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Preparation of bulk Si_3N_4 from tape casting and lamination

Jingxian Zhang [a,*], Feng Ye [b], Dongliang Jiang [c], Mikio Iwasa [a]

[a] *National Institute of Advanced Industrial Science and Technology, AIST Kansai, Osaka 563-8577, Japan*
[b] *School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China*
[c] *The State Key Laboratory of High Performance Ceramics and Superfine Structure, Shanghai Institute of Ceramics, Shanghai 200050, PR China*

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Abstract

Si_3N_4 samples were prepared by tape casting, laminating and hot pressing (HP)/spark plasma sintering (SPS). Initially, the as-received Si_3N_4 powders were chemically treated to improve the dispersion in aqueous media. After surface treatment, a decrease in zeta potential was observed in the basic region. Rheological measurements showed that 40 vol.% Si_3N_4 slips exhibited a well deflocculated state in the presence of the sintering additives. After the addition of binder and plasticizer, Si_3N_4 slurries exhibited a shear thinning behavior. The dried green sheets were smooth and homogeneous on both sides. The Si_3N_4 samples were densified by HP and SPS. A good homogeneity is observed and no single layers can be distinguished in the fracture surface. The mechanical properties were also studied.

Keywords: A. Tape casting; D. Si_3N_4; Zeta potential; Rheology

1. Introduction

Due to their unique combination of excellent properties, Si_3N_4 ceramics are considered the most promising materials for advanced structural applications [1]. However, the widespread use of Si_3N_4 composites has been limited by low mechanical stability (from dry pressing), difficulty in machining, and high manufacturing costs of components, especially for fabricating parts with complex shapes. Colloidal processing has been reported as a cost effective route to prepare ceramic composites of complicated shape with improved stability [2,3]. Various colloidal methods have been tried to prepare bulk Si_3N_4 samples, including direct coagulation casting, slip casting, gel casting etc. [4–9]. The colloidal behavior of silicon nitride-based suspensions in aqueous media has also been studied by many authors [10–13].

It is evidenced that laminated design is a feasible path to increase the strength and the fracture toughness [14,15]. Recently, many researchers show their interest in applying laminated object manufacturing (LOM) technology to build parts from engineering materials such as structural ceramics and composites. LOM is one of the rapid prototyping and manufacturing techniques where a part is built sequentially from layers of paper, green sheets of ceramics, sheets of metal, etc. This technique is especially suitable for producing geometrically complex objects, and for operating with a high degree of automation [16–20].

Tape casting is a well-developed technique for the preparation of ceramic substrates, capacitors and multi-layered composites for electronic industry [21–25]. In recent years, tape casting technique is also reported for the structural design [14,26,27]. However, few papers referred the preparation of bulk Si_3N_4 ceramics from aqueous tape casting sheets [28].

In the present work, Si_3N_4 samples were prepared through aqueous tape casting, laminating, hot pressing (HP) and spark plasma sintering (SPS) sintering technique. The dispersion of Si_3N_4 suspensions was studied in terms of surface charge behavior and the rheological properties. The microstructure, strength and fracture toughness of the as sintered Si_3N_4 sample were also characterized.

* Corresponding author. Tel.: +81 727 519 785; fax: +81 727 519 631.
E-mail address: jx_zh@yahoo.com (J. Zhang).

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Table 1
Impurities in as-received Si_3N_4 powders

Impurities	Content (wt.%)
CaO	0.0329
Fe_2O_3	0.234
Al_2O_3	0.216
MnO_2	0.0161
Y_2O_3	0.0413

2. Experimental procedures

2.1. Starting materials

Commercially low cost Si_3N_4 powders (Shenhai Nitride Company, Nantong, China) were used in this paper. The mean particle size and the specific surface area were 0.42 μm and 11 m^2/g, respectively. The impurities of Si_3N_4 powders were characterized by an X-ray fluorescence spectrometry PW2404 (Philips, Netherlands), see Table 1. Al_2O_3 and Y_2O_3 were used as sintering additives.

