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Spark plasma sintering of α-Si_3N_4 ceramics with MgO–$AlPO_4$ as sintering additives

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Abstract

In this study, a novel sintering method, SPS is applied to prepare α-Si_3N_4 ceramics of different relative densities with MgO and $AlPO_4$ as the sintering additives. The sintering behavior of SPS process is discussed and the factors influencing the relative density of the prepared samples are analyzed. The sintering mechanism is explained by both the reaction between MgO and SiO_2 presenting on the Si_3N_4 powders and solid state sintering of $AlPO_4$. Microstructures of the sintered samples are observed by SEM images and the phase compositions are analyzed by XRD. The mechanical properties of the sintered ceramics are also investigated, as a function of the relative densities. The resultant α-Si_3N_4 ceramics sintered from 1300 °C to 1500 °C show fine microstructure with nearly no grain growth and phase transformation and have a relative high bending strength. The α-Si_3N_4 ceramics with relative density of 58–98% and bending strength of 50–420 MPa are obtained.

Keywords: Silicon nitride; Spark plasma sintering (SPS); Sintering additives; Mechanical properties

1. Introduction

Silicon nitride (Si_3N_4) matrix ceramic has been studied intensively and used in numerous applications as structural and functional ceramic materials because of its superior properties, such as high-temperature strength, good oxidation resistance and low thermal expansion coefficient [1–4]. Silicon nitride is strong covalent chemical bond and has two forms, α and β phases [5]. The unit cell of the α-Si_3N_4 is twice as length as the β-Si_3N_4. The stacking sequence of α-Si_3N_4 is ABCDABCD···, and β-Si_3N_4 is ABAB···. Previous studies focused mainly on totally transformation from α-Si_3N_4 to β-Si_3N_4 and achieving perfect mechanical and thermal properties of silicon nitride by using different sintering additives, and were aimed at obtaining fully dense products [6,7], but a few reported on sintering of α-Si_3N_4 ceramics which could have a promising dielectric application [8]. (It is reported that α-Si_3N_4 has lower dielectric constant than β-Si_3N_4 [9].) Thus, it is significant to fabricate α-Si_3N_4 ceramics and to reveal the microstructure effect on the mechanical properties.

It is known that spark plasma sintering (SPS) is a newly developed sintering method [10] that is similar to conventional hot pressing in configuration, the precursor powders are loaded in a die and a uniaxial pressure is applied during the sintering. However, instead of using an external heating source, densification is enhanced by the use of a pulsed direct current passes through the electrically conducting die and the sample. High-rate and possibly low temperature sintering are indeed characteristics of this sintering method. It is reported that Si_3N_4 ceramic can be sintered in 15 min of heating and holding time, but α to β transformation is not completed within such a short sintering time [11]. It is assumed that the initial temperature of the α to β transformation is about 1400 °C and the completion temperature is about 1800 °C. Otherwise, the SPS technique thus provides us with unique possibilities to manipulate the sintering kinetics. The inherent advantages of SPS technique are the reasons why it is selected in this study.

In the present study, we are motivated to prepare α-Si_3N_4 ceramics of different relative densities doped with sintering additives based on MgO and $AlPO_4$ by SPS technique, and study the correlations between the microstructure and relative density. The purpose of this study is to obtain as clear a correlation as possible between the microstructure and the mechanical properties and in addition, to explore the sintering behavior by SPS technique and sintering mechanism.

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Table 1
Phase and elemental composition of the Si_3N_4 raw material

Material	Si_3N_4 (wt.%)
α phase	>93
β phase	<5
Si_{free}	<0.3
N	>37.0
O	<1.5
C	<0.1
Fe	<0.3

2. Experimental procedure

2.1. Starting materials

The raw materials used in the present study are as follows: α-Si_3N_4 (Tsinghua Ziguang Industries, Beijing, China, the main compositions is listed in Table 1, density 3.26 g/cm^3, particle size 0.5 μm), MgO (Alfa Aesar China Co. Ltd., Tianjin, China, density 3.58 g/cm^3, particle size 0.2 μm, purity = 99.99%), and $AlPO_4$ (Alfa Aesar China Co. Ltd., Tianjin, China, density 2.63 g/cm^3, particle size 0.5 μm, purity = 99.99%).

2.2. Materials preparation

According to Table 2, the powder precursors in various ratios were ball milled in ethanol for 10 h in a nylon jar, using sintered Si_3N_4 grinding media. After the powder mixtures were dried, they were passed through a 100 mesh sieve to eliminate large agglomerates, then loaded in a graphite die with the inner diameter of 32 mm and pre-pressed to some extent and sintered using a SPS system (model-1050, Sumitomo Coal Mining Co. Ltd., Tokyo).

