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Fabrication and dielectric properties of Si_3N_4–MgO–Al_2O_3 by spark plasma sintering technique

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In the present study, α-Si_3N_4 was prepared using MgO and Al_2O_3 as the sintering additives and spark plasma sintering (SPS) technique. The SPS sintering behaviour and mechanism have been discussed. The relationship between the content of sintering additives, sintering temperature, and relative densities of the samples have been analyzed. The phase composition was determined by XRD, the microstructures of the fracture surfaces were observed by SEM and the dielectric properties have been tested. The results suggest that when the sintering temperature is 1300–1500 ºC, the content of sintering additives – 6–10%, the relative density of the sintered samples is 64–96%. When the sintering temperature reaches 1400 ºC, the content of sintering additives 10%, the samples could be fully dense sintered (the relative density up to 95%) The sintering mechanism is liquid phase sintering. The electric permittivity of the sintered samples is 5–8 being in a close relationship with the relative density. The dielectric loss, influenced by the liquid phase, is less than 1×10^{-2}.

Key words: spark plasma sintering; α-Si_3N_4; sintering additive; microstructure; dielectric properties

1. Introduction

Silicon nitride (Si_3N_4) based ceramics have been studied intensively for more than 40 years and used in numerous applications as structural and functional ceramic materials due to its superior properties, such as high-temperature strength, good oxidation resistance, and low thermal expansion coefficient [1–3]. The Si_3N_4 ceramics has the best mechanical and thermo-structural properties for high temperature applications [4]. Previous studies focused mainly on achieving perfect mechanical and thermal properties of silicon nitride [5], and were aimed at obtaining high density products but a few have been reported on dielectric properties.

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Silicon nitride is strong covalently bonded and has two forms: α and β phase [6]. The unit cell of the α-Si_3N_4 structure is twice as long as that of the β-Si_3N_4. The stacking sequence of α-Si_3N_4 is ABCDABCD…, and β-Si_3N_4 is ABAB... It has been reported that β-Si_3N_4 has a higher electric permittivity than α-Si_3N_4 [7]. Thus studying dielectric properties of the material is of importance in view of fabrication of α-Si_3N_4 ceramics.

Spark plasma sintering (SPS) is a recently developed sintering method [8] being 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 with the use of a pulsed direct current passing through the electrically conducting die and the sample. High rates and possibly low temperatures of sintering are characteristic of this method. It has been reported that Si_3N_4 ceramics can be sintered for 15 min of heating and holding, but α to β transformation is not completed within such a short time [9]. It is assumed that the initial temperature of the α to β transformation is about 1400 ºC and the completion temperature is about 1800 ºC. The SPS technique thus provides us with unique possibilities to manipulate the sintering kinetics. The inherent advantages of the SPS technique are the reasons why it has been chosen for this study.

In the present study, we are motivated to prepare α-Si_3N_4 ceramics of various densities doped with mixed additions based on MgO and Al_2O_3 by the SPS technique, and to study correlations between the microstructure and relative densities. In addition, one of the important tasks of this paper is to explore the sintering behaviour and LPS mechanism. The goal of this study is to obtain a correlation as clear as possible between the microstructure and the dielectric properties.

2. Experimental procedure

Materials. Raw materials used in the study were as follows: α-Si_3N_4 rich powder, light magnesia (MgO) powder and aluminum phosphate ($AlPO_4$) powder. In Table 1, the main compositions of α-Si_3N_4 are given. Their grain size is about 1–2 μm. The grain size of commercial MgO was about 0.2 μm, and its purity was up to 99.9%. For Al_2O_3, the grain size was about 0.5 μm and purity was up to 99.9%.

Table 1. Phase and elemental composition of Si_3N_4 raw material, wt. %

Material	α-Phase	β-Phase	Si free	N	O	C	Fe
Si_3N_4	> 93	< 5	< 0.3	> 37.0	< 1.5	< 0.1	< 0.3

Preparation of materials. According to Table 2, the powder precursors in various ratios were mixed uniformly in a three-dimensional mixing for 5~7 h. The mixture was loaded in a graphite die with the inner diameter of 32 mm, pre-pressed and sintered using an SPS system (model-1050, Sumitomo Coal Mining Co. Ltd., Tokyo). Figures 1, 2 show the schematic diagram of the SPS process.