As shown in Table 1, the content of impurity is high in the starting Si_3N_4 powders. To obtain well-dispersed slurries, the surface of Si_3N_4 powders was treated with acidic and alkaline solution in advance. The surface treatment procedure was similar to that reported in literature for Si_3N_4 [29,30], SiC and TiC [31,32]: as-received Si_3N_4 powders were first dispersed in deionized water to obtain a 10 vol.% suspension. The slurry pH was adjusted to ∼5 with HNO_3 (Analytical, Shanghai Chemical Reagent Corporation, China). Then the suspensions were conditioned over a 6 h period before passing a filter to remove water in the slips. After filtration, new suspensions were prepared again at 10 vol.% in deionized water with the slurry pH adjusted to ∼11 using $NH_3{\cdot}H_2O$ (Analytical, Shanghai Chemical Reagent Corporation, China). Another 6 h were allowed for conditioning before removing the solvent again by filtration. The obtained Si_3N_4 cakes were washed using deionized water until the slurry pH was ∼7. Finally, the Si_3N_4 cakes were dried and passed through a 200-mesh screen.

The dispersant was a secondary polyamine, polyethyleneimine (PEI, Acros Organics, M.W. 50-60000). To prevent the flocculation of sintering additives, ammonium salt of citric acid was added. The binder and the plasticizer were polyvinyl alcohol 1788 (Qidong Chemical Plant, China) and glycerol (Analytical, Shanghai Chemical Reagent Corporation, China), respectively. Details about the selection and stability of dispersant were reported in previous papers [31–33].

2.2. Zeta potential test

Zeta potential of as received and as treated Si_3N_4 powders was determined by Zetaplus (Brookhaven Instruments Corporation). Suspensions were prepared by dispersing Si_3N_4 powders (0.01 vol.%) in 0.001 M KCl (Analytical, Puqiao Scientific and Technological Corporation, China) solution. The samples were ultrasonicated and conditioned before measurements. The pHs were adjusted with 1 M HCl (Analytical, Shanghai Chemical Reagent Corporation, China) and 1 M NaOH (Analytical, Shanghai Chemical Reagent Corporation, China).

2.3. Rheological measurements

Rheological measurements were used to characterize the slurry properties. 40 vol.% Si_3N_4 suspensions were prepared in the presence of dispersants by ball milling for 24 h to allow the attainment of an adsorption equilibrium. The testing was conducted under steady shear condition by ascending and descending shear rate ramps from 0 to 400 s^{-1} in 10 min, and from 400 to 0 s^{-1}in 10 min, respectively. To avoid undesired influence from different mechanical histories, fresh samples were pre-sheared for 3 min and left standing for an additional 3 min prior to measurement (SR5, Rheometric Scientific).

2.4. Mechanical properties

Si_3N_4 suspensions were cast onto fixed glass plates at a constant casting speed of 30 cm/min. The gap height was set as 500 μm. The green sheets were cut into a rectangular size (40 mm × 50 mm) and stacked in a graphite die.

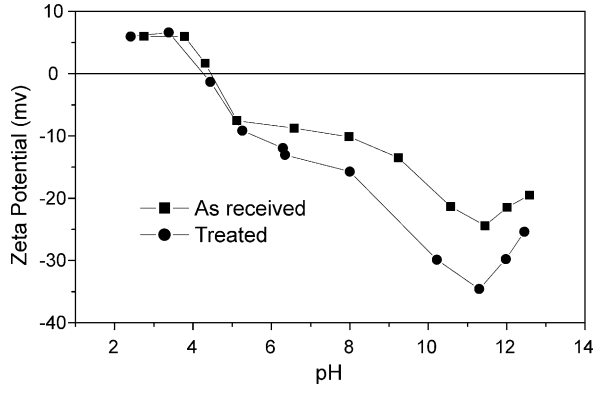


Fig. 1. Zeta potential of Si_3N_4 powders before and after surface treatment.

