

Effects of time, temperature, and pressure on the microstructure of spark plasma sintered silicon carbide

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Silicon carbide is a ceramic material with useful properties that have many potential advanced applications. Achieving a range of desired properties is possible by carefully controlling the microstructure, which itself can be controlled by the spark plasma sintering conditions. We varied three sintering conditions and characterized the resulting microstructure. Our samples did not reach full density, and the densification and grain growth of nano-sized silicon carbide powder did not follow traditional trends. Instead, both features increased simultaneously. We conclude that additional experimentation is necessary to obtain fully dense samples and to characterize the microstructure of nanometer-sized silicon carbide powder affected by spark plasma sintering conditions.

Key words: Silicon carbide, Spark plasma sintering, Densification, Microstructure.

Introduction

Silicon carbide (SiC) holds much promise as an advanced engineering material. It is strong, lightweight, and can withstand elevated temperatures. However, it is difficult to synthesize by traditional methods such as pressureless sintering and hot pressing. Consolidation of ceramic powders by a field-assisted sintering technique (FAST)-specifically, spark plasma sintering (SPS)-is preferred over traditional sintering methods because of its lower temperatures and shorter dwell times [1]. SPS has been identified to cause rapid densification and to preserve grain size [1], but little is known theoretically how the technique accomplishes these results.

Full densification of SiC powders by both traditional methods and SPS are typically achieved with the help of additives. Oxides such as alumina and yttria can provide low-temperature liquid phases necessary for densification, but they result in weak phases at the grain boundaries. Elemental additives such as boron and carbon can also improve densification. Several authors have reported fully dense or near theoretically dense SiC with one or all of these additives [1-8]. SPS of SiC without additives has also been investigated, although most studies report final densities less than

the theoretical density (TD). A few, however, have been successful at reaching full density or near TD [9-12]. A method that produced SiC up to 98% TD was with precursor elements Si and C in powder form [13, 14]. Here, we compare the effects of time, temperature, and pressure on the resulting density, grain size, and crystal structure of nanometer-sized SiC.

Experimental Procedure

SiC nanopowder (NanoAmor, Inc. Houston, TX) with mean particle size of 45-55 nm was ball milled for 24 hours in a 100 ml high-density polyethylene (HDPE) bottle with 5 mm yttria-doped zirconia grinding medium (Union Process, Akron, OH). Five grams of SiC nanopowder was placed within a graphite die-and-punch assembly, shown in Figure 1. All surfaces in contact with the loose powder were lined with grafoil to prevent adherence to the graphite components and aid in sample removal. A felt sleeve was placed around the periphery of the die to minimize radiative heat loss.

The ram platens applied a 5 MPa preload to the punches. Then the SPS chamber (Thermal Technologies, Santa Rosa, CA) was continuously evacuated as argon gas was allowed to fill the chamber. Next, the full load was applied to the rams. After reaching and maintaining the load, pulsed electric current was passed through the graphite punches while an optical pyrometer measured the temperature of the sample through a hole in the side of the die and felt sleeve. The temperature provided

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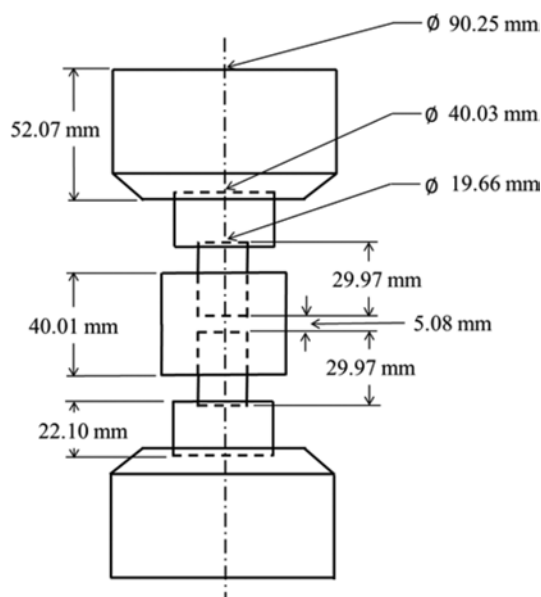


