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Ultra-fast densification of boron carbide by flash spark plasma sintering

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ABSTRACT

A novel method, Flash Spark Plasma Sintering (FSPS), combining flash sintering and electric field assisted sintering was used to densify B_4C ceramics. B_4C powder was densified up to 99.2% in 1 min with limited grain size increase at 1931 °C under an applied pressure of 15.3 MPa. TEM analysis of the grain structure of the resulting ceramics suggests that the Joule heating and sparking initiated by the pulsed current are highly localized to particle interfaces and contribute significantly to the character of densification. We show that plastic deformation under high current and low pressure is the dominant densification mechanism.

Sintering form ceramics from powders as inter-particle pores in the granular material are closed due to atomic diffusion driven by capillary forces [1,2]. Traditionally, sintering of ceramics is performed at high temperatures, with long sintering times, and with either no applied pressure or an isostatic or uniaxial pressure. Such methods however both cause abnormal grain growth and are costly in time and energy [3]. During the past few decades, electric field assisted sintering (EFAS) methods, such as spark plasma sintering (SPS), have been considered as alternative high-efficiency techniques for densification of ceramics, which was elaborated by Risbud et al. [4]. In EFAS, heating is achieved in conductive samples by applying a pulsed DC current to the samples rather than using an external heat source. This internal heating can shorten the sintering time and the energy inputs [5,6]. In particular, lower temperatures and shorter processing times give the possibility to sinter powders to near theoretical density with little grain growth [7].

Recently, a new technique called flash sintering has demonstrated the feasibility of sintering ceramics at low temperatures in a few seconds [8]. Despite significant energy and time savings, however, the conventional furnace preheating needed to initiate the process limited efficiency gains. Grasso and co-workers solved this problem with a new method called Flash Spark Plasma Sintering (FSPS), by which fully dense ZrB_2 was prepared [9]. The ZrB_2 powder was first poured into a graphite die and then partially sintered to 63.6% of the theoretical maximum density, at which point the sample was strong enough to be directly pressed between two graphite punches of an SPS furnace to perform the FSPS experiments. In this final FSPS step no graphite die was employed, so the current passed entirely through the sample. Densification was achieved in less than 35 s. Although FSPS avoids a long conventional preheating treatment, the partial sintering was still of sub-optimal efficiency. Furthermore, the application of FSPS to semiconductor ceramics is limited by their poor conductivity at low temperature. In addition, the ultra-fast heating rate, which presumably drove the exceptional densification, was not measured in those reports.

To close these gaps in understanding and efficiency, we investigate the flash sintering process in more depth. For this purpose, a thin graphite die was designed as shown in Fig. 1a. The powders were poured into the die and sintered by SPS with a constant uniaxial force of 2.7 kN (contact pressure 15.3 MPa). The die was designed with a small cross-sectional area to produce a high current density and hence a rapid heating rate. We hypothesized that the flash sintering of materials from powders to dense bulks would thereby be realized in a short time.

We focused on boron carbide (B_4C) as a model ceramic. B_4C has attracted considerable attention due to its excellent physicochemical properties, such as hardness (it is the 3rd hardest ceramic), low density (2.52 g/cm^3), high melting point (2450 °C), high elasticity modulus, good wear and corrosion resistance, and high neutron absorption ability [10,11]. In addition, B_4C is a high-temperature semiconductor that could potentially be used for electronic applications [12]. Due to strong covalent bonding and high resistance to grain boundary sliding, however, very high temperatures and/or external pressures are typically required to densify B_4C ceramics [13]. Du and co-workers showed that more than 60 min are needed for hot pressing at 1950 °C to approach full-density B_4C under a pressure of 30 MPa [14]. Mashhadi and co-workers found that without an applied pressure, dense B_4C required sintering temperatures as high as 2250–2350 °C [15]. Wei Ji and co-workers sintered dense B_4C in 1750 °C under pressure of 80 MPa in 5 min with a heating rate of 100 °C/min by SPS [16]. In this work, we present a novel method combining flash sintering and electric field assisted sintering

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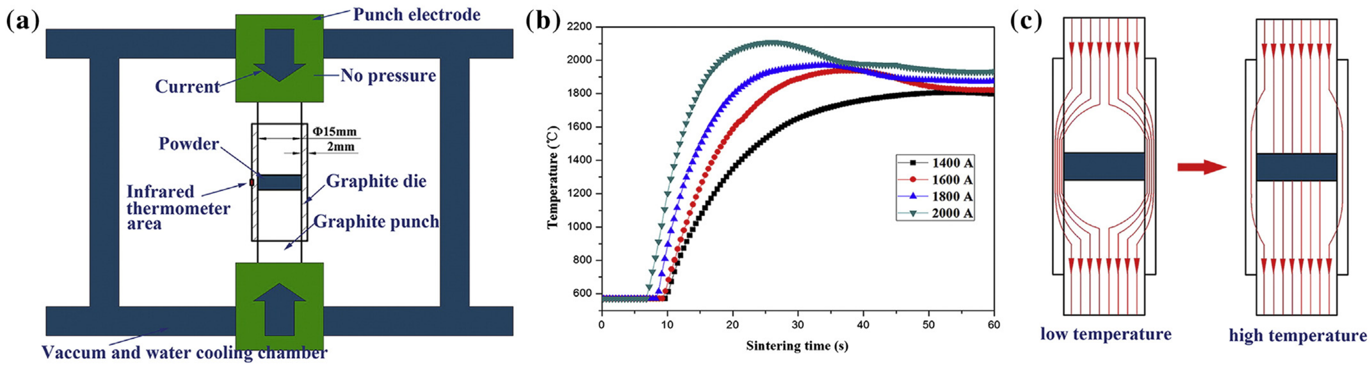

Fig. 1. Schematic representation of the FSPS process. (a) Schematic illustration of the graphite die used for the FSPS. (b) Temperature curves versus time during the FSPS processes with different applied currents. (c) Schematic illustration of the current distributions at low and high temperatures during FSPS processes.

to densify B_4C ceramics at low temperature (1931 °C) and low pressure (15.3 MPa) in 1 min. To evaluate the effect of the ultra-high heating rate in the FSPS process, B_4C was also sintered using self-propagating high temperature synthesis plus quick pressing (SHS/QP), a fabrication technique similar to flash sintering that also produces a high heating rate.