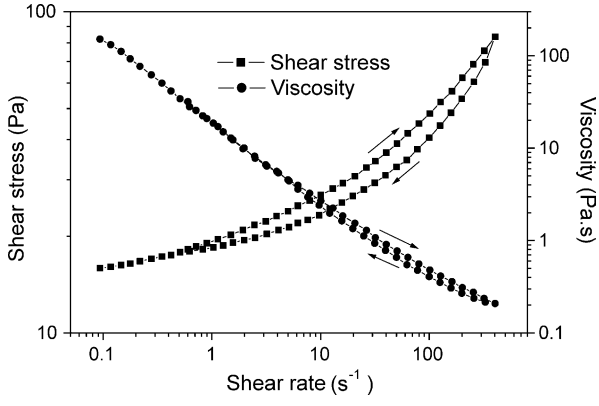


Fig. 2. Rheological properties of 40 vol.% Si_3N_4 slurries with sintering additives.

Table 2
Formulation of Si_3N_4 slurries for tape casting

Materials	Function	vol.%	wt.%
Si_3N_4	Ceramic powder	24.00	48.58
PEI	Dispersant	1.422	0.97
Citric acid ammonium salt	Dispersant	0.31	0.19
Al_2O_3	Sintering additive	0.74	1.86
Y_2O_3	Sintering additive	0.39	1.24
Deionized water	Solvent	64.13	40.56
PVA	Binder	4.83	3.30
Glycerol	Plasticizer	4.17	3.30

Binder removal was carried out in an argon atmosphere. Samples were hot pressed at 1800 °C and 35 MPa in N_2 atmosphere for 0.5 h. The laminated green bodies were also sintered by SPS for comparison. The temperature, pressure and soaking time were 1600 °C, 30 MPa and 3 min, respectively.

Tests of flexural strength were performed by three point bending. Fracture toughness was determined by single-edge-notched beam (SENB) method at room temperature. The microstructure of the specimen was investigated by SEM. The density and open porosity of the sintered samples were measured by the Archimedean method. The starting Si_3N_4 powders and the sintered Si_3N_4 ceramics were also characterized by XRD.

3. Results and discussion

3.1. Aqueous tape casting, lamination and sintering

Zeta potential of Si_3N_4 powders is shown in Fig. 1. The purpose of surface treatment is to remove the impurities

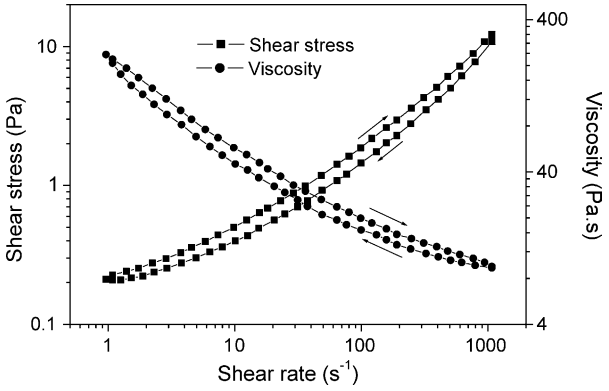
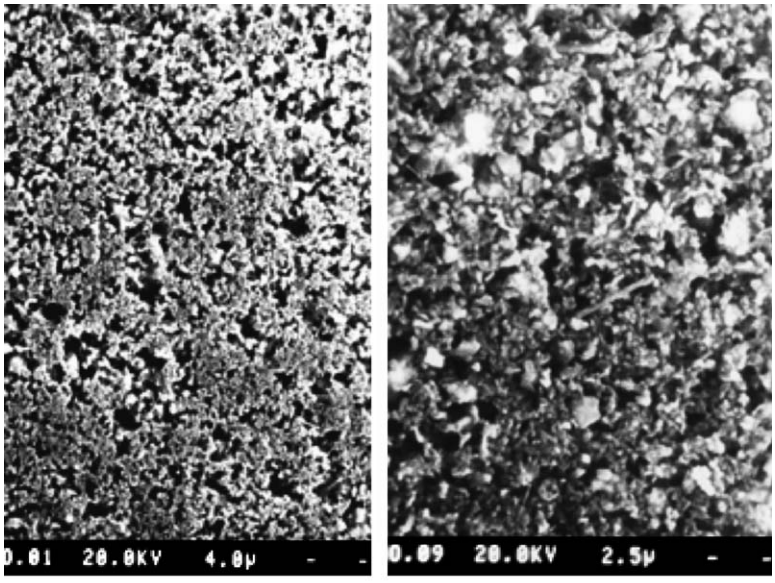


