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Preparation of Si_3N_4 ceramics with high strength and high reliability via a processing strategy

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Abstract

In this study, the preparation of Si_3N_4 ceramics with high mechanical reliability is investigated. The influences of several processing steps on the bending strength and the Weibull modulus are reported including: (i) coating of the Si_3N_4 powder with its sintering aids, (ii) oxidation of the coated powder, (iii) cold isostatic pressing, (iv) gelcasting of the green bodies and (v) gas pressure sintering. It was found that all the aforementioned steps contribute to improvements of strength and reliability of Si_3N_4 ceramics. Via an optimised processing strategy, Si_3N_4 ceramics with a bending strength and a Weibull modulus as high as 944.7 ± 29.5 MPa and 33.9, respectively, could be prepared. Additionally, it was also found that surface modifications, i.e. coating and oxidation of Si_3N_4 powder, increased the rheological properties of the powder suspension in aqueous media, which is favourable for in situ colloidal forming such as gelcasting.

Keywords: Gas pressure sintering; Gelcasting; Mechanical properties; Powders-pretreatment; Pressing; Si_3N_4

1. Introduction

Silicon nitride based ceramics have various excellent properties covering chemical resistance, light weight and excellent mechanical performance at both ambient and elevated temperatures. Therefore, they have attracted an increasing interest as structural materials.[1,2] They have already been put into practical use as e.g. in cutting tools, ball bearings, valves, and turbocharger rotors.[3] However, further fields of application in structural components will be explored, if the reliability of Si_3N_4 ceramics can be improved. Many effective processes, such as coating of the powder with its sintering aids[4] and colloidal forming[5] have been endeavoured respectively to narrow the distribution of fracture strength for Si_3N_4 ceramics. Si_3N_4 ceramics with Weibull modulus as high as 20 were prepared.[6,7] However, for wider engineering applications of this material, even higher Weibull moduli are requested.

The reliability of ceramics is dominated by many factors, such as characteristics of as-received materials, sintering aids, forming process, sintering procedure and surface preparation of test samples. First, the characteristics of the starting powder need to be considered. It is commonly believed that starting powders with smaller particle sizes and narrower particle-size-distribution result in ceramics with higher reliability.

To prepare ceramics with predominantly covalent-bonded powders such as silicon nitride, sintering aids, commonly Y_2O_3 and Al_2O_3, are necessary, since otherwise full density can be hardly achieved.[8] The sintering aids form a liquid phase at rather low temperature and, thus, lower the sintering temperature. Commercial silicon nitride powders always contain an oxygen content typically between 1 and 2.5 wt.%, since the powders are apt to be oxidised to silica or oxynitride in the presence of an oxygen or water-containing atmosphere because of the higher formation enthalpy of silica then that of silicon nitride.[9] During sintering, the silica naturally also acts as a sintering aid, which reacts with other sintering aids and plays an important role in determining the final mechanical properties of silicon nitride ceramics. Because of this, the oxygen content is one of the most important characteristics of silicon nitride powder. Natansohn[10] investigated the effect of powder surface

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modifications on the properties of silicon nitride ceramics and found for oxidised Si_3N_4 powder an oxygen concentration range at which a maximum of the fracture strength is reached.

With the addition of sintering aids, the system becomes a multi-component one. It is important that the sintering aids are blended with the silicon nitride particles as homogeneously as possible.[11] For this reason, mechanical milling of oxides as a means of adding the sintering aids has been commonly used. There are several previous studies on the coating of silicon nitride particles with its sintering aids by precipitation or co-precipitation reactions to improve the homogeneity of the distribution[11–14]. Wang[13] and Kulig[14] found that silicon nitride ceramics obtained from the coated powder attained a higher Weibull modulus compared to materials fabricated from mechanically milled powders with the same composition due to the uniform distribution of the sintering aids in case of coated powder. As a further advantage, the coated particles show the surface characteristics of the coating oxides, which may lead to an improved dispersion in colloidal forming[11] and consequently to increasing homogeneity of green and sintered bodies.

Colloidal forming techniques are commonly accepted to provide a powerful route to improve the reliability of ceramic materials. In his fundamental review, Lange[15] showed that several flaw size distributions, such as soft agglomerates, hard agglomerates and organic inclusions, could be eliminated by colloidal processing technology, which indicated that the reliability of ceramics could be improved by those processes. By centrifugal casting, Huisman[16] prepared alumina ceramics with Weibull modulus as high as 24.

Cold isostatic pressing is another forming process to prepare green bodies with high uniformity and sintering bodies with improved reliability. The application of multiaxial stress is especially favourable for green bodies with initially high heterogeneity and low density. Abe[17] investigated cold isostatic pressing of silicon carbide and found that the Weibull modulus increased with rising pressure during forming due to the achieved homogeneity and density of the green bodies.

