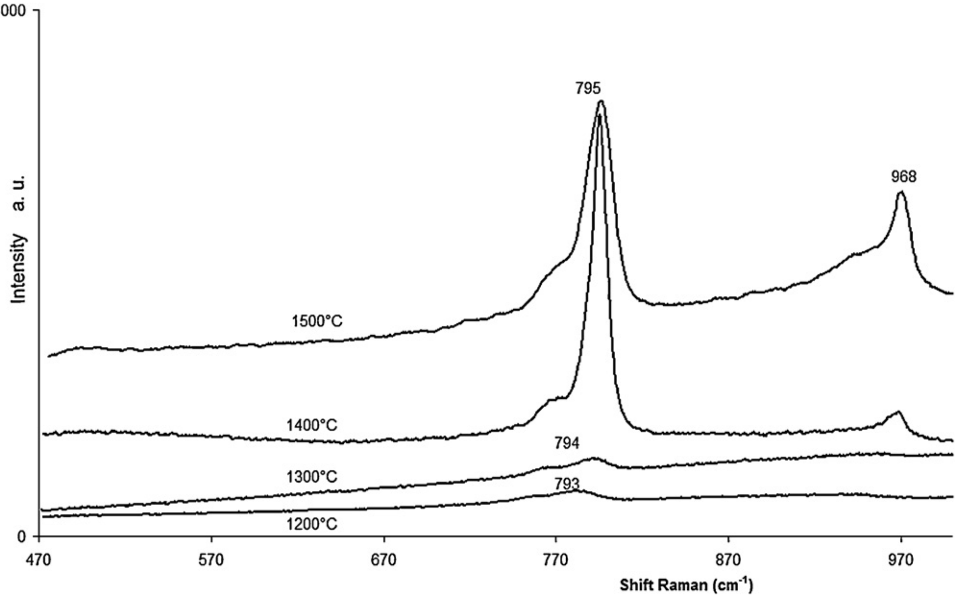

Fig. 7. Raman spectra of samples heat-treated for 1 h at different temperature.

powder is β-SiC. The peak at 793 cm^{-1} belongs to the cubic polytype 3 C.

4. Conclusions

Nanosized β-SiC powder was prepared by carbothermal reduction of freeze-dried gel. Resorcinol and formaldehyde were found to be a promising source of carbon. SiC powder was prepared after heat treatment at relatively low temperature of 1200 °C for 1 h. Excess carbon was not required in this synthesis. The obtained powder consisted of agglomerates of fine SiC crystallites with diameter of ∼20 nm. Heat treatment at higher temperature such as 1400 °C caused an intensive growth of SiC particles and decrease in specific surface area. Prolonged heat treatment at 1200 °C was found to be an effective way to increase the crystallinity of SiC and to retain SiC crystallite size below 30 nm.

Acknowledgement

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