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A Comparison of Sol–Gel Derived Silicon Carbide Powders from Saccharose and Activated Carbon

Lj. Čerović, S. K. Milonjić & S. P. Zec

Vinča Institute of Nuclear Sciences, P.O.Box 522, 11001 Belgrade, Serbia

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Abstract: β-SiC has been synthetised at 1550°C by the reductive heating of gel precursors prepared from silica sol and saccharose or activated carbon as carbon sources. An optimum molar ratio of reactants, C/SiO_2, as well as the mechanism of SiC crystallization, have been investigated for each carbon source applied. The influence of boric acid addition in the starting sol on the properties of SiC powders produced has been elaborated. Boric acid represents a catalyst for the carbothermal reduction of silica within the established range of concentrations which is, in return, dictated by the molar ratio of reactants and carbon source in the system.

1 INTRODUCTION

Silicon carbide (SiC) is a promising structural material for high temperature applications, owing to its excellent chemical and physical characteristics. The Acheson process remains as a basic manufacturing process, but other methods have been applied recently, for the production of more elaborate SiC powders. Among them, the sol–gel process has drawn considerable attention for making homogeneous and highly active SiC powders. Starting materials used in this process are usually alkoxides,[1–3] but colloidal solutions can also be applied as silica precursors.[4] Saccharose, activated carbon, phenolic resin, pitch, etc., are commonly used as external carbon sources. A mixture of Si-alkoxides can also be applied.[5,6] White and coworkers[7, 8] obtained SiC powder from organosilicon polymers, other than alkoxides, which contain carbon and silicon in the same molecule. With this being the case, gel decomposition provided more intimate C/SiO_2 mixture, allowing lower temperatures of synthesis and high surface areas of the as-processed SiC powders to be obtained.

In this study, SiC was prepared from silica sol with saccharose or activated carbon as external carbon sources. The effect of boric acid presence in the system on the surface characteristics of the SiC powders obtained was also studied.

2 EXPERIMENTAL

The silica sol used was prepared by the ion exchange method.[9] It contained 3·7 mass % SiO_2 stabilised at pH= 10·3. The specific surface area of the solid phase was 152 m^2/g and the mean diameter of the SiO_2 particles was 18 nm. Two carbon sources were applied: saccharose, $C_{12}H_{22}O_{11}$, p.a. quality (Merck, Germany) and activated carbon, p.a. quality, with specific surface area of 960 m^2g (Kemika, Croatia). The carbon source was dissolved/mixed in the sol in a quantity adjusted to obtain molar ratio of reactants, C/SiO_2 from 3 to 5. Boric acid, H_3BO_3, was added into the starting sol in the range of 0–13·5 mass %. Gelling was performed by water evaporation with constant stirring. Carbothermal reduction of silica was carried out in a tube furnace using graphite crucibles. Dried, ground gels were heated at 5°C/min in an argon stream (15 litre/h) flowing through the sample,[4] up to 1550°C with 3 h hold. The decomposition of gels was investigated using a thermal

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analyser. The X-ray examination was carried out using a Siemens-D 500 diffractometer with CuKα Ni-filtered radiation. A scanning electron microscope JSM-35 (JEOL, Japan) was used to study the morphology of the powder samples. Specific surface areas (*Sa*) were estimated by the B.E.T. method.

3 RESULTS AND DISCUSSION

Low temperature TG analysis under flowing argon revealed the gel decomposition in the range of 100–600°C, attributed to water loss and saccharose decomposition, depending on the carbon precursor. The total weight loss went up to 90 and 70 mass % for samples with saccharose and activated carbon, respectively. The specific surface areas, measured after the thermal treatment at 1100°C, took values of 920 m^2/g for activated carbon and 34 m^2/g for the carbonaceous product originating from saccharose.