Table 2. The contents [wt. %] of raw powders and theoretical densities of the samples

No.	Contents [wt. %]			Theoretical density [g/cm^3]
	Si_3N_4	MgO	Al_2O_3	
S1	94	4	2	3.283
S2	92	4	4	3.295
S3	90	4	6	3.307

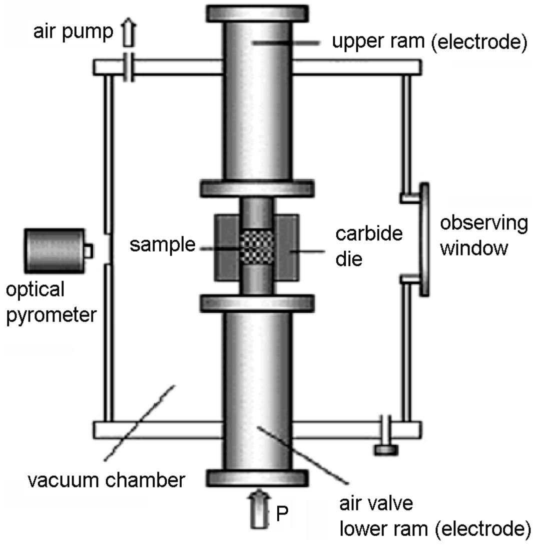

Fig. 1. Schematic drawing of the SPS system

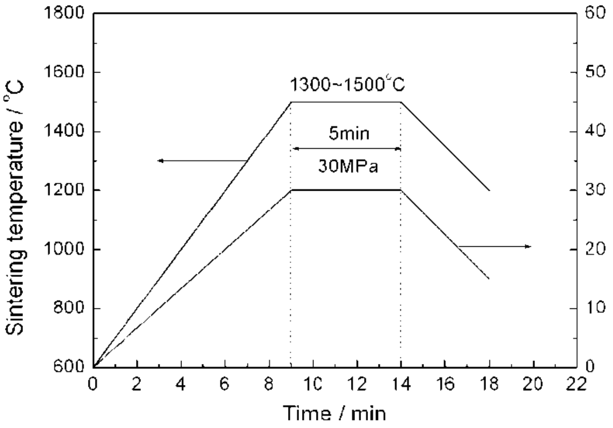

Fig. 2. The schematic diagram of the SPS process

The sintering temperature (1300–1500 °C) of each sample was measured using an optical pyrometer focused on the surface of the graphite die. The average heating rate of about 100 °C/min was maintained up to the sintering temperature and then the temperature was held constant for 5 min. A uniaxial pressure of nitrogen of 30 MPa was applied during the sintering cycle. Then the samples were cooled naturally under nitrogen atmosphere.

Sample characterization. After sintering, the bulk density of the sintered products was determined by the Archimedes immersion method using distilled water. Theoretical densities were calculated in terms of the rule of mechanical mixture. Phase compositions were analyzed by X-ray diffraction (XRD) using a Rigaku-D/Max-ⅢA diffractometer. Cu radiation was used operating at 35 kV and 30 mA. The microstructure of the fractured surfaces was observed by a scanning electron microscope (JSM-5610LV). The dielectric properties of the specimen were measured by the capacitive measuring mode while the test frequency was 1 MHz.

3. Results and discussion

3.1. Sintering behaviour

For the sake of constraining the conversion of α-Si_3N_4 to β-Si_3N_4, the powder mixtures were sintered at 1300–1500 °C. The temperature was measured by an infrared pyrometer at the outer surface of the graphite die. It is believed that the discrepancy (underestimate) of about 150–200 °C exists between the temperature at the surface and that at the interior under such circumstances [10]. So, α-Si_3N_4 can be sintered even at 1500 °C by the SPS.

