



SPARK PLASMA SINTERING OF PLASMA SYNTHESIZED NANOSIZED SiC POWDER

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Spark Plasma Sintering (SPS) of thermal plasma synthesized nanosize powders were studied without removing the free carbon impurities. Instead, SiC was mixed with silicon powder to react with the free carbon during sintering with boron as sintering aids. Density of the resulted disc samples found to be increased with the applied temperature and achieved a maximal 93 % of relative density at 1950 °C after 5 minutes holding time. The obtained samples composed of β -SiC along with a few per cent of un-reacted graphite.

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Introduction

Silicon carbide is an advanced ceramic material that has found widespread application both for structural and electrical purposes.¹ The enhanced mechanical properties and other outstanding features associated with nanosize particles and nanostructured bulk materials has directed an increased interest in manufacturing and sintering of nanosize powders. Several methods for the synthesis of nanosize powders have been developed over the last decades including sol-gel processes,² pyrolysis of silicon-bearing polymers,³ CVD methods,⁴ plasma synthesis⁵⁻⁶ rapid carbothermal reductions,⁷ etc. Nanosize powders require, however, special sintering treatment to retain the nanostructure. During conventional sintering substantial grain coarsening can occur on the account of the relatively prolonged sintering process at high temperatures. Spark plasma sintering (SPS) method is a newly developed technique that enables the compacted powder to be fully densified at a comparatively low temperature, and in a very short time intervals.⁸⁻¹² Several reports have already been published recently on the successful sintering of nanosize SiC by SPS retaining the nano-structured characteristic.^{13,14} In these reports SiC was sintered with addition of various sintering aids in minor amounts. One of the main drawbacks of nanoparticle synthesis methods is that the primary products usually contaminated with carbon and unreacted silica.¹⁵⁻¹⁶ These impurities are usually removed prior to sintering. Carbon is commonly eliminated by heating the sample in a furnace between 600-700 °C under oxidizing atmosphere. Even though SiC is considered to be an oxidation resistant material, during this process oxidation of the surface of silicon carbide particles is inevitable in thermodynamic point of view. In addition, due to the high specific surface area of the nanoparticles the oxygen contamination can also be increased. The formed oxide layer along with unreacted silica particles are easily eliminated by

a subsequent acidic washing. The whole process, however, may lead to substantial yield loss. On the other hand, pure SiC is difficult to sinter due to its highly covalent nature, which results in very slow atomic diffusion. To promote sintering various sintering additives are used. Carbon is routinely employed when solid phase sintering mechanism is aimed. This may pose the question if carbon really has to be completely removed before sintering. In the practice of conventional SiC sintering there are well-developed methods for sintering SiC without removing the carbon. In these cases the compacted form is getting into contact with molten silicon. This way is not viable in advanced sintering methods such as SPS, or at least not in that form.

There has not been any study reported yet on the sintering of carbon contaminated SiC by SPS. In the present work we investigated the sintering behavior of nanosized SiC powders synthesized by thermal plasma processing without removing the free carbon content, which remained in the product after synthesis as an impurity. Unlike conventional sintering technique, silicon is initially mixed into the SiC powder to react with the free carbon remained in the powder. At the high temperature of sintering (>1800 °C) the reaction between silicon and carbon is thermodynamically favored. We investigated the completeness of the above reaction after sintering as well as the porosity of the obtained specimens.

Experimental

Nanosized SiC powder (marked as IMEC powder) was prepared by RF thermal plasma synthesis from solid precursors, namely fine powders of silica and carbon. Experimental details of the procedure were published elsewhere.¹⁷ It was found that the SiC particles were contaminated with non-reacted silica and carbon precursors. The silica was leached out with hydrofluoric acid but the carbon wasn't burnt out for fear the fine silicon carbide may also be oxidized. In this way the starting SiC powder, which was used for sintering had lower oxygen contamination (3 wt. %) but had free carbon content as much as 20 wt.%. Reference tests were also performed using commercial SiC powder (Carborex F1200, Washington Mills). Main characteristics of the tested SiC powders are detailed in Table 1.

