Investigation of the effect of pressure, sintering temperature and time on silicon carbide microstructure

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Received 7 March 2023; Received in revised form 9 June 2023; Accepted 18 June 2023

Abstract

In this research, SiC ceramics were densified via spark plasma sintering (SPS) with 0.5 wt.% B₄C and 1.5 wt.% C additions at temperatures ranging from 1900 to 2000 °C for 5–65 min under 10–50 MPa applied pressure with an intermediate dwell at 1400 °C, and the effects of applied pressure, sintering temperature, and dwelling time were examined. The samples sintered under 50 MPa applied pressure had high density (>99%), and showed high elastic modulus (~420 MPa). However, lower applied pressure caused a decrease in density and elastic properties. The increase of sintering temperature from 1900 to 2000 °C, while sintering time and pressure remained the same, caused grains coarsening. Increasing the dwelling time for the samples sintered at 1900 and 2000 °C showed that sintering at a relatively lower temperature for a longer period of time did not increase grain size significantly. On the other hand, increasing the dwelling time at 2000 °C caused excessive grain growth. The results show that fine-grained highly dense SiC can be produced by spark plasma sintering at 1900 °C for 5 min under 50 MPa.

Keywords: silicon carbide, spark plasma sintering, pressure, sintering temperature, sintering time

I. Introduction

Silicon carbide (SiC) is one of the most favourable high-temperature materials due to its remarkable properties, such as low density, high hardness, high elastic modulus and oxidation resistance [1–9], making it useful for many industrial applications [10–12]. However, SiC should have a high relative density in order to be used in applications requiring superior performance [13,14]. Pressureless sintering, hot pressing and spark plasma sintering are common methods to densify SiC ceramics. Nonetheless, obtaining a high density SiC body is challenging due to its strong covalent bond structure and low self-diffusion coefficient [15–21]. Studies have shown that sintering aids, high temperature and pressure play an important role in obtaining SiC ceramics with high density [22–25]. While sintering aids such as Al₂O₃, AlN, Y₂O₃ and other rare earth oxides cause liquid phase formation [16,17,26], sintering aids such as C, B₄C and BN provide condensation with solid-state sintering [23,27–29]. The addition of C also solves the native oxide layer (SiO₂) problem with SiC [21,29–32]. Using boron and carbon together as sintering aids is a highly preferred method for obtaining fully densified SiC [28,31–35].

In SiC studies that we have conducted for many years, different boron carbide ratios, different carbon sources and ratios, as well as different powder mixing techniques have been tested [5,6,36,37]. It was seen that using less than 0.5 wt.% of B₄C causes grain growth and elongation [37], and adding less than 1.5 wt.% C does not contribute enough to improve the properties of SiC since it is insufficient in removing the native oxide layer of SiC. On the other hand, the addition of more than 1.5 wt.% C adversely affects the properties of SiC, since it has too much residual C [6,36]. As a result of the studies, it was observed that the addition of 0.5 wt.% B₄C and 1.5 wt.% C to SiC improves the density, mechanical and elastic properties of SiC. In addition to these studies, it is essential to examine the effect of sintering conditions on the properties of SiC.

This paper presents the results of an evaluation of the effects of applied pressure, sintering temperature and
dwell time on the microstructure of SiC with 0.5 wt.% B₄C and 1.5 wt.% C additives sintered via spark plasma sintering (SPS) in order to produce fine-grained highly dense SiC.

II. Experimental

98 wt.% SiC (1.5 µm, Saint Gobain, Niagara Falls, New York), 0.5 wt.% B₄C (0.6 µm, HD-20, H.C. Starck GmbH & Co, Germany) and 1.5 wt.% C (100 nm, amorphous, Lamp black, Fisher Scientific) were mixed by ball milling in ethanol with SiC media in a polyethylene container for 24 h. After that, the slurry was dried using a hot plate.