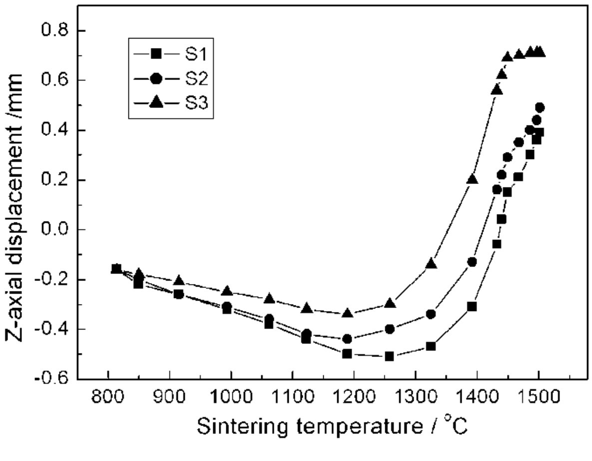

Fig. 3. The temperature dependence of Z-axial displacement (sintering at 1500 °C)

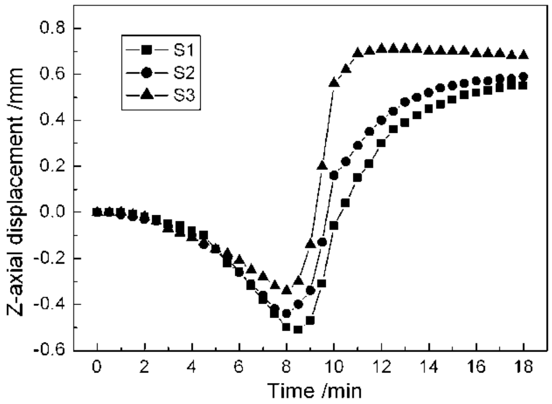

Fig. 4. The time dependence of *Z*-axial displacement (sintering at 1500 °C)

The consolidation behaviour is best represented by the shrinkage concurrently measured during sintering. An example of such a dependence on the amount of additive in the powder mixtures is shown in Figs. 3 and Fig. 4, representing the temperature dependence and the time dependence of Z-axial displacement measured directly

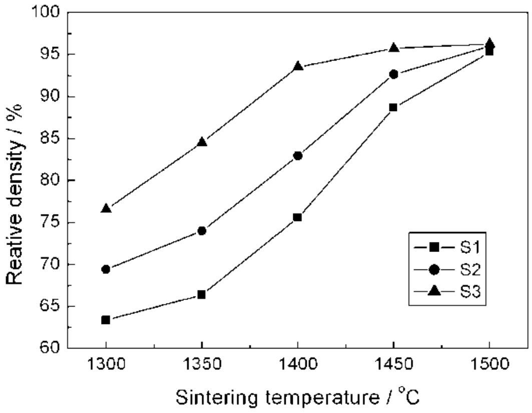

Fig. 5. The effect of sintering temperature and content of sintering additives on the relative densities of the sintered samples

from the SPS system. In all these cases, the sintering temperature was 1500 °C. The additive reduces the thermal expansion during sintering and the more of the additive is added, the more obvious this phenomenon is. Furthermore, the starting sintering temperature is lower (1200 °C) upon addition of MgO and Al_2O_3 (Fig. 3). With a high additive level (e.g., S3, 10 wt. %), the densification is completed in a very short time, at 11 min according to Fig. 4, and at a relatively low temperature (1400 °C), which is a behaviour typical of liquid-phase sintering. On the other hand, with a low additive level (e.g., S1, 6 wt. %), liquid phase sintering alone is not enough to bring the material to high density at low temperature due to the lack of a continuous liquid phase. In such a case, the shrinkage does not stop during the sintering process and the consolidation of this material is not finished even at 1500 ºC.

The relative densities of S1–S3 samples at various sintering temperatures and the content of sintering additives are shown in Fig. 5. The relative densities show sharp variation against the sintering temperature from 1300 ºC to 1500 ºC. Relative density from 64% to 96% was obtained when the content of the sintering additive was from 6% to 10% and the sintering temperature varied from 1300 ºC to 1500 ºC. We can conclude that when the content of Al_2O_3 or the sintering temperature reached certain values, the material could be compactly sintered and the relative density changed a little. In this way, the density can be controlled by using different content of sintering additives and sintering temperature.

3.2. Microstructure

Fig. 6 shows the SEM observation of fractured surface of the sintered samples. It can be seen that the volume of pores decreased remarkably from S1 to S3 when the sintering temperature was 1400 ºC. These results are in agreement with those shown in Fig. 5. It is worthy to note that almost no β-Si_3N_4 was observed and the grain size was about 1 μm, which indicates there was no obvious grain growth in the SPS process.