Fig. 3. Rheological properties of 24 vol.% Si_3N_4 slurries in the presence of binder and plasticizer.

(see Table 1) as well as the physically adsorbed hydroxide (water) and ammonia groups on the Si_3N_4 particle surface, and to increase the silanol site density. After surface treatment, Si_3N_4 particles did not show obvious change in pH_{IEP}, indicating that only physical adsorbed groups are removed from the surface. However, the zeta potential of as treated Si_3N_4 powders showed a significant decrease in strong basic region, suggesting the increase in surface silanol density, this can be further related to the decrease of the adsorbed hydroxide (from impurities in Table 1) and ammonia groups, as evidenced in literature [30].

Based on the study in a previous paper [13], Si_3N_4 suspensions can be stabilized around pH 9.3 with 1.2 wt.% PEI as dispersant. But it is difficult to stabilize the sintering additives (Al_2O_3 and Y_2O_3) simultaneously at the above-mentioned pH just using PEI as dispersant. In literature, citric acid was reported as an effective dispersant for Al_2O_3



(a) (b)

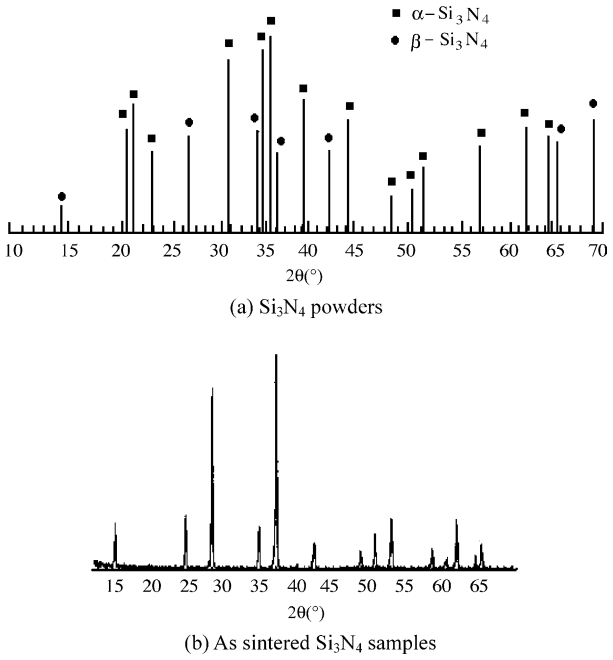
Fig. 4. SEM micrographs for dried tapes (a) bottom surface and (b) top surface.

in aqueous media [34]. As citric acid is an acidic dispersant, it is effective for shifting the IEP of the sintering additives toward more acid region. Consequently, the flocculation around pH 9.3 can be avoided. In this paper, citric acid was added in its ammonium salt form to help stabilizing the suspensions. Viscosity measurement showed that citric acid ammonium salt did not show obvious influence on the stability of Si_3N_4 powders. The viscosity of 40 vol.% Si_3N_4 slurries in the presence of sintering additives is characterized by rheological measurement, see Fig. 2.

In the presence of citric acid ammonium salt, Si_3N_4 slurries exhibited slight shear-thinning behavior, see Fig. 2. This shear thinning behavior might come from the high molecule weight of dispersant because of the contact with neighboring chains [35]. Free polymers might also induce weak flocculation [36,37]. As shown in Fig. 2, the up and down curves of viscosity were almost convergent in the whole shear rate range, showing that the time dependence effects were very limited, and the slurries were in its well deflocculated state.