Many sintering techniques, such as pressure-less sintering[18], hot pressing[4], hot isostatic pressing[19] and gas pressure sintering[20] were applied to prepare silicon nitride ceramics. It is well known (i) that it is generally difficult to obtain Si_3N_4 materials with full density by pressure-less sintering, (ii) that hot pressing results in anisotropic materials and (iii) that hot isostatic pressing is a costly technology. Gas pressure sintering outbalances these techniques to prepare Si_3N_4 ceramics with high reliability since it combines the advantages of preparing a material with high density, high homogeneity and at relatively low cost.

In the past five years, we tried to prepare high-reliability silicon nitride ceramics by colloidal forming processes. Good results were obtained by combining the coating of Si_3N_4 with its sintering aids and gelcasting[21] and by combining surface oxidation of the powder and gelcasting[22]. This paper aims to demonstrate our recent results of producing high-reliability Si_3N_4 via processing strategy using a combination of coating, oxidising, gelcasting, cold isostatic pressing and gas pressure sintering.

2. Experimental procedure

2.1. Materials and reagents

The silicon nitride powder used (H. C. Starck, M-11, Germany) consists to 91.7% β-phase. It exhibits a specific surface area of 12.85 $m^2\ g^{-1}$ and a mean particle size of 430 nm. The major impurities in the powder are C and O with 0.20 and 1.44 wt.%, respectively, and a total metal content (Fe + Al + Ca) of 0.058 wt.%. $Y(NO_3)_3{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$, co-precipitated with NH_3H_2O, were applied as precursors of Y_2O_3–Al_2O_3 sintering aids coated on the surface of silicon nitride particles. De-ionised water was employed as a reacting medium and, followed by alcohol, as a washing liquid in the coating process. Powders yttria and alumina (Jiangsu Wuxian Special Ceramics Plant, China) with a purity of 99%, were used as sintering aids for uncoated silicon nitride powder. Acrylamide [$C_2H_3CONH_2$] (AM) and *N,N′*-methylenebisacrylamide [$(C_2H_3CONH)_2CH_2$] (MBAM) were applied in the gelcasting process as monomers for polymerisation, which was initiated by an initiator, ammonium persulfate [$(NH_4)_2S_2O_8$], and accelerated by a catalyst, *N,N,N′,N′*-tetramethylethylenediamine (TEMED). All of the materials and reagents were chemically pure.

2.2. Surface modification of silicon nitride powder

To adjust the colloidal characteristics of the silicon nitride powder and the properties of the resultant ceramics, the as-received powder was coated with its sintering aids and then oxidised in air.

The coating process of Si_3N_4 particles with Y_2O_3–Al_2O_3 sintering aids is shown in Fig. 1. The precursors $Y(NO_3)_3{\cdot}6H_2O$ and $AlCl_3{\cdot}6H_2O$ were firstly dissolved in de-ionised water at a concentration of 0.4 mol/l followed by 2 h stirring. The resulting clear liquid is called the "coating solution". Secondly, as-received Si_3N_4 powder was dispersed in de-ionised water to prepare an aqueous Si_3N_4 suspension with solids loading of 10 wt.% and with a basicity of pH 10 adjusted by addition of $NH_3{\cdot}H_2O$. The suspension was then stirred and ultrasonically agitated for 4 h to achieve high homogeneity. Afterwards, a certain amount of coating solution was dripped with a rate of 10 drops/min to the suspension, which was vigorously stirred and kept constant at pH 10