6.5 g of the dried powder mixture was placed into a 20 mm diameter graphite die with graphite punches and densified via spark plasma sintering method (Thermal Technology SPS 10-4). The samples were sintered under argon at temperatures ranging from 1900 to 2000 °C with a heating rate of 200 °C/min for 5–65 min under 10–50 MPa applied pressure under vacuum. An intermediate dwell for 5 min at 1400 °C was added to the sintering schedule to allow the C to react with native SiO₂ on the SiC surface, thereby removing it from the surface. The reaction between SiO₂ and C is described by the following equation [24,32]:

\[
\text{SiO}_2 + 3 \text{C} \rightarrow \text{SiC} + 2 \text{CO(g)}
\] (1)

The sintering conditions for each sample are shown in Table 1.

The densities of the specimens were determined using the Archimedes’ method. Ultrasound analysis was used to measure the samples’ elastic properties. Then, samples were sectioned into small pieces using a diamond coated saw and polished to a 0.25 µm finish using Buehler-Ecomet 250-Grinder-Polisher. The samples were etched in a mixture of 20 g KOH, 20 g K₃Fe(CN)₆, and 60 ml DI water (modified Murakami method) to highlight the SiC grains. The microstructures of the samples were analysed using a Zeiss Sigma field emission scanning electron microscope (FESEM) and energy dispersive spectroscopy (SEM-EDS) was performed with Oxford EDS. The grain sizes were measured using an image analysis software (Lince 2.4.2e) by the linear intercepts method.

III. Results and discussion

3.1. Effects of applied pressure

Figure 1 shows the FESEM images of the samples sintered by applying different pressures at the same temperature (1900 °C) and time duration (15 min). In all samples, the SiC grains show similar size and shape. The SiC grains are relatively small and have equiaxed grain shapes. Furthermore, the samples have small amounts of unreacted B₄C and C. The most sig-

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significant difference in these samples is the amount of porosity. With the increase of applied pressure, the number of pores decreased. The samples sintered at 10 MPa show significant porosity. The samples sintered at 20 and 30 MPa have moderate porosity and the samples sintered at 40 and 50 MPa have few pores. The amount of porosity affects the density values of the samples.

The density and average grain size changes as the function of applied pressure are given in Fig. 2. With the increase in applied pressure from 10 to 50 MPa, the density values increased from 2.94 to 3.18 g/cm³ (Fig. 2). Barick et al. [38] observed a similar trend when increasing the pressure from 25 to 75 MPa. Feng et al. [39] sintered SiC without pressure at 2000 °C with purified SiC powder. They obtained ceramics with visible porosity, relative density of 98% and the average grain size of 6.5 µm. These results showed that applying pressure and finding an optimal pressure is vital to obtaining high density ceramics with fine unimodal grain size distribution [39].

The Young’s modulus (E), shear modulus (G), and bulk modulus (K) values of the samples can be seen in Fig. 3. While the sample sintered under 10 MPa has an elastic modulus of 347 GPa, the sample sintered under 50 MPa pressure has an elastic modulus of 418 GPa. Since the elastic modulus has a close relationship with density, reducing the porosity results in an increased elastic modulus value [40,41].

3.2. Effects of sintering temperature

In Fig. 4, FESEM images of the samples sintered for 5 min at 50 MPa and different temperatures are shown. The samples sintered at 1900, 1925 and 1950 °C show very similar microstructures to each other. These samples have relatively small and equiaxed SiC grains. Furthermore, evenly dispersed non-reacted B₄C and C secondary phase particles can be seen in the images. This can also be seen in the EDS analysis results of the sample sintered at 1900 °C for 5 min in Fig. 5. When looking at the samples sintered at 1975 and 2000 °C, differentiation in microstructures was observed.
Figure 4. FESEM images at 5000× magnification of samples spark plasma sintered under the pressure of 50 MPa at:
   a) 1900 °C, b) 1925 °C, c) 1950 °C, d) 1975 °C and e) 2000 °C for 5 min

Figure 5. EDS images of SiC sample sintered at 1900 °C for 5 min: a) SE2 image of polished surface of SiC sample, b) EDS mapping of Si element, c) EDS mapping of C element and d) EDS mapping of B element

Figure 6. Average grain sizes as a function of sintering temperature; corresponding densities are indicated with red numbers

The density and average grain size of the samples sintered at different temperatures are given in Fig. 6. Grain growth was observed with an increase in temperature, with the average grain size increasing from 2.10 to 5.23 µm when the temperature increased from 1900 to 2000 °C, respectively. Maitre et al. [42] sintered SiC with addition of B₄C and C at 1950 °C for 5 min via SPS, but the relative density only reached 97.1%, demonstrating that finding optimum sintering conditions for SiC is essential to obtaining high densities.