It was noticed that the mechanism of β-SiC crystallization depended on the carbon origin. With saccharose being the carbon source, the formation of SiC started timidly at 1300°C and became intensive at 1400°C (Fig.1). The crystallization process took place entirely within the glass-like matrix and well-defined diffraction peaks for crystalline SiO_2 were never observed. On the contrary, in the case of gels prepared from activated carbon, the crystallization of β-SiC started at 1400°C and proceeded via carbothermal reduction of excellently crystallized SiO_2 (cristobalite) (Fig.2). These differences were attributed to the molecular intimacy of the SiO_2/C mixture obtainable only in the gels prepared with saccharose. Carbon obtained from external C source-saccharose, behaved as if it had been internal to silicon, similar to the polymer precursors of SiC.[8]

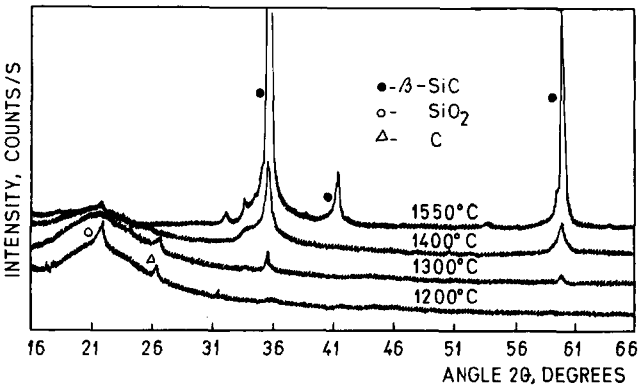

Fig. 1. Diffraction patterns of saccharose derived SiC gel precursor, prepared using $C/SiO_2=4$ with an addition of 1·0 mass % H_3BO_3, after thermal treatment.

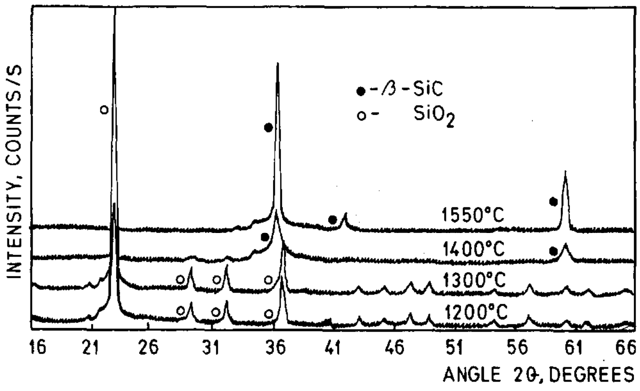

Fig. 2. Diffraction patterns of activated carbon derived SiC gel precursor, prepared using $C/SiO_2=3$ with an addition of 0·7 mass % H_3BO_3, after thermal treatment.

After synthesis at 1550°C, a relative quantity of β-SiC and unreacted reactants in the powder samples was studied through the ratio of diffraction peak areas of all β-SiC reflections appearing in diffraction pattern, ΣP_{SiC}, to the diffraction peak areas ascribed to unreacted reactants, $\Sigma P_{residue}$ (Tables 1 and 2).

Table 1. Properties of saccharose derived β-SiC powders, synthetised at 1550°C/3h

Molar ratio (C/SiO_2)	H_3BO_3 (mass %)	ΣP_{SiC} (arb. units)	$\Sigma P_{residue}$ (arb. units)	Relative quantity SiC (mass %)	Crystallite size (nm)	*Sa* (m^2/g)
	0	4766	301	94·0	18	31
3	2·3	4450	532	89·5	35	25
	5·5	5222	305	94·5	37	8
	0	3640	1130	76·4	25	255
	1·0	3559	1609	68·9	21	300
	3·0	5236	293	94·7	36	21
4	5·5	5546	410	93·1	41	8
	8·1	5374	240	95·7	39	10
	11·0	5375	254	95·5	38	5
	13·5	5392	439	93·5	41	<1
	0	4890	470	91·2	34	80
5	3	5245	388	93·1	34	59

Table 2. Properties of activated carbon derived β-SiC powders, synthetised at 1550°C/3h