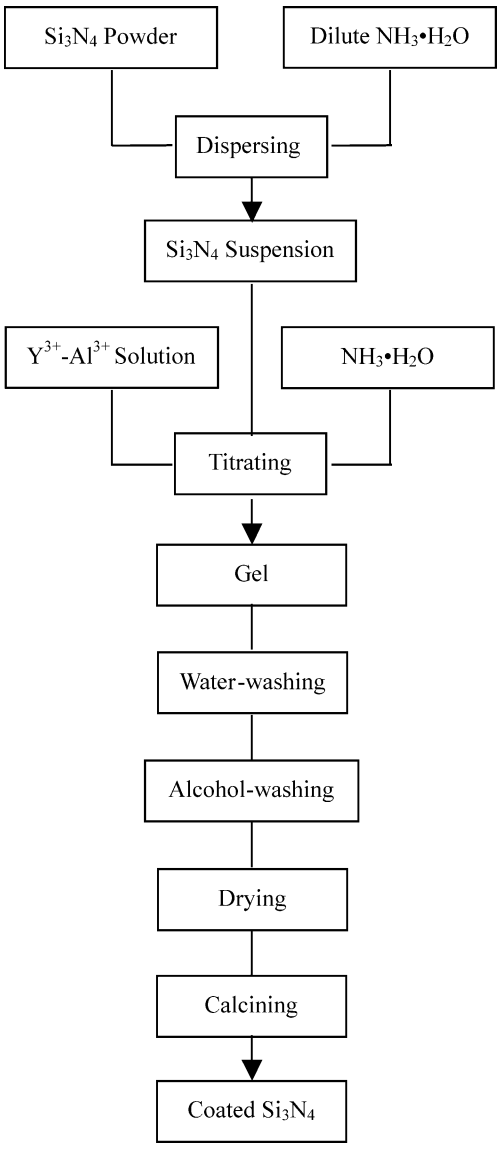


Fig. 1. Process for coating of Si_3N_4 powder with sintering aids.

by simultaneous addition of concentrated $NH_3{\cdot}H_2O$. The mixture was kept stirred for another 30 min after the coating solution was completely added. Nitrate and chlorine ions as well as de-ionised water were totally eliminated by washing and filtrating for 4 times with de-ionised water and another 4 times with alcohol. The resultant Si_3N_4 powder coated with yttrium-aluminium hydroxides was then dried at 80 °C for 24 h and passed through a sieve (100 mesh) followed by calcination in N_2 for 2 h. Pure yttrium-aluminium hydroxides were also prepared, analysed by differential thermal analysis (DTA), calcined at different temperatures and detected by X-ray diffraction to determine a proper calcination temperature for the Si_3N_4 powder. The content of sintering aids was adjusted to 7.5 wt.% Y_2O_3 and 2.5 wt.% Al_2O_3. After calcination, the coated silicon nitride powder was sieved with a 100 mesh and oxidised at 600 °C for 3 or 6 h in air to reach a certain oxygen content on the surface of the powder which corresponds to a silica layer. For comparison, as-received silicon nitride powder was also oxidised at 600 °C for 3 h in air.

2.3. Forming and sintering

Gelcasting was applied to prepare silicon nitride green bodies with high homogeneity, which can be further improved by subsequent cold isostatic pressing. The gelcasting process used was similar to that of previous studies[23,24]. First, Si_3N_4 powder with 7.5 wt.% Y_2O_3 and 2.5 wt.% Al_2O_3 was suspended with TMAH as dispersant in the premixed solution of AM and MBAM. The suspensions with a pH value of 10.5 ± 0.2 were degassed for 5 min after rolling for 24 h in polyethylene bottles using alumina balls as milling media. The slurry was degassed for another 3 min, when the initiator and catalyst were added. All the above operations were carried out at room temperature. Afterwards, the slurry was cast into a nonporous mold, which was then kept at 60–80°C. After consolidation, the green bodies were demolded and dried under controlled humidity to avoid cracking and non-uniform shrinkage due to rapid drying. Subsequent binder burnout was carried out at 600 °C for 3 h in air followed, if necessary, by cold isostatic pressing for 1 min at a pressure of 200 MPa.

Gas pressure sintering (GPS) of the green bodies was performed in a KCE furnace (FPW 180/250-2200-100-SP, KCE Corp., Germany). The GPS schemes were as follows: 1750 °C for 1.5 h under a nitrogen pressure of 0.3 MPa and then 1900 °C for 1.0 h (sample SN5), 1.5 h (samples SN1–SN4), 2.0 h (sample SN6) or 2.5 h (sample SN7) under a nitrogen pressure of 6 MPa with both heating and cooling rates of 10 °C /min.

2.4. Characterisation and reliability evaluation

The transformation temperature of yttrium-aluminium hydroxides to their oxides was tested by TGA/DTA (Setaram PC92, France). X-ray diffraction (XRD, D/Max IIIB, Rigaku, Japan) was applied to determine the completeness of the transformation. The nature of the coating layers was observed by transmission electron microscope (TEM, JEM-200CX, Japan). The oxygen content was measured by inert gas pulse, while the viscosity of the silicon nitride suspensions with different solids loading was examined by a rotational rheometer (MCR300, Physica, Germany).

Bulk densities of the resulting green bodies and ceramic bodies were measured via the Archimedes principle. The microscopic morphology of green bodies and the fracture surfaces were also observed by scanning electron microscopy (SEM, JSM-6301F, Japan). Specimens for bend tests with final dimensions $3\times4\times36$ mm were ground and polished longitudinally with diamond pastes to a finish of 0.5 μm and lightly bevelled on the

long edges of the tensile surface. Bending tests were performed on 20 specimens per batch using the three-point bending method with a 30-mm-span at a cross head speed of 0.5 mm/min. Weibull moduli were estimated based on the two-parametric Weibull distribution.

