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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 2725–2728
www.elsevier.com/locate/jeurceramsoc

Densification of SiC by SPS-effects of time, temperature and pressure

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Received 27 April 2006; received in revised form 4 October 2006; accepted 16 October 2006
Available online 21 November 2006

Abstract

Temperature, holding time and conditions of pressure application, three of the most important spark plasma sintering (SPS) parameters, have been reviewed to assess their effect on the densification and grain growth kinetics of a pure commercially available submicrometer-sized silicon carbide powder. Experiments were performed in the 1750–1850 °C temperature range with holding time from 1 to 10 min. Two pressure setups were used: one with pressure (75 MPa) applied at 1000 °C and the other with ultimate pressure applied at sintering temperature. Experimental data highlighted the fact that temperature and holding time have a different impact on grain growth and densification. Diffusion and migration mechanisms that promote grain growth were found to be strongly dependent on temperature, the latter being linked to pulsed current intensity. Conditions of pressure application suggest that the ultimate pressure applied at higher temperature increases densification by keeping small surface contact between particles.

Keywords: Spark plasma sintering; SiC; Grain size

1. Introduction

In the field of thermomechanical materials used in aeronautic and nuclear applications, silicon carbide (SiC) is one of the best solutions because of its low density, high hardness and high decomposition temperature. The main difficulty lies in sintering. A number of aids are used to promote SiC densification, but certain glassy phases at grain boundaries may be detrimental to the desired performance. Indeed, mechanical properties are lowered.[1–4] To reach full density with pure SiC, it was decided to use a relatively new process that is, field activated sintering, also known as spark plasma sintering (SPS). The SPS process allows various types of powders to be sintered.[5–9] It relies on pulsed DC current passing through an electrically conducting pressure die containing the sample. Uniaxial pressure is applied during sintering. The main benefit is that full density can be reached fairly easily, the whole experience taking only a few minutes. Silicon carbides has already been processed by SPS, with sintering additives such as Al_4C_3 and B_4C[10] or with mechanical alloyed SiC powder.[11,12] The aim of this study is to assess the evolution of SiC grain size and density versus temperature, holding time and pressure on a commercial powder.

2. Experimental

The SiC HC Starck grade B 17, with a mean grain size of 0.5 μm and a low oxygen concentration (∼1.2%, manufacturer data), was used in this project. Two SPS machines were used, i.e. Sumitumo-2050 (Arrhenius Laboratory, Stockholm, Sweden) and Sumitumo-2080 ("Plateforme Nationale de Frittage Flash", CNRS, Toulouse). The first series of samples were prepared on the former machine and the final one on the latter. The SiC powder was loaded into graphite dies with an inside diameter of 8 and 12 mm. Temperature was automatically raised to 600 °C, then monitored and regulated by an optical pyrometer aiming at the die surface. A heating rate of 100 °C/min between 600 and 1600 °C, and then 50 °C/min up to the final temperature was systematically used. Each sample was weighed to get pellets of ∼5 mm in thickness at maximum densification. Pressure setup, initially set at 50 MPa at room temperature follows two protocols: (1) 75 MPa pressure applied when maximum temperature is reached (Sw); (2) 75 MPa applied since 1000 °C (To). In each case, pressure was released at the end of the holding time and the cooling rate down to 1000 °C was

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doi:10.1016/j.jeurceramsoc.2006.10.005

Table 1
Temperature (°C) and holding time (min) sintering parameters for 75 MPa pressure applied at 1000 °C and sintering temperature for To and Sw, respectively, together with experimental density (g/cm^3), relative density (%) and grain size (μm)

Process	Samples	T (°C)	Holding time (min)	Experimental density (g/cm^3)	Relative density (%) ($d_{SiC\ theor.}$ = 3.217 g)	Grain size (μm)
Sw	1	1750	5	2.48	77	0.5
	2	**1780**	**1**	**2.51**	**78**	**0.5**
	3	1780	5	2.44	76	0.7
	4	**1780**	**10**	**2.82**	**88**	**0.8**
	5	1850	1	2.34	73	1.5
	6	**1850**	**5**	2.95	**92**	**2.0**
To	7	1750	1	2.23	69	0.5
	8	1750	5	2.21	69	0.6
	9	1750	10	2.29	71	0.7
	10	**1780**	**1**	**2.33**	**72**	**0.5**
	11	1780	5	2.24	70	0.7
	12	**1780**	**10**	**2.36**	**73**	**1.0**
	13	1850	1	2.45	76	1.5
	14	**1850**	**5**	**2.41**	**75**	**2.5**
	15	1850	10	2.58	80	3.0

Examples discussed are in bold.

around 400 °C/min. The graphite layer due to die protection was removed. Density of the final specimens was determined according to Archimedes' principle and compared to SiC theoretical density.[13] Samples were systematically controlled using X-ray powder diffraction. Microstructure was investigated via scanning electron microscopy (using a JEOL JSM-6700 F).