Molar ratio (C/SiO_2)	H_3BO_3 (mass %)	ΣP_{SiC} (arb. units)	$\Sigma P_{residue}$ (arb. units)	Relative quantity SiC (%)	Crystallite size (nm)	*Sa* (m^2/g)
	0	4345	199	95·6	31	8·7
3	0·7	4383	326	93·1	20	15·3
	2·4	4941	257	95·0	32	3·3
	8·1	5472	270	95·3	44	—
	0	5355	204	96·3	35	115·4
4	0·7	4743	435	91·6	29	83·5
	2·4	4502	237	94·9	26	186·9

Poorly crystallized β-SiC with a significant remainder of SiO_2 (cristobalite) was obtained in samples with saccharose using the stoichiometric molar ratio of reactants, $C/SiO_2 = 3$ (Fig.3). Raising the molar ratio of reactants up to 4 resulted in a better crystallinity of the dominant phase and a significant portion of an amorphous residue. Introduction of a higher amount of carbon, $C/SiO_2 = 5$, led to even better crystallized SiC, according to the corresponding peak intensities, and an amorphous residue increase (Fig.3). The recorded residue increase was due to the greater molar ratio of reactants applied cf. the stoichiometric case. Prolonged isothermal heating of the samples did not contribute to further conversion of reactants, but only to the growth of the primary SiC crystallites. In our experiments, the maximum obtainable temperature of synthesis of 1550°C was obviously not high enough for completing the carboreduction of silica. Under such conditions, the molar ratio of reactants $C/SiO_2 = 4$ was chosen as an optimum one. In the case of gels prepared from activated carbon as a carbon source, the optimum molar ratio of reactants was found to be $C/SiO_2 = 3$, when very well crystallized β-SiC and a negligible residue of unreacted reactants were produced (Table 2).

An introduction of 5·5 mass % of H_3BO_3 into the starting sol in the samples with saccharose, prepared according to the optimum molar ratio established, caused a beneficial change in its diffraction pattern, as shown in Fig.4. According to literature[4] the presence of boric acid contributes to the conversion rate of silica, leading to better crystallinity and yield of as-processed SiC powders. Upon heating, H_3BO_3 decomposes to B_2O_3 which is throughly miscible with SiO_2. At such a low temperature (451±1°C) the mixture of B_2O_3 and SiO_2 shows a liquid as one of the phases.[10] Respecting the equilibrium concentration for SiO_2 and B_2O_3 at the temperature of synthesis of 1550°C, a formation of the liquid phase occurs in the system. Migration of silica particles through the gel matrix is enhanced, allowing more frequent and efficient contacts between SiO_2 and C, for the same period of time and at the same temperature, compared to the solid state reaction. It has been determined in the system with saccharose that, for the optimum molar ratio of reactants, H_3BO_3 represents a catalyst for the carbothermal reduction of silica in the range of concentrations between 3·0 and 11·0 mass %.

Although the synthesis of SiC from gels with activated carbon proceeded with greater conversion

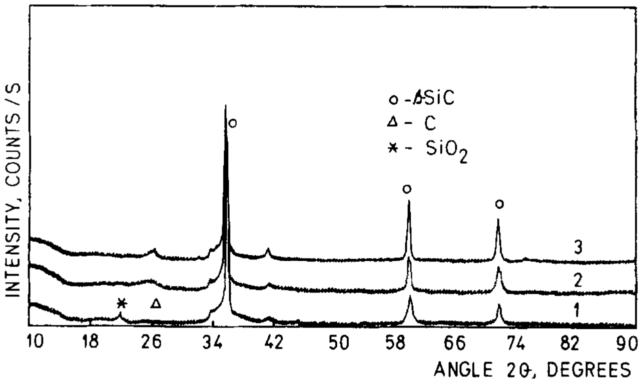

Fig. 3. Diffraction patterns of saccharose derived SiC powders, synthetised at 1550°C using different molar ratio of reactants: (1) C/SiO_2=3, (2) C/SiO_2=4 and (3) C/SiO_2=5.