3. Results and discussions

3.1. Influence of surface modification on the colloidal properties of Si_3N_4 powder

Coating followed by oxidation is applied to modify the surface characteristics of Si_3N_4 powder, and, thus, its rheological performance. For the coating process, a proper calcination procedure should be determined for the transformation of Y–Al hydroxide to Y–Al oxide on the surface of the powder. DTA and XRD were selected for this aim. that The DTA curve of pure yttrium-aluminium hydroxides reveals an exothermic peak at 892 °C, which corresponds to the transformation temperature (Fig. 2). However, calcination of the hydroxides at 900 °C for 2 h in nitrogen does not result in crystalline oxides; only when calcined at 1000 °C for 2 h, the resulting products are clearly crystalline (Fig. 3).

TEM micrographs of Y–Al oxide coated Si_3N_4 particles are shown in Fig. 4. It can be noticed in this figure that a layer of nano-sized precipitates is closely attached to the surface of large Si_3N_4 particles and the thickness of precipitates varies from about 5 to 40 nm. A more careful observation of the figure shows that the surface of small Si_3N_4 particles is not completely covered by precipitates. This is a typical feature for the coating of sub-micron powder with nano-sized precipitates, since the smallest Si_3N_4 particles are also in the nano-size regime. However, colloidal characteristics and rheological properties of the surface-modified powder are still obviously adjusted.

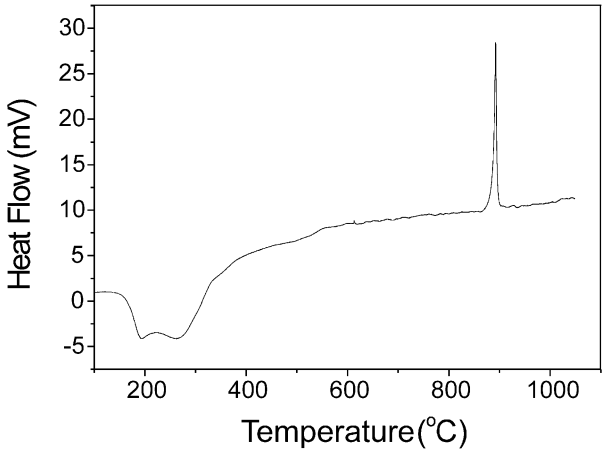


Fig. 2. TGA curve of transformation from Y–Al hydroxide to Y–Al oxide.

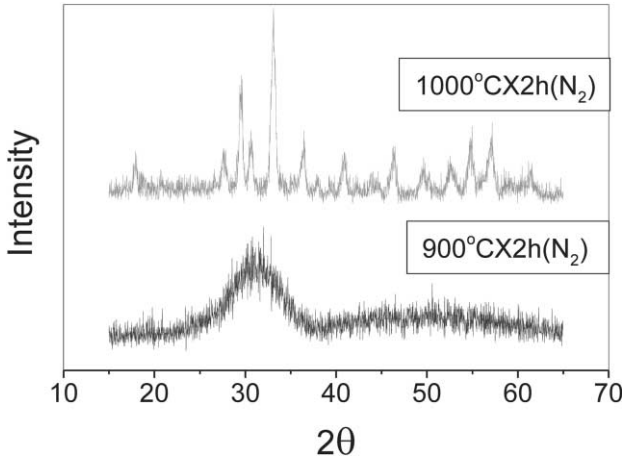


Fig. 3. XRD patterns of Y–Al hydroxides calcined at different temperatures.

As reported in previous studies,[21,25] the Zeta potentials of coated Si_3N_4 particles are rather complex. Unlike any curve of pH-dependent Zeta potentials for Al_2O_3, Y_2O_3 or Si_3N_4, the Zeta potential for coated Si_3N_4 powder possesses three isoelectric points (IEP), i.e. three "charge" reversals in the pH range, which indicates an inadequate coverage of Y–Al oxides on the surface of Si_3N_4 particles, as observed by TEM. Anyway, the dispersability of the powder could be improved by coating.[21] Previous studies also demonstrate that the dispersion of Si_3N_4 powder is enhanced after it is oxidised below 850 °C in air.[22] In the current study, it is found that the dispersity of the coated and oxidised (600 °C×3 h in air) powder is improved compared to the as-received state (Fig. 5). At a pH value of 10.5±0.2, the viscosity of slurries from coated and oxidised Si_3N_4 powder with the same solids loading in