Fig 1. Diagram of the graphite die and punch assembly. The sample powder is placed in the center and surrounded on all sides by grafoil sheets.

feedback to control the pulsed current amplitude. The pulsing continued in order to maintain the maximum temperature for the prescribed hold, after which the current was discontinued and the load was released. Displacement, temperature, load, current, and voltage were measured and recorded by a computer data-acquisition system. The sample cooled to room temperature before the chamber was vented and the sample was removed. The sample was cleaned of any grafoil residue using a wire brush. Sample mass and physical dimension measurements were taken. X-ray spectra were obtained with Cu K-alpha radiation from a Siemens/Bruker D-5000. The SPS conditions for

each sample are listed in Table 1. The samples were divided into four groups, each having one independent variable. The temperature was varied for samples 1-3. The dwell time was varied for samples 4-8. The pressure was varied for samples 5, 9, and 10. The load removal and cooling routines were varied for samples 5, 10, 11, and 18.

Results and Discussion

Figure 1(a, b) shows the interior of samples 1 and 18 after cutting and polishing. The micrographs show an interconnected network, providing evidence of incomplete densification. The individual grains are difficult to observe. Sample 18 contains much larger pores than sample 1. The density, grain size, and crystal structure of each sample are listed in Table 1. The density of all samples was much lower than typical of SiC processed by SPS [1-12]. However, we did not use sintering additives, nor did we match all experimental variables presented in the literature. Since we measured the density by the geometric method, our measurement included all voids and open porosity within the sample. Some samples contained grains larger than the initial as-received size, and some were smaller. The measured average grain size sat at the upper edge of the size range of the as-received powder, but several measurements were below the as-received size. Figure 1(c) shows the X-ray spectrum of a sample after sintering. The spectra and the associated analysis indicate that the SiC was cubic. The as-received SiC powder was also cubic. This result is consistent with previous work [15], which found that transformation from the cubic to hexagonal crystal structure occurred at temperatures higher than 1800 °C.

Table 1. Effect of temperature, dwell time, pressure, and load removal on density, grain size, and crystal structure.

Sample	Temperature (°C)	Dwell Time (Minutes)	Pressure (MPa)	Loading	Density (% TD)	Grain Size (nm)	Crystal Structure
1	1800	0	50	Load removed at 1700 °C	64.3	57.6	Cubic
2	1700	0	50	Load removed at 1700 °C	56.1	31.1	Cubic
3	1600	0	50	Load removed at 1700 °C	68.5	27.1	Cubic
4	1700	0	50	Load removed at 1700 °C	63.6	65.8	Cubic
5	1700	1	50	Load removed at 1700 °C	57.2	52.2	Cubic
6	1700	2	50	Load removed at 1700 °C	55	35.1	Cubic
7	1700	3	50	Load removed at 1700 °C	52.8	32.1	Cubic
8	1700	4	50	Load removed at 1700 °C	66.2	63.9	Cubic
5	1700	1	50	Load removed at 1700 °C	57.2	52.2	Cubic
9	1700	1	60	Load removed at 1700 °C	64.8	40.5	Cubic
10	1700	1	70	Load removed at 1700 °C	66.1	58.7	Cubic
10	1700	1	70	Load removed at 1700 °C	66.1	58.7	Cubic
11	1700	1	70	Load removed at 1000 °C	69.3	63.0	Cubic
5	1700	1	50	Load removed at 1700 °C	57.2	52.2	Cubic
18	1700	1	50	Load removed at 1000 °C	70.9	133.4	Cubic