In the presence of PEI and citric acid ammonium salt, 50 vol.% Si_3N_4 slurries were prepared for the subsequent tape casting process. Then the binder solutions (13 wt.%) and the plasticizer were added, the content of them was similar to that reported in literature [33]. The formulation of the tape casting slurries is shown in Table 2. After the addition of binder and plasticizer, the rheological properties were also characterized, see Fig. 3.

As shown in Fig. 3, Si_3N_4 slurries exhibited a shear-thinning behavior with slight time-dependent effects. This rheological behavior is requisite for the tape casting process [38]: during passing the blade, the viscosity decreases; and immediately after casting, the slurry retains its high viscosity, which could help to reduce the mobility of the constituents and preserves a homogeneous distribution of the ceramic particles.

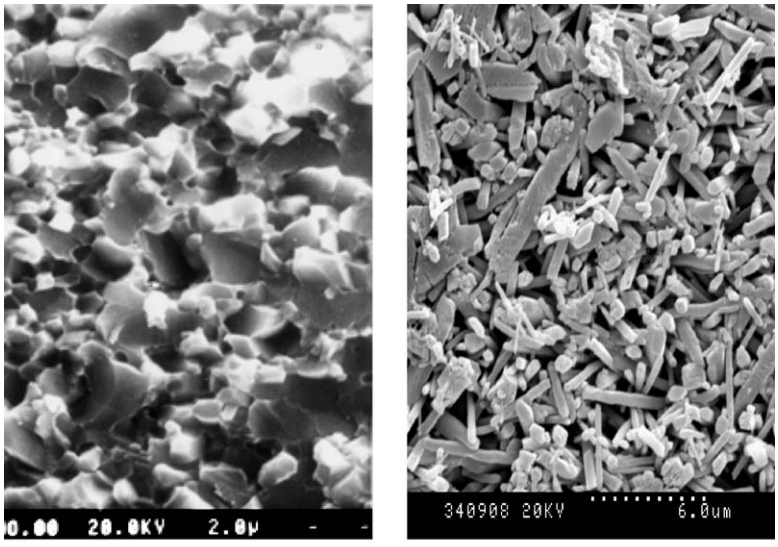


(a) Si_3N_4 powders

(b) As sintered Si_3N_4 samples

Fig. 5. XRD pattern of Si_3N_4 powders and sintered Si_3N_4 samples.

The microstructure of the green sheets is shown in Fig. 4. Both sides of the tapes had a smooth and homogeneous surface. The bottom surface, which was contacted with the carrier, was much smoother than the top one. The relative density of the green sheets was 52.1%. The tapes could be easily laminated due to the good flexibility. After lamination, binder removal and sintering by HP and SPS, the samples were further characterized in terms of microstructure and mechanical properties.



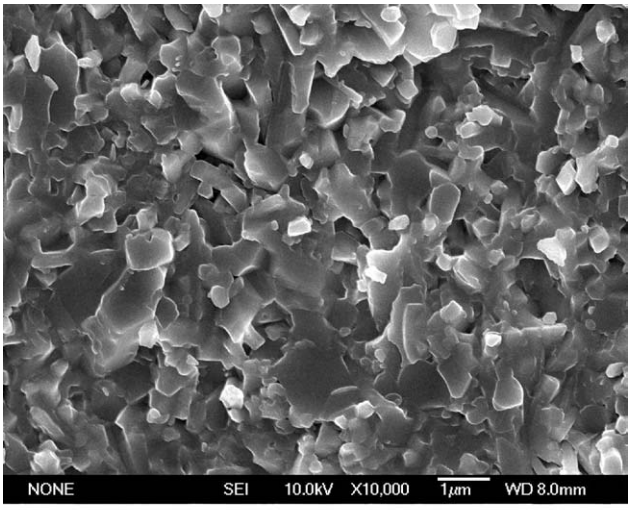
(a) (b)

Fig. 6. SEM images of Si_3N_4 samples sintered by HP (a) fracture surface and (b) polished and etched surface.