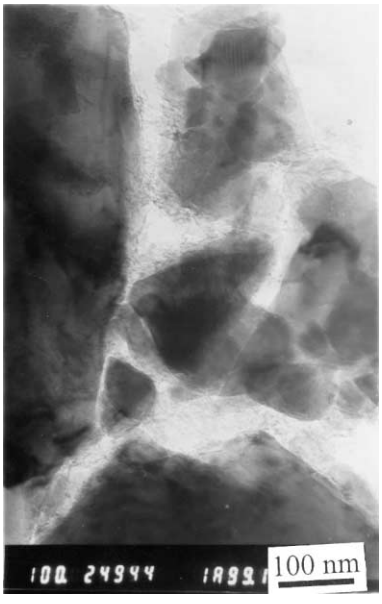


Fig. 4. TEM micrograph of coated Si_3N_4 particles.

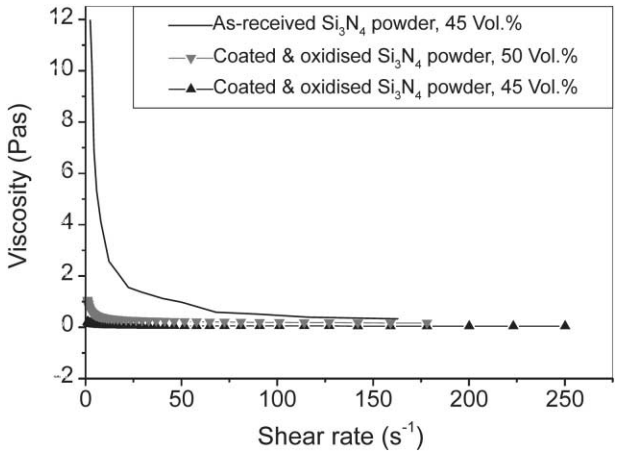


Fig. 5. Rheological curves for the suspensions of as-received and surface modified (coated and oxidised) Si_3N_4 powders.

comparison with original Si_3N_4 slurry is greatly decreased. When the solids loading is increased up to 50 vol.%, the viscosity of the coated and oxidised Si_3N_4 slurry is still much lower than that of the as-received Si_3N_4 slurry although it has a lower solids loading of 45 vol.%. The reason is complex, but it is commonly believed that oxides on the surface of non-oxides such as Si_3N_4 lead to surface properties similar to that of oxides, which exhibit good dispersability in aqueous media.[3,26]

3.2. Influences of coating, CIP and oxidation on the properties of Si_3N_4 ceramics

In previous studies,[21,22] it was found that relative to dry pressing of original Si_3N_4 powder with mixed sintering aids, both gelcasting of Si_3N_4 powder with coated sintering aids and gelcasting of oxidised powder with mixed sintering aids were able to prepare Si_3N_4 ceramics with higher bending strength and reliability. So it was concluded that coating and oxidising as well as gelcasting is beneficial for the resulting properties of the material. In this study, we combined coating, oxidation, gelcasting and CIP to prepare Si_3N_4 ceramics and to investigate their influences on the final properties of the material. There were four batches of Si_3N_4 specimens, each one corresponding to a processing strategy listed as follows:

SN1 : mixing sintering aids + oxidation (600 °C × 3 h) + gelcasting + GPS

SN2 : coating sintering aids + oxidation (600 °C × 3 h) + gelcasting + GPS

SN3 : coating sintering aids + oxidation (600 °C × 3 h) + gelcasting + CIP + GPS

SN4 : coating sintering aids+oxidation (600 °C × 6 h) + gelcasting + CIP + GPS

The GPS scheme was 1750 °C for 1.5 h under a nitrogen pressure of 0.3 MPa and then 1900 °C for 1.5 h under a nitrogen pressure of 6 MPa. The processing strategies and their results are shown in Fig. 6 and Table 1.

The surface oxygen contents of the Si_3N_4 powders in Table 1 do not include those of Y–Al oxides coated on the surface of the powder. The original Si_3N_4 powder contains 1.44 wt.% oxygen, 0.72 wt.% in the bulk and

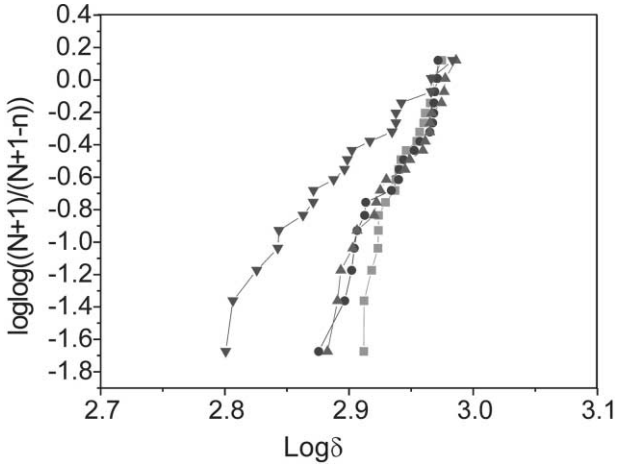


Fig. 6. Properties of Si_3N_4 ceramics with different processing schedules. ▼: SN1, ▲: SN2, ●: SN3, ■: SN4.