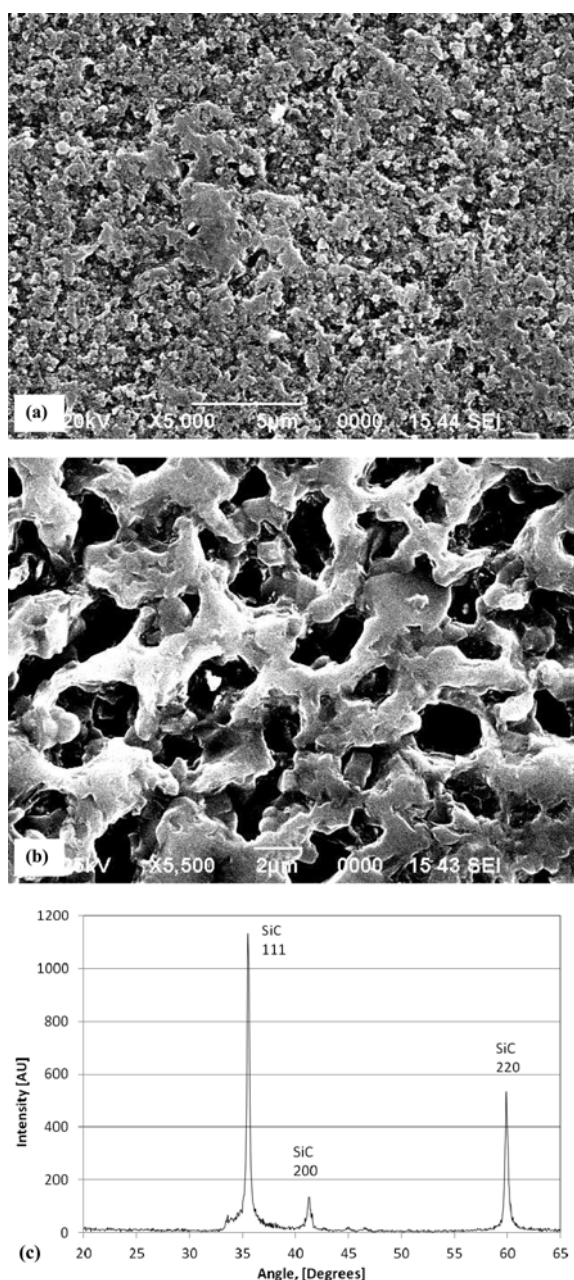


Fig. 2. (a) SEM micrograph of sample 1 sintered at 1800 °C, 0 minute dwell, and 50 MPa pressure. An interconnected network of SiC is evident, indicating incomplete densification. Pores are < 1 μm. (b) SEM micrograph of sample 18 sintered at 1700 °C, 1 minute dwell, and 50 MPa pressure. Pores are > 1 μm. (c) X-ray spectrum of SiC after sintering showing expected reflections.

Effect of sintering temperature

Between samples 1, 2, and 3, a maximum density was achieved at the sintering temperature of 1600 °C. There appeared to be no correlation between the temperature and the density, because the density values obtained at 1600 °C and 1800 °C were similar while the density value at 1700 °C was lower. The correlation between temperature and grain size matched what was expected. The smallest grain size occurred at 1600 °C, and the largest grain size occurred at 1800 °C. The

increasing grain size concurrent with increasing temperature was assumed to be caused by the longer sintering duration. The temperature had no effect on the crystal structure of the SiC. All samples remained in the cubic form during the sintering processes.

Effect of dwell time

The highest density among samples 4, 5, 6, 7, and 8 was achieved during the 4 minute dwell time. The lowest density among these same samples was achieved during the 3 minute dwell time. The correlation between the density and dwell time was as expected. As the dwell time increased the density decreased, except for sample 8, which increased in density. Sample 8 may have increased in density because the longer dwell time allowed for the oxide layer to be reduced, thus promoting diffusion.

The largest grain size measured among these samples was obtained during the zero-minute dwell time, and the smallest grain size was obtained during the 3 minute dwell time. In general, the grain size decreased as the dwell time increased. This trend was opposite of what was expected. The trend may have been caused by a decrease in surface oxidation during longer dwell times, thereby reducing the particle diameter. However, sample 8 did not follow the trend; it instead increased in grain size while also having the longest dwell time. Typically, a longer sintering duration results in grain growth, so sample 8 behaved as expected. The diameter of the grains in sample 4 after zero-minutes dwell time were larger than the as-received powder grains (45–55 nm), which was attributed to the additional oxide layer.