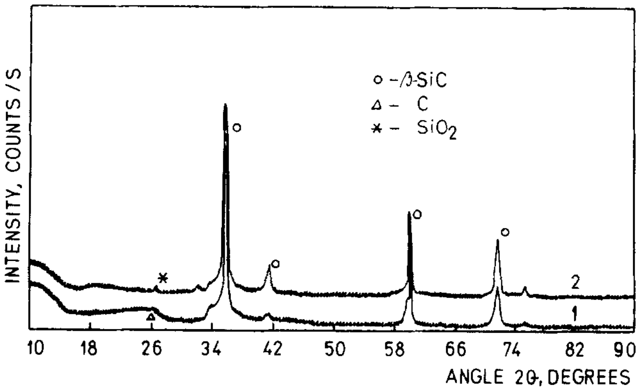

Fig. 4. Diffraction patterns of saccharose derived SiC powders, synthetised at 1550°C using C/SiO_2=4, (1) without H_3BO_3 and (2) with 5·5 mass % H_3BO_3.

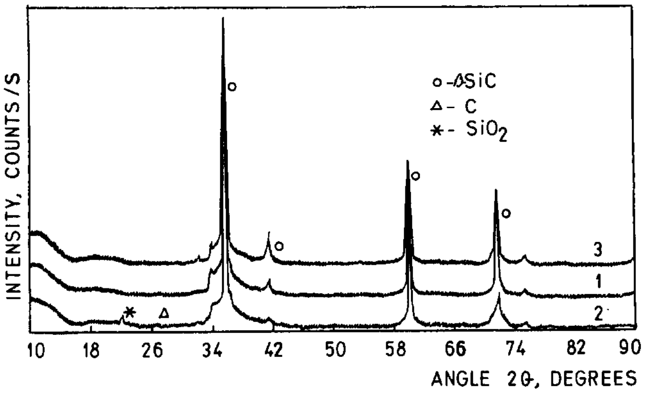

Fig. 5. Diffraction patterns of activated carbon derived SiC powders synthetised at 1550°C, using $C/SiO_2=3$, (1) without H_3BO_3, (2) with 0·7 mass % H_3BO_3 and (3) with 2·4 mass % H_3BO_3.

rate than when using saccharose, the presence of boric acid in this system was found to be beneficial as well (Fig.5). The optimum interval of the boric acid concentrations for the samples with activated carbon starts at 2·4 mass % and exceeds the value of 8·1 mass %. A H_3BO_3 content lower than 2·4 mass % retards the carbothermal reduction and increases the remainders of the reactants. It is worth mentioning that the same amount of boric acid does not lead to the same degree of crystallization when using different molar ratios of reactants. Introducing 2·4 mass % H_3BO_3 when applying stoichiometric molar ratio to the gels with activated carbon, much better crystallized β-SiC was produced than when using $C/SiO_2 = 4$ (Fig.6). Similar observations were registered when comparing the diffraction patterns of the samples prepared from saccharose using $C/SiO_2 = 4$ and $C/SiO_2 = 5$ upon addition of 3·0 mass % H_3BO_3 (Fig.7). An optimum amount of boric acid appears to be specific for each system, thus should be determined separately for each one.

The sixth columns of Tables 1 and 2 list the crystallite sizes measured on the (111) reflection of β-SiC using Schrerrer's formula and Warren's method[11] for the instrumental broadening correction. The crystallite size is obviously very dependant on the amount of H_3BO_3 in the system.

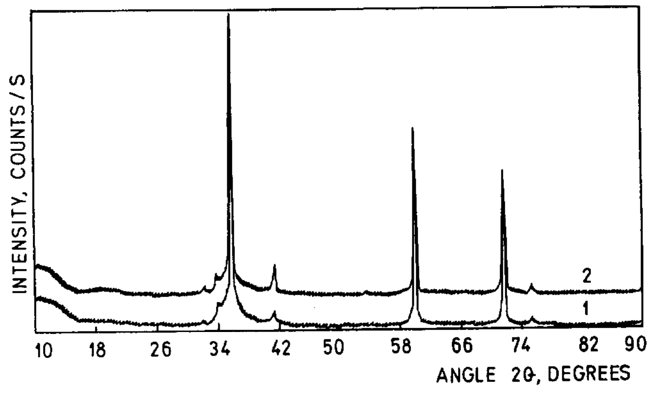

Fig. 6. Diffraction patterns of activated carbon derived SiC powders synthetised at 1550°C/3h, with addition of 2·4 mass % H_3BO_3, using (1) $C/SiO_2=3$ and (2) $C/SiO_2=4$.