Table 1
Results for influences of coating, oxidizing and CIP on properties of Si_3N_4 ceramics prepared by gelcasting

No.	Surface oxygen content of Si_3N_4 powder (wt.%)	Adding sintering aids by	CIP	Relative density (%)		Bending strength (MPa)	Weibull modulus
				Green bodies	Sintering bodies		
SN1	2.94 (600 °C×3 h)	Mixing	No	47.7	99.0	773.5±95.1	8.6
SN2	2.73 (600 °C×3 h)	Coating	No	47.7	98.9	814.5±68.5	12.4
SN3	2.73 (600 °C×3 h)	Coating	Yes	64.2	98.8	868.9±59.8	15.1
SN4	3.64 (600 °C×6 h)	Coating	Yes	64.2	99.2	877.2±40.5	22.8

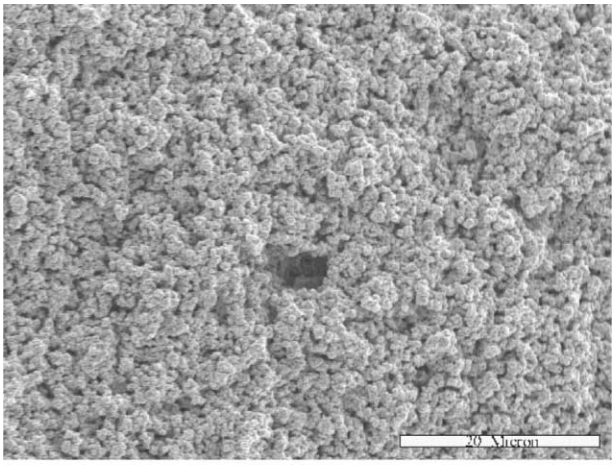
0.72 wt.% on the surface. When oxidised at 600 °C for 3 h in air, the oxygen content on the surface of the original powder is up to 2.94 wt.%, while that of the coated powder is up to 2.73 wt.%. The latter is a little smaller than the former, which indicates that the coated layer on the surface of Si_3N_4 powder inhibited to a certain extent the oxidation of the powder. The restraint of existing layers on the further oxidation of Si_3N_4 powder is also illustrated by the influence of the oxidation time at 600 °C: for 3 and 6 h the increments are not proportional to the oxidation times.

Even though there is a small difference in the oxygen contents of the Si_3N_4 powders for SN1 and SN2, it can be assumed that the main contributor to higher reliability of SN2 relative to SN1 is the addition of sintering aids via coating. There are three advantages of coating Si_3N_4 powder with its sintering aids for aqueous gelcasting : (1) modification of the surface characteristics of Si_3N_4 particles to improve their dispersability and, thus, the homogeneity of its slurry; (2) uniform distribution of sintering aids in green bodies to promote sintering processes;[3] (3) partial separation of the surface of Si_3N_4 powder from the aqueous media with high basicity to avoid the formation of macro-pores in green bodies.[21] Those advantages result in uniform Si_3N_4 green bodies, homogeneous sintered bodies and consequently high reliability of the material.

