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Materials

Comparative study of β-Si_3N_4 powders prepared by SHS sintered by spark plasma sintering and hot pressing

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Abstract: β-Si_3N_4 powders prepared by self-propagating high-temperature synthesis (SHS) with additions of Y_2O_3 and Al_2O_3 were sintered by spark plasma sintering (SPS). The densification, microstructure, and mechanical properties of Si_3N_4 ceramics prepared using this method were compared with those obtained by hot pressing process. Well densified Si_3N_4 ceramics with finer and homogeneous microstructure and better mechanical properties were obtained in the case of the SPS technique at 200°C lower than that of hot pressing. The microhardness is 15.72 GPa, the bending strength is 716.46 MPa, and the fracture toughness is 7.03 MPa·$m^{1/2}$.

Key words: self-propagating high-temperature synthesis (SHS); hot pressing; spark plasma sintering (SPS); silicon nitride; mechanical properties

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1. Introduction

Spark plasma sintering (SPS) is a new process [1] that offers a means by which ceramics can be sintered very rapidly to full density. It is similar to conventional hot pressing (HP), in that it is carried out in a graphite die, but the heating is done by means of direct currents of about 4 to 8 kA, pulsed by a patented powder generator, applied through electrodes at the top and bottom of the die punch. The powders are heated initially by spark discharge between the particles. The temperature may be measured by an optical pyrometer focused on the surface of the die or by means of a thermocouple placed inside the die [2-5].

Silicon nitride (Si_3N_4) is a material well known among engineers for its high strength, toughness, resistance to corrosion, low mass, and ability to withstand high temperatures-all of which make it suitable for the toughest jobs. Nevertheless, the relatively higher cost of ceramic components when compared to metallic counterparts is a large obstacle that hampers its wider acceptance. Therefore, an important developing direction of Si_3N_4 ceramics is to lower its production cost while maintaining its performance advantages [6, 7]. Ge *et al.* [8] has done substantial researches of the use of the SHS method for the production of Si_3N_4 powders, and has prepared high-quality, low-cost Si_3N_4 powders. To give full play to the advantages and potential of this material, the spark plasma sintering and hot pressing process of β-Si_3N_4 powders synthesized by SHS with the addition of Al_2O_3 and Y_2O_3 as sintering additives were investigated. The β-Si_3N_4 powders synthesized by SHS (self-propagating high-temperature synthesis) were characterized. The densification, microstructure, and the mechanical properties of Si_3N_4 ceramics sintered by the two processes were compared in this study.

2. Experimental

2.1. Raw materials and compaction

The SHS of β-Si_3N_4 powders (self-prepared) after acid washing were mixed with 6.67wt% Y_2O_3 (purity>99wt%, d_{50} (mean grain size)= 3.528 μm, Yuelong Chemical Industry, China) and 3.33wt% Al_2O_3 (purity>99wt%, d_{50}=2.553 μm, Yuelong Chemical Industry, China), and then wet-milled in alcohol for 2 h with ZrO_2 balls in polyethylene jars. After drying, the powder mixtures obtained were sieved to 100 mesh screen, and then dry-pressed uniaxially in a steel die to form cylindrical bodies of ϕ40 mm×10 mm at 30 MPa. Furthermore, the commercial Stark M II Si_3N_4 was also used and mixed in the same manner.

2.2. Sintering process

A novel sintering method, spark plasma sintering

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was applied to densify the self-propagating high-temperature synthesis (SHS) of β-Si_3N_4 powder. For comparison, hot pressing was also used for composite processing.

The powder mixtures were placed in a cylindrical carbon die with an inner diameter of 40 mm, and were compacted in a spark-plasma sintering apparatus, Dr. Sinter 1050 (Sumitomo Coal Mining Co., Japan), in a vacuum atmosphere. The schematic diagram of the SPS system is shown in Fig. 1. The sintering temperature was set to 1500°C, the holding time was set to 5 min, and the compact was furnace-cooled. The heating rate was 100°C·min^{-1} when the heating temperature was below 1000°C, and then the heating rate was 30°C·min^{-1}. The pressure was 20 MPa and this was applied at 200°C and retained to the sintering temperature.