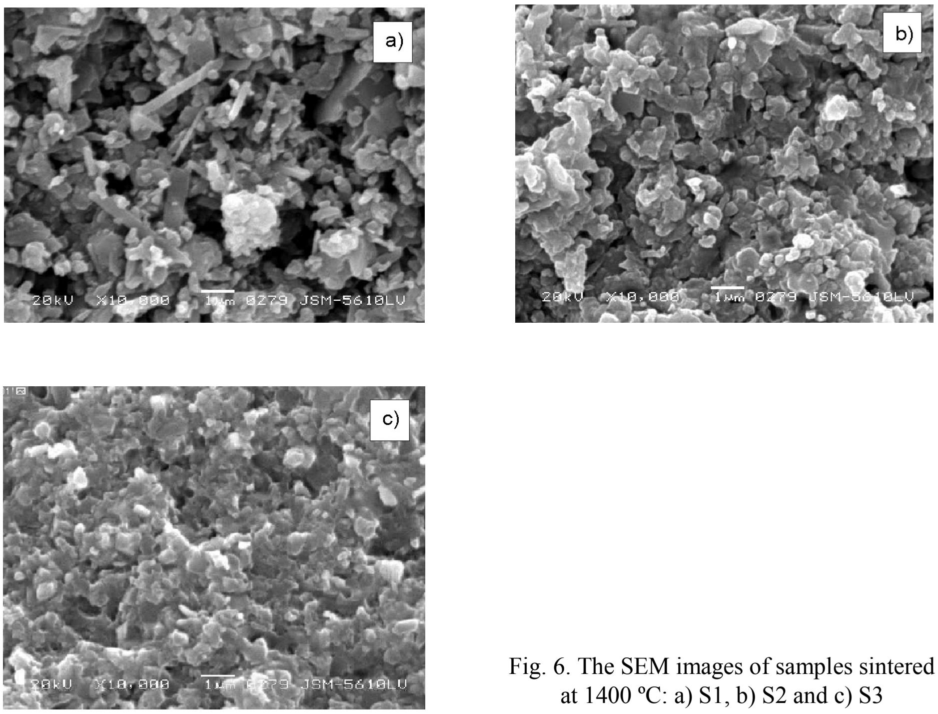

Fig. 6. The SEM images of samples sintered at 1400 ºC: a) S1, b) S2 and c) S3

Previous analyses prove that this sintering phenomenon is supposed to be due to liquid phase sintering [11], which is induced by the reaction among the components of the mixture. During the sintering process, the liquid phase attempts to occupy the lowest free energy position. Thereby, it flows to the smaller capillaries, which have the highest energy per unit volume. When there is not enough liquid to fill all the pores, the liquid tends to pull the particles together to minimize the free energy. So the increase in densification is attributed to the capillary forces exerted by the liquid phase on the solid particles. This effect results in the rearrangement stage and rapid initial densification.

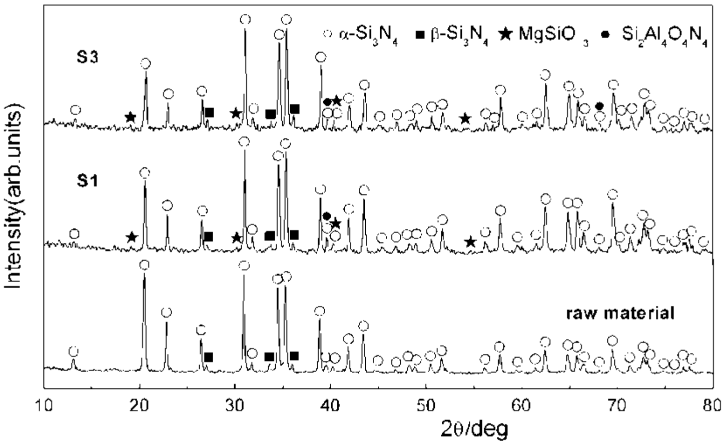

Fig. 7. The X-Ray diffraction patterns of sintered S1, S2 and Si_3N_4 samples of raw material at 1500 °C

The identified phases for all compositions of samples S4 sintered from 1300 °C to 1500 °C are presented in Fig. 7, which are α-Si_3N_4, β-Si_3N_4, $MgSiO_3$ and $Si_2Al_4O_4N_4$ (β-sailon). The XRD indicates that the major phase is α-Si_3N_4, and that the sintered samples basically preserve the characters of the starting powders.