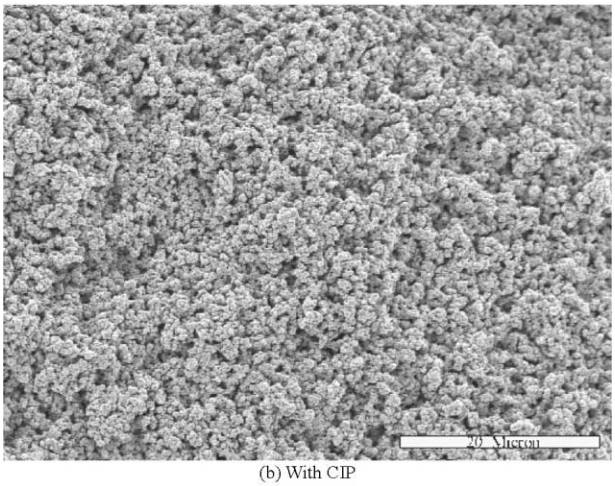
In Table 1, the influence of CIP on bending strength and reliability of Si_3N_4 ceramics gel-cast from coated and oxidised Si_3N_4 powder becomes evident by comparing SN2 and SN3. Bending strength and Weibull modulus of the former are 814.5 ± 68.5 MPa and 12.6, while those of the latter are measured to be 868.9 ± 59.8 MPa and 15.1, which indicates that CIP obviously improves the reliability of the material. This can be explained by analysing the microstructures of green bodies obtained with and without CIP, as shown in Fig. 7. Si_3N_4 powder is chemically unstable in aqueous media, especially in alkaline solution. There were millimeter-sized macro-pores in Si_3N_4 green bodies formed during gelcasting if the processing condition was not properly controlled. By decreasing the pH value of the slurry and coating of the Si_3N_4 powder with its sintering aids, green bodies free of macro-pores were prepared.[27] However, there are still some micron-sized pores in the green body, as shown in Fig. 7(a). After CIP, not only the micro-pores in the bodies disappears, but also the relative density of the green bodies increases, as can be seen from Fig. 7(b), both of which further optimises the homogeneity of the green bodies and final ceramics. Accordingly, the reliability of the material rises.

Table 2
Properties of Si_3N_4 ceramics with various second holding time in two-stage GPS

No.	The second hold time (h)	Relative density (%)	Bending strength (MPa)	Weibull modulus
SN5	1.0	98.9	915.9 ± 52.0	18.7
SN4	1.5	99.2	877.2 ± 40.5	22.8
SN6	2.0	99.0	944.7 ± 29.5	33.9
SN7	2.5	98.0	804.2 ± 77.9	10.8



(a) Without CIP



(b) With CIP

Fig. 7. Micrographs of coated and oxdized Si_3N_4 green bodies by gelcasting.

Comparison of SN3 and SN4 reveals the influence of the oxygen content of Si_3N_4 powder on bending strength and reliability of Si_3N_4 ceramics, as shown in Table 1. The bending strength of Sample SN3 and SN4 are almost the same, while the Weibull modulus of the latter is 22.8, which is much more than that of the former as 15.1. Just like coating and CIP, oxidisation influences much on the reliability rather than the strength of the Si_3N_4 based ceramics. The coated Si_3N_4 powders for SN3 and SN4 were oxidised at 600 °C for 3 and 6 h in air, which leads to a surface oxygen content of 2.73 and 3.64 wt.%, respectively. The surface oxygen content of Si_3N_4 powder is due to silica, which also acts as a sintering aid and plays an important role on sintering and densification of green bodies and the properties of the ceramic. Natansohn [10] investigated the role of surface oxygen and

found that there was an optimal oxygen content at which the fracture strength of Si_3N_4 reaches its maximum. He found that the approach was only effective when the oxygen content was adjusted by thermal treatment, i.e. oxidation of silicon nitride powder. Other means of oxygen adjustment, such as silica additions or chemical and physical treatment, did not result in Si_3N_4 based ceramics of equivalent properties[10]. Whether this is the case for the material under investigation remains to be clarified in future. Further investigations are also needed to ascertain the optimal surface oxygen content of the coated Si_3N_4 related to maximum strength and reliability of Si_3N_4 ceramics. However, the sintering scheme was optimised in this regard, as discussed below.