The sintering temperature of 1300–1500 °C of each sample was measured by an optical pyrometer focused on the surface of the graphite die. An average heating rate of 100 °C/min was maintained up to the sintering temperature and then the temperature was held constant for 5 min. A uniaxial pressure of 30 MPa and a nitrogen (N_2) atmosphere were applied from the start to the end of the sintering cycle. The sample was cooled naturally in the nitrogen (N_2) atmosphere after the sintering period finished.

2.3. Sample characterization

After sintering, the bulk density of the sintered products was determined by Archimedes' immersion method using distilled water as media. The true densities of the samples with different amount of sintering additives were calculated by using the mixture law and the density of Si_3N_4 (3.26 g/cm^3), $MgSiO_3$ (4.09 g/cm^3) and $AlPO_4$ (2.63 g/cm^3) were used. The phase compositions were analyzed by X-ray diffraction (XRD) using a Rigaku-D/Max-III A diffractometer. Cu radiation was used and operated at 35 kV and 30 mA. The microstructure of the fractured surfaces was observed by scanning electron microscopy (SEM). The specimens were machined into test bars with a dimension of 3 mm × 4 mm × 35 mm for bending strength measurement before a three-point-bending test was conducted at a loading rate of 0.5 mm/min on a universal testing machine. All surfaces of the test bars were finally polished and the edges were beveled. Each final value was averaged over three measurements.

Table 2
The ratio (wt.%) of raw powders of every sample

No.	Si_3N_4	MgO	$AlPO_4$
S1	94	4	2
S2	92	4	4
S3	88	4	8
S4	80	4	16

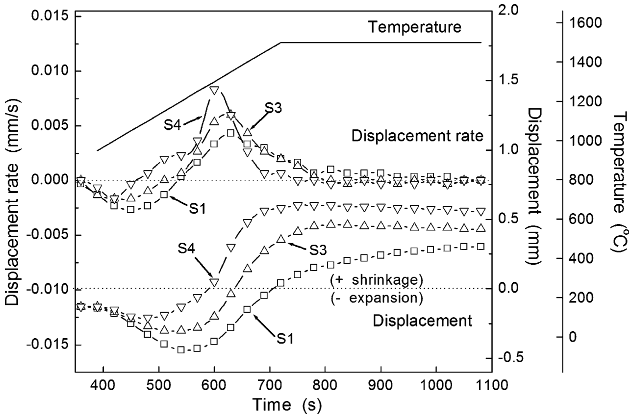

Fig. 1. Dependence of sintering behavior on different additive amount at 1500 °C.

3. Results and discussion

3.1. Sintering behavior

For sake of constraining the conversion of α-Si_3N_4 to β-Si_3N_4, the powder mixtures are sintered at a low temperature of 1300–1500 °C. The temperature is measured by an infrared pyrometer at the outer surface of the graphite die. It is believed that a discrepancy (underestimate) of about 150–200 °C exists between the temperature at the surface and that at the interior under such circumstances [12]. So, α-Si_3N_4 can be sintered even at 1500 °C by SPS.

Consolidation behavior is best represented by the shrinkage and shrinking rate concurrently measured during the sintering. An example of the dependence as a function of the amount of additive in the powder mixtures is shown in Fig. 1. In all these cases the sintering temperature is 1500 °C. From the displacement curves, all the sintered samples show first expansion at low temperature due to the thermal expansion of the powders and then shrinkage because of the sintering of the samples. The starting sintering temperature is lower by adding $AlPO_4$, 1100 °C according to Fig. 1. With a high $AlPO_4$ level (e.g., S4, 16 wt.%), densification is completed in a very short time and relative low temperature (1400 °C) after the peak shrinking-rate is reached, which suggests that $AlPO_4$ performs good sintering behavior. While with a low $AlPO_4$ level (e.g., S1, 2 wt.%), sintering is attributed mainly to the effect of MgO which is not enough to bring the material to high density at low temperature. In this situation, consolidation of this material is finished at 1500 °C.

The relative density of S1–S4 as a function of different sintering temperatures and content of sintering additives is shown in Fig. 2, respectively. It can be seen from Fig. 2 that the relative densities show sharp variation against the sintering temperature from 1300 °C to 1500 °C when the content of the $AlPO_4$ is 2 wt.% (S1) and 4 wt.% (S2), while when the content of $AlPO_4$ is 8 wt.% (S3) and 16 wt.% (S4), this phenomenon is from 1300 °C to 1400 °C. For S3 and S4, the relative densities fluctuate little when the sintering temperature is from 1400 °C to 1500 °C. Samples with the relative density from 58% to 98% are acquired.