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Microstructural differences and formation mechanisms of spark plasma sintered ceramics with or without boron nitride wrapping

Yun Tang, Jia-Xiang Xue,* Guo-Jun Zhang,* Xin-Gang Wang and Chang-Ming Xu

State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Shanghai 200050, China

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Two different modes of placing powders in a graphite die were used in a spark plasma sintering system: loading a conductive green body (zirconium nitride, ZrN, or titanium nitride, TiN) into a non-conductive bed (boron nitride) or loading the ZrN or TiN powders into the die directly. The ceramics obtained, which had completely different morphologies, have been characterized in this work. Through experimental and theoretical analysis, possible formation mechanisms of microstructural differences have been proposed.

Keywords: Spark plasma sintering; BN-wrapped; Microstructure; Grain boundaries; Grain growth

Spark plasma sintering (SPS) is a novel sintering process which is characterized by a rapid heating rate using a pulsed electric current with the simultaneous application of external pressure. It is also a promising technique for powder consolidation, and has been applied in the preparation of ceramics and composites [1–3], metals [4,5] and functional materials [6,7]. Numerous experimental and theoretical investigations into the sintering mechanism of SPS have been reported.

The inventor of this process, Tokita [8], maintained that, for conductive materials, an electric field can excite a spark discharge and even plasma between conducting particles. This spark discharge and/or plasma can remove any adsorbed species from the surfaces of particles, leading to the enhancement of densification. It is now generally accepted that an electric discharge occurs between powder particles on the microscopic level.

However, the sintering mechanism for non-conductive materials is still under debate. For example, both Wang et al. [9] and Tomino et al. [10] have suggested that pulsed electric current sintering on non-conductive samples (such as Al_2O_3) is similar to the hot-pressing process. The pulsed current mainly flows through the die and heats the graphite mold by Joule heating. The heat is then transferred to the powder compact inside. However, a number of different views have also been proposed. Shen et al. [11] indicated that the densification of Al_2O_3 was greatly enhanced by exposure to a pulsed direct current. The discharge caused by the electric field set up by a pulsed direct current can still take place. Zhang and Fu [12] introduced the application of software ANSYS with the finite element method to an electromagnetic field in an empty vacuum chamber during SPS treatment, and confirmed the existence of a pulsed magnetic field and an electric field during the SPS process of a non-conductive material.

Even though it remains unclear whether a spark discharge is generated between non-conducting particles or what the sintering mechanism is for non-conductive materials in the SPS system, the ways that the pulsed current influences the SPS mechanism for the two kinds of material (i.e. conductive or non-conductive) are definitely different. For conductive materials, conventional SPSed ceramics can be obtained when loading the powders into the die directly. However, if the conductive green body is wrapped with non-conductive powders, no pulsed current or only a very weak one will pass through the body. What kind of ceramic microstructure will then be obtained, and how will a pulsed electric current influence the microstructure of the conductive ceramic inside?

In our present work, the two different modes of placing powders in the graphite die were used: loading

* Corresponding authors; e-mail addresses: jx.xue@mail.sic.ac.cn; gjzhang@mail.sic.ac.cn

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a conductive green body (zirconium nitride, ZrN, or titanium nitride, TiN) into a non-conductive bed (boron nitride, BN) and loading ZrN or TiN powders into the die directly. The ceramic specimens obtained were subjected to density measurement, microstructure observation and Vickers hardness test with a view to characterization. The microstructural differences between the ceramics with and without BN wrapping were investigated and the possible formation mechanisms were proposed by analysis.

The main characteristics of raw materials are listed in Table 1. The consolidation was conducted with a spark plasma sintering system (Dr. Sinter® 2040, Sumitomo Coal Mining Co., Tokyo, Japan) in a vacuum. The temperature was automatically raised to 600 °C, then monitored and regulated by an optical pyrometer aimed at the die surface. A heating rate of 100–400 °C min^{-1} was systematically used. The pressure was initially set at 30 MPa above 1000 °C, and was increased to 50 MPa when the maximum temperature was reached. The pressure was released at the end of the holding time, and the cooling rate down to 1000 °C was around 400 °C min^{-1}. For ZrN, the final temperature was held at 1500 or 1600 °C for a dwelling time of 5 min. To further confirm the microstructural differences, the same experimental process was followed for TiN sintered at 1500 °C.