3. Results

3.1. Relative density

All samples were analyzed (Table 1), but for the sake of clarity, discussion is mainly focussed on samples Sw2, 4 and 6 and To10, 12, and 14. Density of these various pellets shows important differences versus the applied process. In general Sw samples exhibit a relative density approximately 10% more than To samples. From 1750 to 1850 °C, density rises from 77% up to 92% for Sw samples and from 69% to 80% for To samples. A significant difference (10%) is found in Sw2 (1780 °C/1 min/78%) and To10 samples (1780 °C/10 min/72%) or Sw6 (1850 °C/5 min/92%) and To14 (1850 °C/5 min/75%) (Fig. 1).

3.2. Microstructure

Samples treated with the same sintering parameters exhibit a similar grain morphology. The micrograph of To10 sintered at 1780 °C shows that matter necks are clearly formed (Fig. 2d). Most grains are approximately 0.5 μm in size with, apparently, a softened surface. Porosity appears to be of the open and closes type. Longer holding time (10 min) at the same temperature (1780 °C) produced To12 in which matter necks grew, leading to an enlarged grain size up to 1.0 μm (Fig. 2e). Porosity can still be found inside the specimen, but much closed type. Using the same sintering parameters (1780 °C), the Sw process leads to specimen Sw4 in which both microstructure and porosity have drastically changed. Open porosity seems to have disappeared and is replaced by closed porosity. No matter necks can be found, grains being stuck together. In spite of these modifications, the mean grain size remains around 1.0 μm as in the To process sample (To12).

At 1850 °C, mean grain size increases up to 2.0 μm (Fig. 2f) for a To process sample (To14). Except for size, grain morphology is similar to that observed at lower temperatures with their slightly bigger matter necks and softened surfaces. Porosity still exhibits bigger trapped pores. In order to confirm change of grain size, a similar experiment has been made with same sintering parameters as Sw6 (1850 °C/5 min), but with an 8 mm diameter dies. Grain size for that sample was around 2.4 μm, for a relative density of 85%.

4. Discussion

4.1. Effect of pressure conditions

Comparing the results between both pressure application procedures (P-Sw and P-To) reveals major differences in terms of

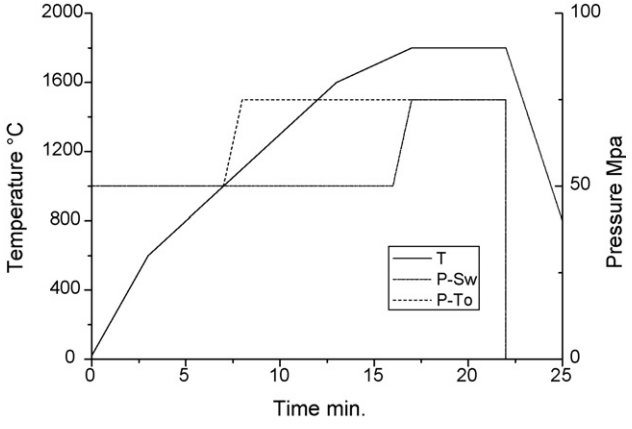

Fig. 1. Temperature rates and temperatures of pressure application: protocole To (P-To) pressure applied at 1000 °C, and Sw (P-Sw) pressure applied at 1800 °C.