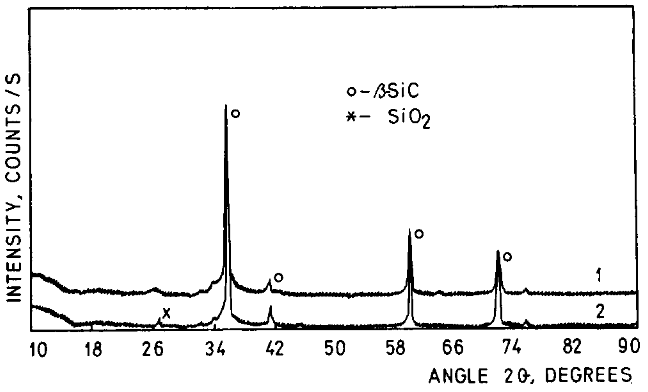

Fig. 7. Diffraction patterns of saccharose derived SiC powders synthetised at 1550°C/3h, with addition of 3·0 mass % H_3BO_3, (1) using $C/SiO_2=5$ and (2) $C/SiO_2=4$.

SEM observations revealed quite heterogeneous microstructure of as-received SiC powders, which was, in general, independant of carbon origin. It

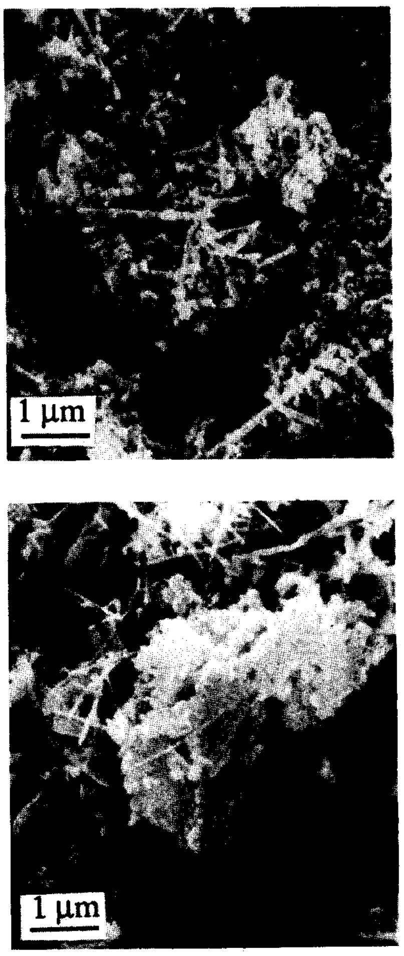

Fig. 8. SEM micrographs of (a) saccharose and (b) activated carbon derived SiC powder/whiskers mixture.

consisted of a combination of SiC agglomerated powder and whiskers (Fig.8). The powder/whisker ratio, as well as the whiskers' morphology, is tightly determined by the boric acid content in the system. The presence of whiskers should be related to the SiO_2–B_2O_3 liquid phase formation, but can not be explained via the conventional vapor–liquid–solid (VLS) mechanism.[12] The whiskers' formation and morphology have been elaborated and discussed in detail elsewhere.[13, 14]

It has been noticed that spherical particles of SiC obtained from activated carbon were firmly bonded and twice as big as those originating from saccharose (Fig.9). Coarse, porous and of exceptional activity, activated carbon particles offer good opportunities for packing at least 1000 times smaller silica particles. On the other hand, carbon particles obtained upon $C_{12}H_{22}O_{11}$ decomposition are at a molecular level comparable with silica particles. As a result, much finer SiC powder particles are produced.