The Young’s modulus (E), shear modulus (G), and bulk modulus (K) values of the samples can be seen in

Figure 7. Elastic properties of samples sintered at different temperatures
### 3.3. Effects of dwelling time

Figure 8 shows FESEM images of the samples sintered at 1900 °C for 5–65 min and Fig. 9 shows the density and average grain size of the samples. All of the samples spark plasma sintered at 1900 °C show microstructures with essentially equiaxed grains. With increased sintering time, there was a slight increase in the grain size. However, extreme grain growth did not occur. With the increase in dwell time from 5 to 65 min, the grain size of the samples increased from 2.10 to 3.71 μm.

Figure 10 shows FESEM images of the samples sintered at 2000 °C for 5–45 min and Fig. 9 shows the corresponding density and average grain size. All of the samples that were sintered at 2000 °C for 5, 15, and 25 min possess microstructures with mainly equiaxed grains of similar size. There is some elongation of grains observed in each sample, but it is not extreme. The grain size only increased from 5.23 to 5.48 μm when dwell time was increased up to 25 min. In contrast, the samples sintered for 35 min (7.63 μm) and 45 min (9.64 μm) display very large grains with very high aspect ratios. There is also a difference in the distribution of secondary phase particles in these samples. In the 5, 15, and 25 min samples the inclusions tend to be located primarily at the grain boundaries while they also appear within the large grains of the 35 and 45 min samples.

When comparing the samples sintered at 1900 and 2000 °C, a longer time at the lower temperature did not affect the grain size in a significant way. Contrarily, higher temperatures resulted in coarser grains. Since the samples sintered at 2000 °C have already reached high density, waiting for a long time at high temperature caused excessive growth in the grains.
The Young’s modulus ($E$), shear modulus ($G$), and bulk modulus ($K$) values of samples can be seen in Fig. 11. The samples sintered at 1900 and 2000 °C at all dwelling times reached high density. Therefore, the elastic properties of the samples are extremely close to each other. As it was mentioned, porosity reduces the elastic properties, but the effect of grain size on the elastic properties could not be determined. Even though the average grain sizes of the samples increased with increasing dwelling time, their elastic properties did not change in value.

IV. Conclusions

SiC samples with an addition of 0.5 wt.% $\text{B}_4\text{C}$, and 1.5 wt.% C were spark plasma sintered at temperatures ranging from 1900 to 2000 °C, for 5–65 min under 10–50 MPa applied pressure with an intermediate dwell at 1400 °C. All samples sintered at 50 MPa showed high density (>99%), and the elastic properties of these samples were very similar to each other. However, a significant decrease was observed in the densities and elastic properties of the samples sintered at lower pressures.

Samples sintered at 1900 °C for 15 min for 10–50 MPa applied pressure showed that increasing the applied pressure from 10 to 50 MPa decreased the amount of porosity in the samples, and slightly reduced the grain sizes.

Examining the effect of sintering temperature, the results showed that samples sintered at 1900–1950 °C have similar microstructures, with small and equiaxed SiC grains, while samples sintered at 1975–2000 °C showed microstructures with coarser grains.

When comparing samples sintered at 1900 and 2000 °C for 5–65 min, even if the samples were sintered for a long time at 1900 °C, there was not a significant difference in grain size. However, excessive grain growth was observed in the samples when the sintering time was extended at 2000 °C.

Based on these findings, it was observed that variations in applied pressure during spark plasma sintering resulted in changes in porosity, increased sintering temperatures lead to both increased average grain size as well as increased grain aspect ratio, and increased sintering time at lower temperatures resulted in isotropic
grain growth while longer dwell times at higher temperatures lead to anisotropic grain growth.

Acknowledgments: The research was sponsored by the National Science Foundation I/UCRC Award No. 1540027. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the National Science Foundation or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein. Additional funding was provided by the Materials for Extreme Dynamic Environments program sponsored by the US Army Research Laboratory Cooperative Agreement (W911NF-12-2-0022).

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