Among these samples, the density and grain size followed similar trends for increasing dwell times, but were opposite of what was expected. Both the density and the grain size decreased. Traditionally, smaller grain sizes correlate to a higher density, and vice versa. One reason for this may be that our samples had not reached near enough to full density for the traditional correlation to take effect. All samples remained in the cubic form during sintering. This result was the same for all dwell times.

Effect of pressure

The highest density among samples 5, 9, and 10 was obtained at the pressure of 70 MPa, and the lowest density among them was obtained at the pressure of 50 MPa. The trend between the pressure and density matched what was expected. We found as pressure increased, the density increased. The largest grain size among these samples occurred during the 70 MPa load, and the smallest grain size among them occurred during the 60 MPa load. There was no trend between pressure and grain size. We did not expect the grains to grow at high pressures, but the largest grains were from the sample subjected to the highest pressure. The

crystal structure of the SiC did not change during the sintering, but remained cubic at all pressures.

Among these samples, there was no correlation between density and grain size. However, between the sample at the lowest pressure and the sample at the highest pressure, both the density and grain size increased. We expected the grain size increase to result in a lower density, but we did not observe this. An explanation for this result could be the effect of the added pressure. The driving force provided by the pressure may have increased the density more than the larger grains decreased it. The only variance from this trend was for the 60 MPa load, for which the grain size shrunk and the density increased.

The SEM images did not indicate grain growth or increasing density. Neither the density nor grain size measurements differed by large amounts, which may have been why it was difficult to compare them visually. The changes in density and grain size may have been smaller than the measurement error, so effects of the different pressures may not have been noticeable. Alternatively, the pressure variations may not have been wide enough to affect the density or grain size.

Effect of load removal

Table 1 compares the density, grain size, and crystal structure of the samples that had the load removed at 1700 °C to those with the load removed at 1000 °C. As in the previous experiments, all other sintering parameters remained the same. The densities increased in both samples for which the load was removed after reaching 1000 °C. The density increase was smaller between samples 10 and 11 as compared to the density increase between samples 5 and 18. The grain size increased similarly within each pair; the grain size increase between samples 10 and 11 was much smaller than the increase between samples 5 and 18. We noted that the correlation between increasing density and increasing grain size was not typical. Traditionally, a grain size increase results in a density decrease. The load removal and cooling pattern did not have any influence on the crystal structure of the samples. All of the samples were in the cubic form before and after sintering.

Conclusions

This study investigated the effect of spark plasma sintering parameters on the microstructure of nanometer-sized silicon carbide. Our results show that full densification was not achieved for these samples. Furthermore, the grain size changed during processing. In summary, we observed: 1) higher sintering temperatures caused grain growth, 2) longer dwell times caused density and grain size to decrease, 3) higher pressure caused higher density, 4) the temperatures, dwell times, and pressures used in this

study did not cause a change in the silicon carbide crystal structure, 5) retaining pressure until samples had cooled to 1000 °C caused higher densities and grain-size growth, and 6) scanning electron micrograph micrographs were inadequate for determining grain size measurements, so the measurements were obtained by X-ray peak profiling and size analysis.

The microstructure did not appear to match traditional correlations for sintered ceramics. In particular, we observed simultaneous grain size and density increases. We believe this can be attributed to partial sintering of the silicon carbide, which led to less than fully dense samples having a microstructure that contained necked grains. The grains were allowed to grow during sintering, but the porosity decreased.

Future work should focus on producing fully dense samples without the use of additives, and recording the effects of spark plasma sintering conditions on those samples. It will also be beneficial to test additional spark plasma sintering conditions such as die size, heating rate, and atmosphere, which also may influence the microstructure. Finally, it will be important to discover fundamental aspects of spark plasma sintering that may reveal the mechanisms of densification and grain growth.

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