Uniaxial hot-press sintering was performed in a graphite resistance-heated furnace. Each specimen was placed in a BN-coated graphite die and sintered for 1 h under a pressure of 20 MPa in a flowing nitrogen atmosphere. The heating temperature was 1700°C. The heat rate was 15°C/min up to the desired temperature, and the compact was furnace-cooled after the holding time. These processing conditions were determined according to the previous studies.

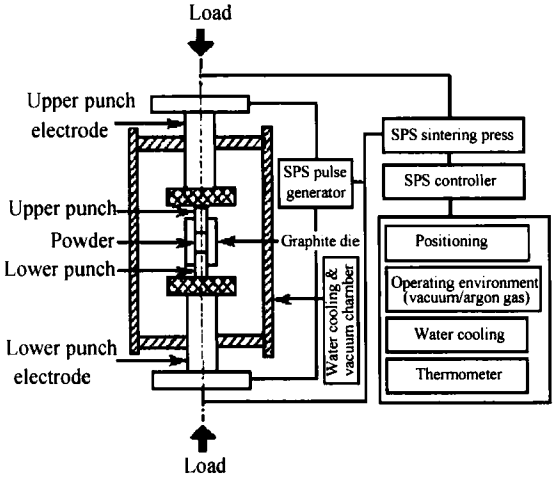

Fig. 1. Schematic diagram of the SPS system.

2.3. Measurements

The bulk density of the sintered compact was evaluated using the Archimedes method. For measuring the bending strength, bar shaped specimens of 3 mm×4 mm×36 mm were cut from the sintered body such that the stress face was perpendicular to the pressing direction. The tensile surface of the specimen was ground and polished by synthetic diamond lapping pastes to a mirror plane. The three-point bending strength measurement was conducted with steel fixtures at a crosshead speed of 0.5 mm/min, with a span of 30 mm (CDW-5). Microhardness values were measured by a Vickers indenter (MH-6) with a load of 9.8 N for 10 s. The fracture toughness, K_{IC}, was determined by the length of the cracks caused by the Vickers indentations.

The morphology of the Si_3N_4 microstructure was characterized using scanning electron microscopy (SEM: Cambridge-S360) after the surfaces of the polished specimens were etched in the molten NaOH for 4 min and then covered with a thin layer of carbon to avoid charging. The crystalline phases were identified by X-ray diffraction (XRD: Dmax-RB) using Cu K_α radiation at 40 kV and 150 mA.

3. Results and discussion

3.1. SHS of β-Si_3N_4 powder characterization

The X-ray diffraction spectrum of the SHS of Si_3N_4 powders after washing with water and a proper acid to remove thimbleful unreacted Si and metal impurity such as Fe and Ca is shown in Fig. 2. It can be seen that the crystalline phases were composed of mainly the β-phase and a minor amount of the α-phase. The β-ratio of Si_3N_4 (β-Si_3N_4/(α-Si_3N_4+β-Si_3N_4)), R_β, in the prepared powders can be evaluated according to the following equation by means of X-ray diffraction [9]:

$$R_\beta = \left[1.4434\times\frac{I_\beta(101)}{I_\beta(101)+I_\alpha(201)} - 0.4434\times\left(\frac{I_\beta(101)}{I_\beta(101)+I_\alpha(201)}\right)^2\right]\times 100 \quad (1)$$

The result of the calculation was that R_β was 97.6%. The morphology of the SHS of β-Si_3N_4 powders after acid washing was observed by SEM and is shown in Fig. 3. It exhibited an integrated rod-like morphology with a diameter of 0.2-0.5 μm and a length of 2-5 μm.

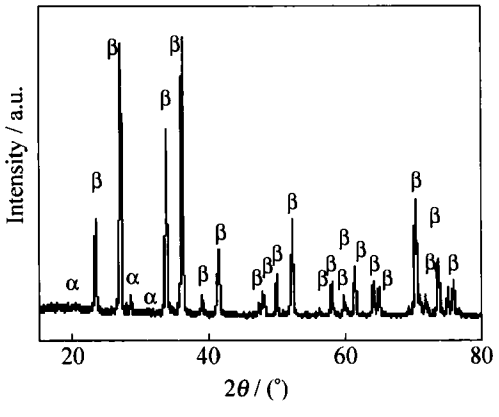

Fig. 2. XRD pattern of Si_3N_4 powders synthesized by SHS.