It has been found in current experiments that the molar ratio of reactants, carbon source applied and the amount of boric acid determine the values of the specific surface areas and colour of powders obtained. All powder samples obtained from activated carbon were light green when their specific surface areas (*Sa*) were less than 9 m^2/g. Dark green coloured samples had the following range of specific surface area values: 9 $m^2/g < Sa < 15$ m^2/g. Samples prepared with saccharose were of a different colour. When 32 $m^2/g < Sa < 1$ m^2/g, samples were quite pale. Unreacted carbon contributed to an increase in *Sa* and to a darker colour. So, powders with specific surface areas in the range of 32–80 m^2/g were grey or black, if their specific surface areas took the values $Sa > 250$ m^2/g. Experimental results, as well as subsequent literature data, confirm that the purity of SiC samples can be estimated by their specific surface area values and colour.

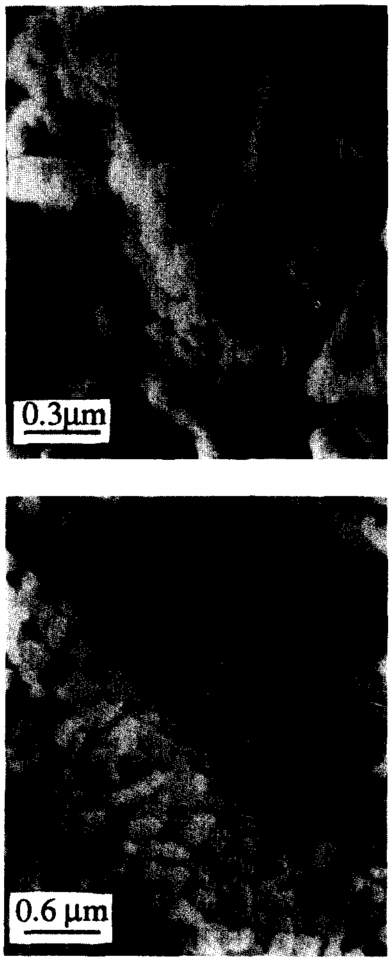

Fig. 9. SEM micrographs of (a) saccharose and (b) activated carbon derived SiC powder.

Ault and Robertson[15] claim 99·8 mass % SiC to be light green. With decreased purity, the colour changes to dark green (99·5 mass % SiC) over black (99 mass% SiC) to gray (90 mass % SiC). Tanaka and Kurachi[2] reported yellow β-SiC, claiming single β-SiC crystals to be yellow. Julbe et al.[4] synthetised light green SiC powder, dark grey SiC with a carbon residue and a powder/whiskers combination which was white. Milewski *et al.*[16] investigated the colour and morphology of β-SiC whiskers as a function of molar ratio of reactants. So, the obtained whiskers were black, grey, white, dark green, and even blue.

4 CONCLUSIONS

β-SiC was synthetised at 1550°C by a sol–gel method from a colloidal solution of silica and saccharose (or activated carbon) as the external carbon source. The stoichiometric molar ratio of reactants, $C/SiO_2 = 3$, was established as an optimum for the preparation of gels with activated carbon. In saccharose derived gels, $C/SiO_2 = 4$ was selected as the most suitable molar ratio of reactants. With saccharose being the carbon source, the formation of SiC starts at 1300°C and proceeds entirely within the glass-like matrix, similar to organosilicon polymers. On the contrary, in the system with activated carbon, SiC commences to generate at 1400°C via carbothermal reduction of well crystallized silica.

Boric acid is a catalyst for the carbothermal reduction of SiO_2 increasing the yield and crystallinity of β-SiC produced. Respecting the optimum molar ratio of reactants, the beneficial H_3BO_3 concentrations range from 3·0 to 11·0 mass % and from 2·4 to 8·1 mass % for the systems with saccharose and activated carbon, respectively.

Microstructures of SiC powders obtained from saccharose and activated carbon are, in general, similar, consisting of an agglomerated, spherical powder/whiskers mixture. Spherical SiC particles derived from activated carbon are bonded together and of twice the diameter (d= 0·4 μm) of those originating from saccharose (d=0·2 μm).

Specific surface areas and colour of the SiC powders produced are tightly determined by the carbon source, molar ratio of reactants applied and amount of boric acid in the system.

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