Table 1. Specifications of SiC powders used in sintering tests

SiC Powder	Phases	Specific area, m ² ·g ⁻¹	Mean size, μm	Purity (wt%)				
				SiC	Free C	Si	O ₂	Fe
Commercial	α	0.6	3	98.3	0.25	0.35	0.60	0.10
IMEC	β	54	0.035		~20	<0.1	3.1	0.17

Boron (H.C.Starck) and silicon (Aldrich) additives were mixed with SiC powders in a ball mill using ethanol. The mechanism by which boron facilitates sintering is still under discussion¹⁸⁻¹⁹ but its beneficial effect is indisputable, while carbon has the role to remove the oxygen from the surface of SiC particles. The additives and their ratio in particular tests are given in Table 2. Finally the mixtures were dried by infrared heating for 1 hour.

The SPS consolidation was carried out using a HP D5 apparatus (FCT GmbH, Germany). 3 grams from each mixture were put into a cylindrical graphite die having an inner diameter of 20 mm. A vacuum of 3 Pa was maintained in the chamber. The powders were uniaxial pressed throughout the sintering process with 30 MPa up to 600 °C, above that it was increased to 50 MPa. A degassing treatment was performed at 600 °C for 5 minutes. The maximum sintering temperatures were selected to be 1850 °C and 1950 °C with a heating rate of 100°C min⁻¹. A soaking time of 5 minutes were applied at the sintering temperature. In one test an extra holding time was applied at 1600 °C for 5 minutes. It is reasoned by our previous tests that showed an increased densification rate at this temperature. In each case, pressure was released at the end of the holding time and specimens were cooled down to room temperature in the die. The experimental parameters including temperature, applied load and sample displacement were measured continuously during sintering. The temperature was controlled by an infrared pyrometer that focused to a hole drilled in the upper graphite punch thereby only a few millimetres from the sample surface. Linear shrinkage of the powder compacts during the SPS process was continuously monitored by displacement of the punch rod.

The sintered samples were cleaned by grit blasting then analyzed for microstructure by scanning electron microscopy (SEM Hitachi HR-SEM S4800 and Philips XL30 model a) and phases by X-ray powder diffraction (XRD, Siemens D5000 diffractometer) using CuKα radiation. Density of the specimens was measured by Archimedes method in distilled water.

Results

Figure 1. shows the linear shrinkage of the different SiC disc samples against temperature during SPS treatment. The starting temperature of reduction can be assessed from the diagram. However, it was determined more precisely using the differentiation of the deformation curves (Table 2). It can be noticed that without sintering aids densification started at much higher temperature (TS) as compared to the other tests. This temperature (TS) considerably decreased by addition of boron and carbon to SiC powder. Using the plasma synthesized nanopowders (IMEC) the densification

shifted down at even lower temperatures. From Fig. 1 one can also compare the sintering tests with respect to their final shrinkage. Maximum reduction was determined at the end of the soaking time at the highest sintering temperature. Analyzing these values it can be observed that tests carried out at 1850 °C had almost the same reduction, while the best densification was obtained using nanosized powder at 1950 °C.

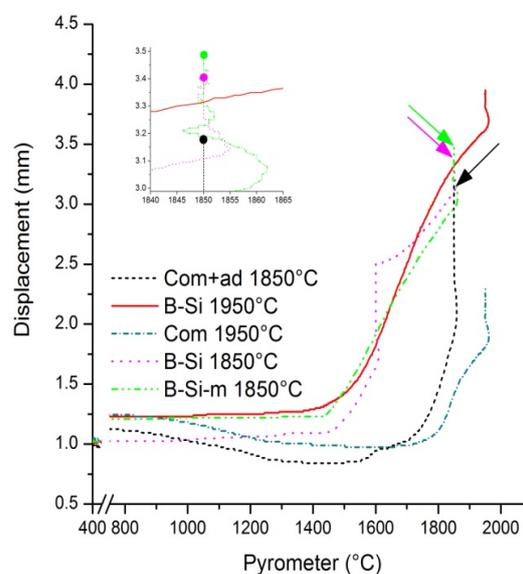


Figure 1. Linear shrinkage of the sintered samples against temperature.

X-ray diffraction plots of commercial and IMEC powders sintered at different temperatures are shown in Fig. 2. No phase changes occurred in any sample during sintering.

The commercial powder that composed of α-polytypes (6H and 12H) no any phase change was presumed. However, the plasma synthesized SiC powder composed of β-polytypes. The β to α phase formation is common at high temperatures especially in the presence of traces of α-polytypes that facilitate this transformation as nuclei. Even though, in tests No 3-5 using IMEC powder no such β-to-α transformation was detected. Similar observations were reported in other papers,²⁰⁻²² as well.