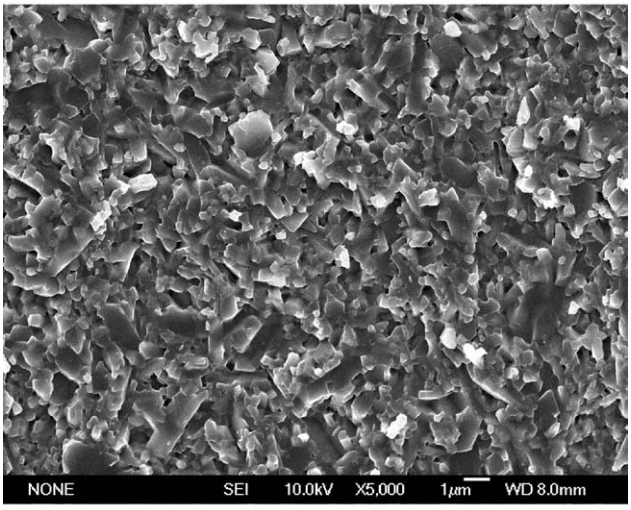
3.2. Microstructure and mechanical properties

XRD analysis of the starting Si_3N_4 powders and the sintered Si_3N_4 ceramics is shown in Fig. 5. In the starting powders, there are 80 wt.% β-Si_3N_4 and 20 wt.% α-Si_3N_4 phase. After sintering, only β-Si_3N_4 is observed without the second phase.

The microstructure of the hot pressed and SPS sintered Si_3N_4 samples are shown in Figs. 6 and 7. After sintering, a good homogeneity is observed for the HP and SPS sintered sample, and no single layers can be distinguished in the fractured surfaces. The grain size in the SPS sintering samples is smaller than that in HP sintered ones. Many rodlike grains appeared in the fracture surface of both samples. The rodlike grains can improve the fracture toughness and the reliability of the as produced ceramics, obvious through crack deflection, crack bridging and grain pullout.



(a) x10000



(b) x5000

Fig. 7. Fracture surface of Si_3N_4 samples sintered by SPS.

Table 3
Mechanical properties of Si_3N_4 samples

Sinter method	Strength (MPa)	Toughness (MPa $m^{1/2}$)	Density (%)	Open porosity (%)
HP	725 ± 26	7.6 ± 0.4	3.18	0.28
SPS	650 ± 23	8.1 ± 0.3	3.15	0.22

The fracture mode is primary an intergranular type. It is interesting that the sample sintered by SPS showed a preferring growth of elongated Si_3N_4 grains although it is sintered very quickly and soaked for only 3 min.

The mechanical properties of Si_3N_4 samples were shown in Table 3. Si_3N_4 samples under different sintering conditions exhibit different properties. The bending strength of HP samples (725 MPa) was higher than that of the SPS samples (650 MPa). However, the fracture toughness of the HP samples was lower than the SPS ones. The density of both samples was similar.

This difference in mechanical properties can be well correlated to the microstructure of Si_3N_4 sample. The higher fracture toughness of SPS samples can be related to the smaller grain size of them. However, for SPS sintering, due to the quick densification process, some pores will be trapped in the sample and lead to the decrease in density. Consequently, the bending strength is decreased too.

4. Conclusions

Surface treatment can increase the surface charge density of Si_3N_4 particles in basic pH region. Si_3N_4 suspensions exhibit well stabilized state in the presence of sintering additives. After tape casting and drying, both sides of green sheets were smooth and homogeneous. Both HP and SPS methods were proved to be effective for densifying Si_3N_4 samples. The sintered samples exhibited a homogeneous microstructure. Si_3N_4 samples sintered by SPS exhibited a higher fracture toughens while a lower strength than that sintered by HP.

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