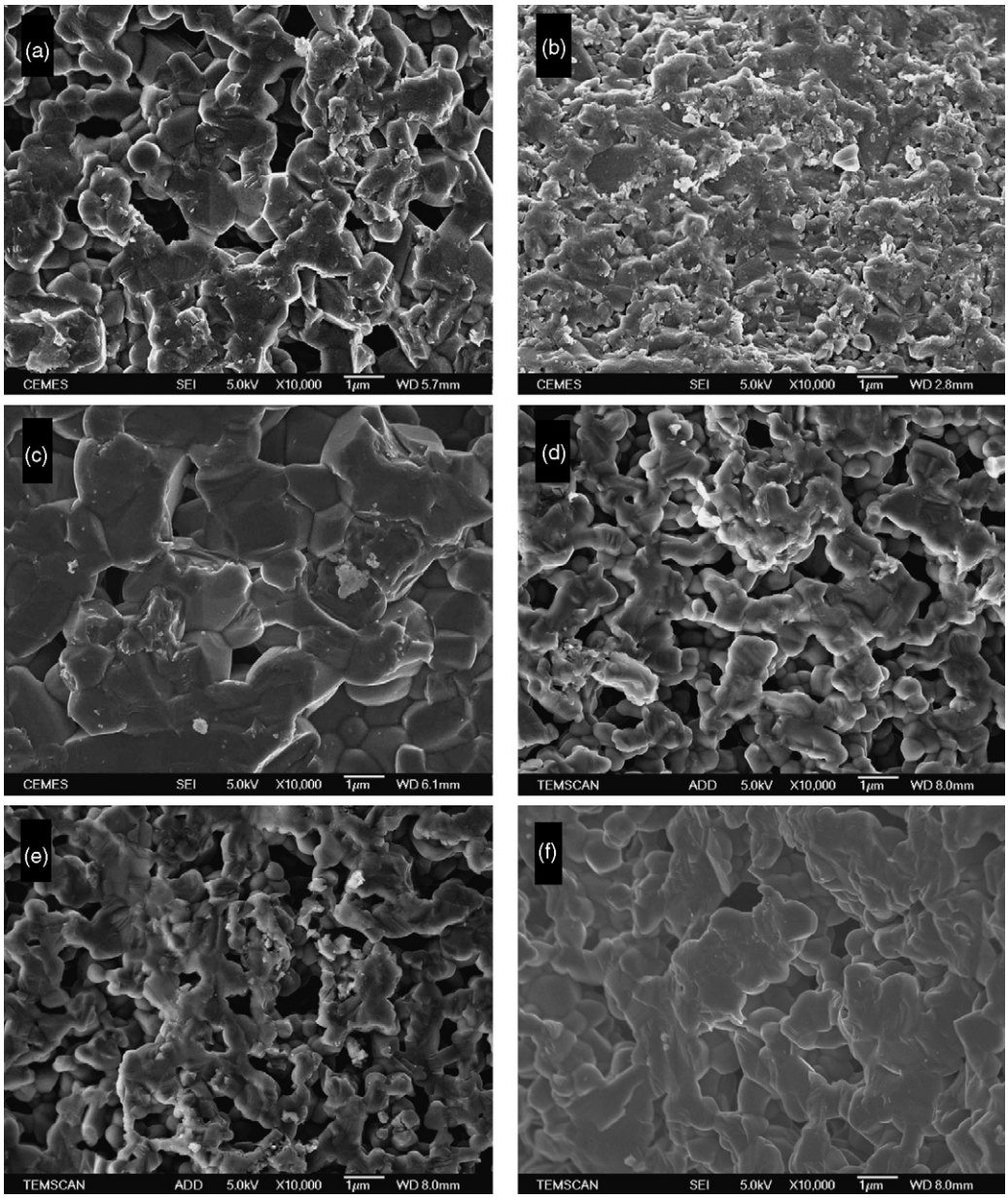

Fig. 2. SEM fracture micrographs of the SiC pellets Sw-2, 4 and 6 in (a–c) and To-10, 12, and 14 in (d–f).

density and grain cohesion inside pellets. It is suggested that after pressure applying at 1000 °C (To-process), the difference in density could be due to the impossible removal of close porosity with increasing temperature. For samples sintered with the Sw-process, this porosity is removed when the grain's surface is sufficiently softened, which can be explained by two different points of view. First, SiC grains have on their surface a thin oxide layer,[14] that could explain the soften aspect on grain surface. Second, this could also be linked to the heating procedure, where high intensity electric pulses of more than 1000 A under 4–5 V, pass through specimens, thereby inducing an electric discharge between the grains small contact surface. The smaller the contact areas, greater the effect becomes. In the To-process, grains are already in contact and attached, creating a broader surface. Thus, the previous phenomenon as well as the final density are reduced. It is reasonable to assume that another phenomenon occurs after some time. Given the Joule effect, die and graphite parts heat samples by radiation effects.

Finally, the morphology and size grains are equivalent in To-samples and Sw-samples although microstructure and density are different.

4.2. *Effect of holding time and temperature*

At given temperatures, density and grain size increase with holding time in both processes, but this is not achieved in the same manner. At 1780 °C, grain size increases by approximately 40% when holding time is prolonged from 1 to 10 min whereas for a 5 min holding time and temperature evolving from 1750 to 1850 °C, size increases by approximately 200%. It appears

that temperature plays a greater role in grain size than holding time. In the SPS technique, temperature is linked to DC current pulse intensity and die size. Thus, it is reasonable to assume that diffusion mechanisms are enhanced by current intensity.

Density appears to be promoted by a combination of holding time and temperature because it increases with both experimental parameters. These results are almost equivalent to conventional sintering processes. One main difference lies in duration, which is drastically reduced.

5. Conclusions

Densifications of selected SiC powder based on several protocols focused on temperature, pressure holding time and temperature–pressure application have been obtained using the spark plasma sintering technique. Mean grain size of the powder was 0.5 μm. The SiC was densified up to 92% at 1850 °C with a 5 min holding time and under 75 MPa. This study allowed us to determine that the temperature of the ultimate pressure (T_{up}) is a major parameter in powder densifications; this temperature T_{up} must be close to maximum temperature, here 1800 °C for 1850 °C at the end of the process. In this case, grain morphology and size remain unchanged. Density increases with holding time and temperature.

These results will be used to fine-tune the SPS technique parameters for the densification of SiC nanopowders, SiC composites bases and to investigate sintering mechanisms during SPS process.

Acknowledgements

This work was funded by the joint research program "ISMIR" between CEA and CNRS. The authors acknowledge Dr. M. Johnsson from University of Stockholm, G. Vaux and G. Loupias from CEA-Saclay. We are grateful to Pr. M. Nygren (University of Stockolm) for his invaluable help during experiments and for his fruitful advices.

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