According to Suzuki²⁰ for obtaining pure β-SiC ceramics the powder has to be free of stacking faults. During SPS the applied lower temperature and shorter sintering time was not sufficient for such a phase change. Other studies also confirm this observation. Beyond SiC, graphite was present in minor amount, too, while silicon was not detected in the XRD plot at all.

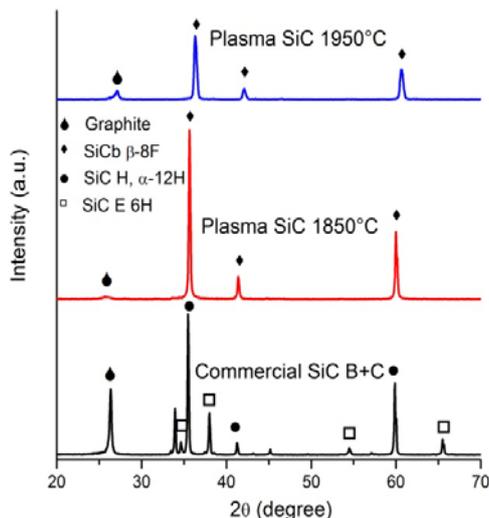


Figure 2. XRD plots of the sintered disc samples.

Discussion

The relative densities of the sintered products are listed in Table 2. These are in good agreement with the maximum values of the reduction curves in Fig. 1. It is apparent that the commercial SiC without additives hardly sintered in particular conditions; the final density was close to the green

density. The difficulties in sintering pure SiC are well known. Pressure-less sintering can be hardly viable without sintering aids. Even using the conventional pressurized techniques such as hot pressing or hot isostatic pressing high sintering temperatures ($T \geq 2100$ °C) and long soaking times (≥ 30 min) are required. There are, however, reports [13-14] of achieving almost full density SiC without sintering aids using SPS owing to the increased surface diffusion and plastic deformation caused by the electric discharges between particles. Applying the same conditions in our test, intensive densification of pure SiC began above 1760 °C. However, the shrinkage finished after 5 min of soaking at 1950 °C. The commercial SiC was failed to achieve similar densification probably because of its micron sized character. The SEM image (Fig. 3.a) of the sintered body of commercial SiC shows a rather porous structure. In this stage of sintering only neck formation began among particles.

Boron and carbon addition to commercial SiC reduced the starting temperature of densification to 1540 °C. In addition, the sintering temperature also decreased to 1850 °C and the sintered body achieved significantly much higher final shrinkage. The relative density obtained under these conditions is in line with other reports.¹³ Indeed, SEM image of the sintered product (Fig. 3.b) shows that although neck formation has been finished, pores can be still observed in the microstructure.

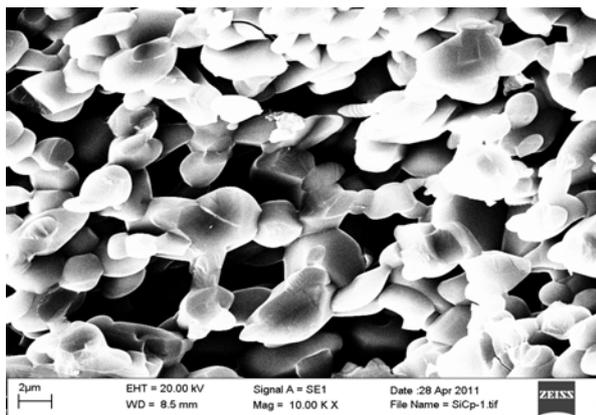


Figure 3a. SEM images of the fracture surface of sintered samples (a) commercial SiC sintered at 1950 °C.

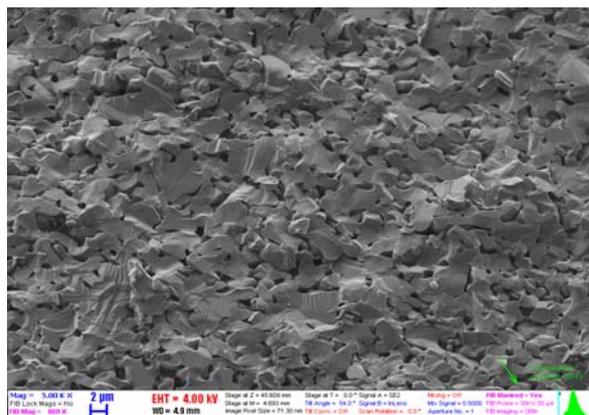


Figure 3b. SEM images of the fracture surface of sintered samples, (b) commercial SiC with B and C sintering aids sintered at 1850 °C.