The product of the identified $MgSiO_3$ and $Si_2Al_4O_4N_4$ illustrates the sintering mechanism that the liquid phase promotes the mixture powders adherence [12, 13], which to some extent confirm certain mechanical properties of the sintered samples.

3.3. Dielectric properties

Electric permittivities of sintered samples are closely dependent on their relative densities as shown in Fig. 8. The value of ε is between 4.5 and 8.5. Since pores contain trapped gases of low conductivities, samples with low relative densities show low electric permittivities, as is clearly seen in Fig. 8. It is known that ε of α-Si_3N_4 is about 5.6 and of β-Si_3N_4 is about 7.9. Low sintering temperature helps to constrain the conversion of α-Si_3N_4 into β-Si_3N_4; the lower temperature can also reduce the production of the liquid phase. These factors made the obtained samples maintain the properties of the initial powder. When the relative density is the same, ε increases by increasing the content of sintering additives, from 6 wt. % to 10 wt. %. This could be attributed to the amount of liquid phase which has a larger ε and tanδ. On the other hand, as can be seen in Fig. 9, the dielectric loss is less than 1×10^{-2} and it increases with increasing relative density when the content of sintering aids is low, i.e. 6 wt. %. However, when the content of sintering aids is high, i.e. 10 wt. %, because of the more generated polar liquid which is filled in the trapped gas, it first decreases and then increases by increasing the relative densities. This is how the liquid phase affects tanδ.

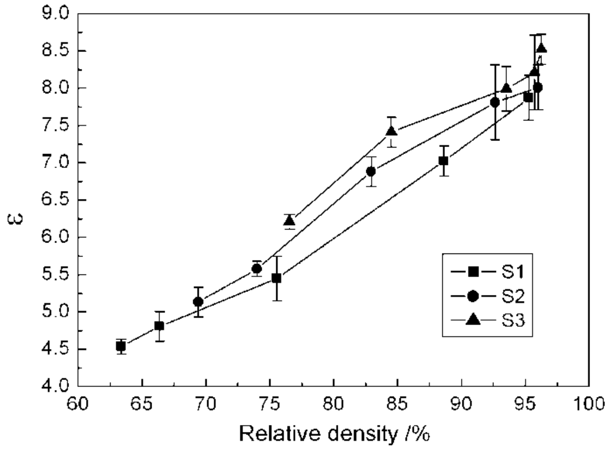

Fig. 8. Electric permittivities of the sintered samples vs. relative densities

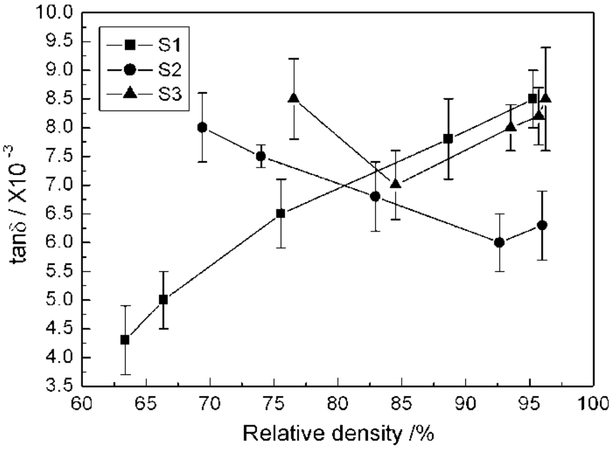

Fig. 9. Dielectric losses of the sintered samples vs. relative densities

4. Conclusions

- Relative density alters from 64% to 96% when the content of the sintering additives changes from 6% to 10% and the sintering temperature from 1300 ºC to 1500 ºC, which enables us to prepare α-Si_3N_4 matrix ceramics for various applications by adjusting the density of the samples. Nearly no grain growth and β-Si_3N_4 are observed by SEM.
- The main sintering mechanism of α-Si_3N_4 matrix ceramics by adding MgO and Al_2O_3 could be attributed to liquid phase sintering.
- Electric permittivity of a sintered sample lies in the range of 4.5–8.5 and has a close correlation with the relative density. Dielectric loss is less than 1×10^{-2} and is influenced by the liquid phase.

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