A schematic drawing of the two different modes of placing powders is shown in Figure 1. In mode (a), a cylindrical pellet of ZrN or TiN with a diameter of 10 mm was first shaped in a uniaxial die press at 5 MPa, then placed in the central zone of the graphite die (20 mm in diameter) with electrically insulating pure BN powders wrapped around it. (The height of BN in the upper and lower layers was 3 mm.) For mode (b), ZrN or TiN powders were loaded directly into a graphite die with an inside diameter of 20 mm, as is the conventional way for the sintering process. The stack height of the ZrN or TiN samples was 5 mm in both modes, to facilitate the subsequent analysis between two sintering conditions.

After sintering, the graphite layers on the surface and the whole BN-wrapped layers of the obtained specimens were removed by grinding. Density measurements were conducted using Archimedes' method after boiling the samples in distilled water for 3 h and cooling down to room temperature. The morphologies of the fracture surfaces of the samples were investigated by scanning electron microscopy (SEM; Hitachi S-570, Tokyo, Japan). The hardness of the samples were measured using the Vickers indentation technique by applying a load with a dwell time of 15 s. Ten indentations were performed to obtain the average hardness value.

Table 1. Main characteristics of the starting powders.

Powder	Supplier	Variety	Particle size (μm)	Purity (%)
ZrN	Beijing Dk Nano technology	fcc	0.5	95
TiN	Hefei Kaier Nano	fcc	0.02	>99
BN	Sanxing, Gongyi, China	hcp	–	>99.5

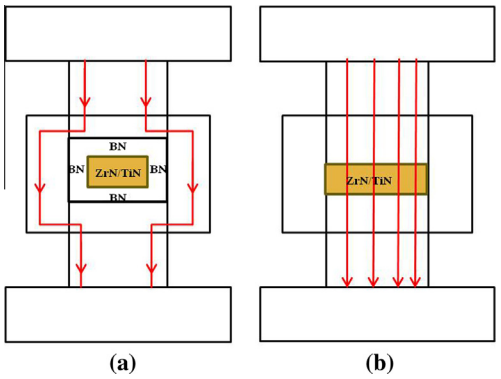

Figure 1. Schematic of two different modes of placing powders in graphite dies. The red arrows represent the direction of the pulsed electric current in the two systems.(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

According to the mode of powder placement, the sintered samples were nominated as ZrN@BN, TiN@BN, ZrN and TiN, respectively.

The SEM morphologies of the fracture surfaces of the SPSed ceramics are shown in Figure 2. It can be easily seen that significant differences existed between the BN-wrapped and unwrapped ceramics. The morphology of the ZrN@BN and TiN@BN sintered at 1500 °C exhibited a loosely bonded interface between spherical-like grains, which was quite distinct from the grains being stuck together in the ZrN and TiN. When the sintering temperature was higher, at 1600 °C, the connection of crystalline grains in the ZrN@BN was relatively tighter, but still weaker than that of the ZrN sample. This difference in grain boundaries is also

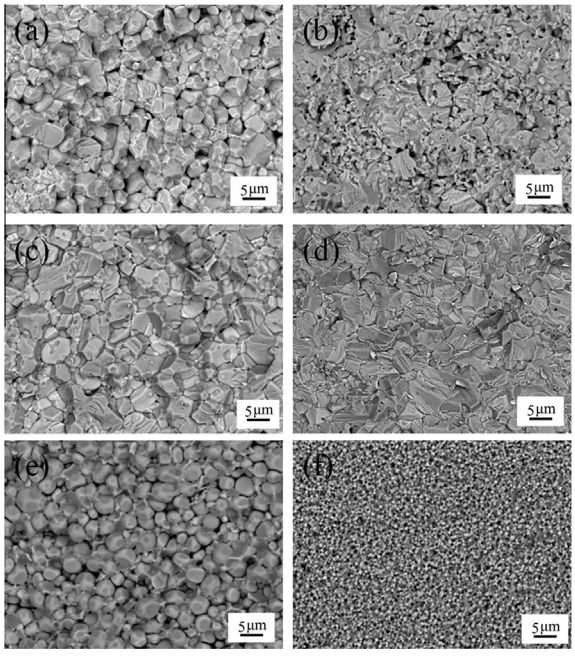

Figure 2. SEM micrographs of fracture surfaces of SPSed ceramics: (a) ZrN@BN sintered at 1500 °C, (b) ZrN sintered at 1500 °C, (c) ZrN@BN sintered at 1600 °C, (d) ZrN sintered at 1600 °C, (e) TiN@BN sintered at 1500 °C, (f) TiN sintered at 1500 °C.