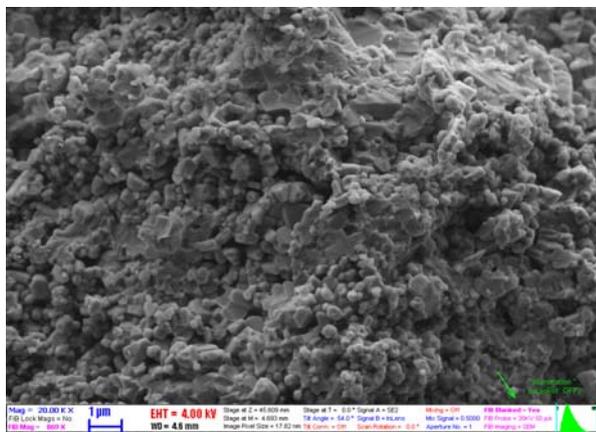


Figure 3c. SEM images of the fracture surface of sintered samples (c) nanosized SiC with B and Si sintering aids sintered at 1850 °C.

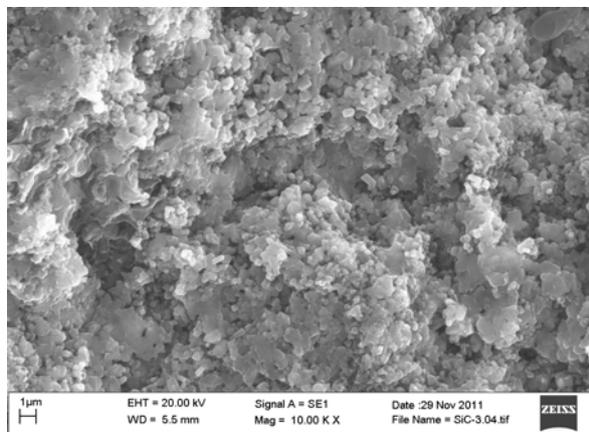


Figure 3d. SEM images of the fracture surface of sintered samples, (d) nanosized SiC with B and Si sintering aids sintered at 1950 °C.

In sintering experiments using IMEC nanopowders, densification started at still lower temperatures of 1420–1440 °C. Interesting, however, that final reduction of IMEC powder sintered at 1850 °C did not exceed that of commercial SiC mixed with additives (Fig. 1). Even the relative densities of the sintered bodies were similar for the commercial and the IMEC powders. It is because of the excess carbon that was not completely reacted with the silicon in experiment No. 3. Comparing the SEM images of these samples (Fig. 3.b-c) great difference can be observed in the grain size. Although the porosity of the disc samples was identical, the nanosize structure could be retained on sintering of plasma synthesized IMEC powders. Variation in the heating schedule during sintering by inserting a new holding step at 1600 °C corresponding to the temperature of highest densification rate did not lead to higher overall densification either.

Table 2. Sintering conditions and relative densities of the SPS sintered ceramics

SiC powder	Additives, wt%	Sintering temperature, °C	Relative density, %
Commercial	no	1950	64
Commercial	B-0.6 C-3	1850	85
IMEC	B-0.6 Si-10	1850	84
IMEC	B-0.6 Si-10	1600	81
IMEC	B-0.6 Si-10	1950	94

The highest relative density was obtained on sintering the nanosized powder at 1950 °C (Test No. 5). Densification started similarly to the previous two tests at 1420 °C, but it had a more distinctive peak above 1600 °C. The lack of silicon in the XRD plot suggests that it reacted with the free carbon in the starting powder and formed SiC. It also revealed that silicon additives did not cause any lag in sintering time due to the reaction between silicon and the free carbon. The SEM image of the sample (Fig. 3.d) exhibits a dense product seemingly free of pores.

Conclusion

In the present study nanosized monolithic SiC ceramic was prepared by SPS method using plasma synthesized SiC nano-powders containing considerable amount of carbon as an impurity. We found that the silicon powder initially added to SiC along with some boron reacted with the free carbon to form SiC. According to this way a 93 % relative density was obtained after 5 minutes of sintering at 1950 °C. The sintered disc sample composed of β -SiC phase and minor amounts of free carbon. As compared to micro sized commercial SiC powder with 0.25 wt.% of free carbon similar densities were achieved with nanosized SiC powder. However, in the latter case nanosized microstructure was formed. The result showed that instead of removing the excess carbon from the nanosized powders, they could be sintered by SPS in short time by adding silicon powder.

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