Commercial B_4C powder (Mudanjiang Diamond Boron Carbide Co., Ltd., China) with average particle size of 2.36 μm was used as the starting material. The SPS machine (PAS, Plasma Assisted Sintering, Ed-Pas-III) was used in this study. This unit can record the shrinkage, temperature and current in real time. The pulsed DC current (1400 A–2000 A) with a DC pulse sequence of 12:2 was applied in 5 s when the sintering began. The sintering time was controlled in 1 min, then the specimens were naturally cooled down to room temperature. To reduce the heat loss radiating from the thin graphite die, a graphite felt was wrapped around it during sintering. The temperature of the FSPS process was monitored with an infrared thermometer focused on the surface of the graphite die, as shown in Fig. 1a. Due to the thin wall, that measurement is approximately the specimen temperature [17].

The SHS/QP process was carried out in a homemade instrument as depicted in Fig. 3a. B_4C powder was uniaxially pressed in a steel die into disk at 20 MPa. The Ti (particle size <45 mm, 99% purity) and C (particle size <2 mm, 99% purity) powders (300 g) were mixed in a 1:1 M ratio. After drying, the mixture was pressed into a cylinder with a B_4C body first placed in the center. The B_4C body was covered by a thin sheet of graphite foil to separate it from the reactants. The following highly exothermic SHS reaction was then driven:

$$Ti + C \rightarrow TiC. \tag{1}$$

During the reaction, the temperature of the B_4C was measured by an embedded thermocouple. When the temperature reached maximum, a mechanical pressure of 20 MPa was applied. The pressure was maintained for 2 min and then released. The sample was then allowed to cool before removing it from the apparatus.

Densities of the samples were measured using the Archimedes method with deionized water as the immersion medium. The specimen surfaces were electrochemically etched in 1 wt.% NaOH solution after polishing with a diamond suspension down to 0.25 μm. The fracture surface and etched microstructures of the specimens were observed using scanning electron microscopy (SEM, Hitachi 3400). The grain size for each sample was measured with the linear intercept method using at least 300 grain data points. Detailed microstructure was observed using transmission electron microscopy (TEM, JEOL JEM-2010HT).

The FSPS curves of the specimens with different applied currents are shown in Fig. 1b. The temperature shows a sudden increase to the maximum value followed by a sudden decline and finally a plateau until sintering finishes. We explain this observation by considering the evolution of material resistivity with temperature and vice versa temperature with resistivity (due to Joule heating). As a high-temperature semiconductor, the resistivity of B_4C decreases sharply with the increase in temperature. The spatial current distributions during the FSPS process at low and high temperatures are depicted in Fig. 1c. While the current will initially avoid the insulated specimen in favor of the graphite die, as temperature increases and the semiconductor conductivity rises it will across both the specimen and the graphite die. The sudden increase in conductivity when the specimen is heated by the graphite die is a signature of flash sintering [18]. When the current begins passing through both the specimen and the graphite die, the total power declines ($W = I^2R$, W power, I current, R resistance) and the temperatures thereby fall. Eventually a steady state is reached where the temperature and electrical resistivity are constant. The final steady-state sintering temperatures are 1781 °C, 1822 °C, 1875 °C and 1931 °C as shown in Fig. 1b.

The dependence of applied current on displacement and time are plotted in Fig. 2a. These curves represent the real-time shrinkage profiles during densification of the powder compacts. Shrinkage is initially negligible, beginning to slowly increase once FSPS begins. Total shrinkage increases as the applied currents are increased. SEM images (Fig. 2c–f) show the microstructure of B_4C sintered under 1400, 1600, 1800 and 2000 A applied currents. In agreement with the displacement curves, porosity decreases with increasing current. While open pores persist in the sample with applied currents of 1400 and 1600 A, only closed pores can be observed at 1800 A and fully dense bulks are produced at 2000 A. The relative densities of B_4C sintered with 1400, 1600, 1800 and 2000 A are 83.8%, 92.7%, 96.9% and 99.2% (Fig. 2b). Nearly fully dense B_4C is fabricated in 1 min at 1931 °C and a pressure of 15.3 MPa.

The temperature curve of the SHS/QP process is shown in Fig. 3b. Compared with FSPS, the SHS/QP process has a nearly identical heating rate, higher sintering temperature and pressure, and longer sintering time. The resulting B_4C sample, however, only had a relative density of 94.3%, as shown in Fig. 3c. The FSPS process' sintering conditions (heating rate, sintering temperature, pressure and sintering time) alone therefore are not enough to produce the observed densification; properties of the applied pulsed current must therefore play an important role. As proposed by J. Narayan, densification and the onset of flash sintering are thought to be driven by local Joule heating at the grain boundaries [19]. The enhancement of conductivity at high temperatures creates a positive feedback loop of increasing current and thereby accelerating heating. If uncontrolled by limiting the current flow, this effect inspires selective melting at grain boundaries. That in turn leads to faster atomic diffusion at particle–particle interfaces than the bulk and therefore faster densification at a given material-averaged temperature. In addition, the pulsed current can cause sparking during FSPS. These sparks can bridge grains, locally promoting mass transport as has been previously demonstrated [20]. These high-current-density sparks also further promote the Joule heating.