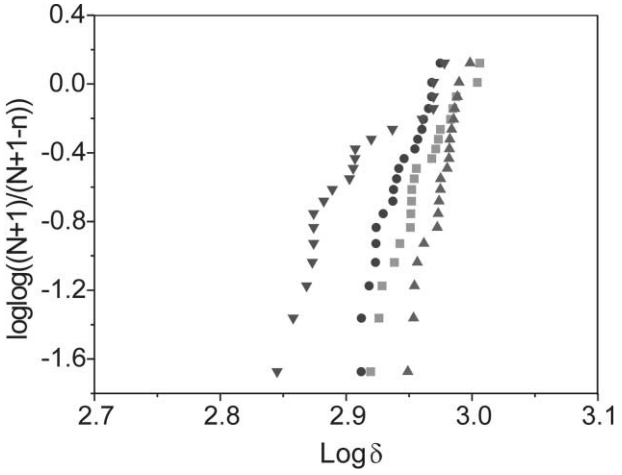
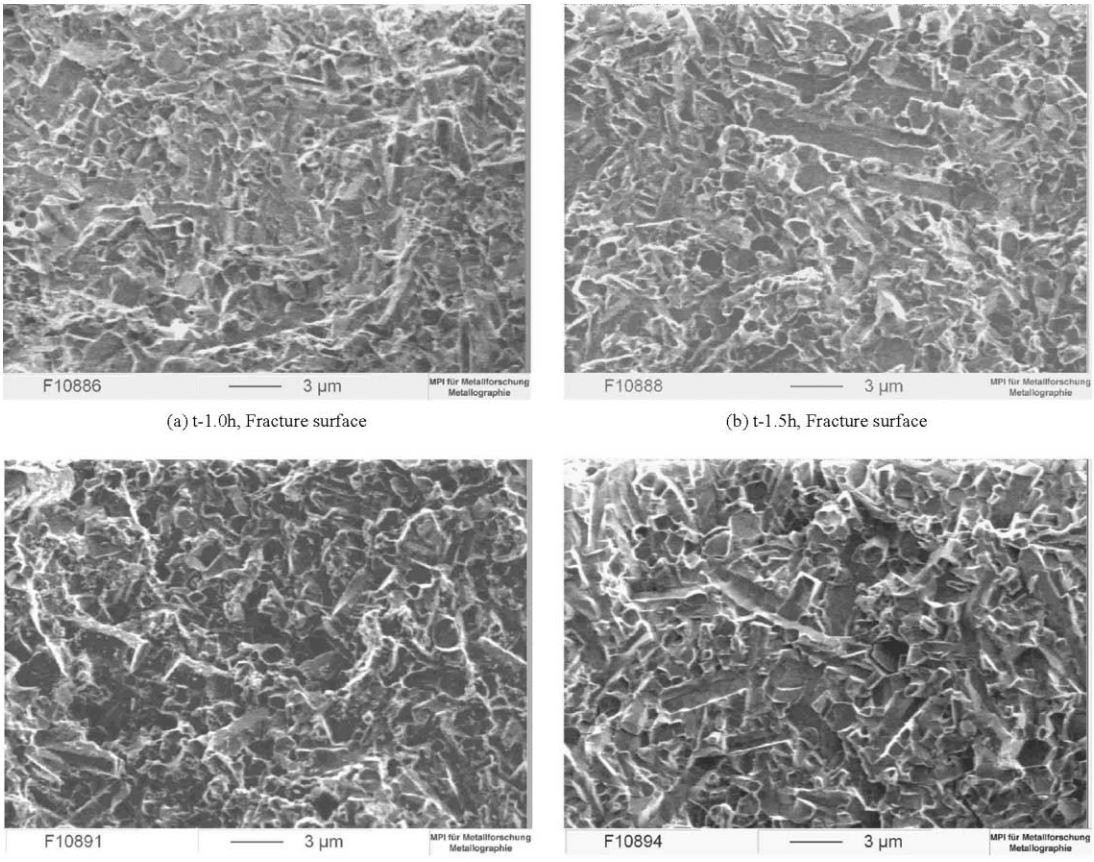


Fig. 8. Properties of Si_3N_4 ceramics with different holding times in two-stage GPS. ■: SN4, ●: SN5, ▲: SN6, ▼: SN7.

3.3. Influence of GPS scheme on the properties of gel-cast Si_3N_4 ceramics

In order to determine an optimal GPS scheme for Si_3N_4, three additional schemes with various second holding times were selected beside that of SN4, which are as follows: 1750 °C×0.3 MPa (N_2)×1.5 h + 1900 °C× 6 MPa (N_2) ×1.0 h (SN5), 2.0 h (SN6) and 2.5 h (SN7). The resulting properties of Si_3N_4 sintered with those schemes are shown in Table 2 and Fig. 8.

As can be seen from Table 2, a maximal bending strength as high as 944.7 MPa (Batch SN6) could be achieved, and the differences in bending strength for SN4, SN5 and SN6 are relatively small. There is also a maximum of the Weibull modulus as high as 33.9 (Batch SN6), but the differences in Weibull modulus are relatively large. This means that in the current investigation the sintering scheme has much influence on the Weibull modulus, but little effect on bending strength of



(a) t-1.0h, Fracture surface

(b) t-1.5h, Fracture surface

(c) t-2.0h, Fracture surface

(d) t-2.5h, Fracture surface

Fig. 9. Micrographs of Si_3N_4 ceramics with various second holding times t in the two-stage GPS.

the material. Micrographs of fracture surfaces of the ceramics are shown in Fig. 9. It can be seen from (a) to (d) in Fig. 9 that there is a more obvious evidence of roughness and pull-out on the fracture surface of the sample SN6 with the highest Weibull modulus. According to previous studies, high Weibull modulus is theoretically and experimentally connected to a strong R-curve effect.[28,29] Previous studies also found that bridging and pullout was one of major reasons for the R-curve behaviour.[30,31] Therefore, both toughening mechanisms are proposed to be also dominant factors for the high reliability of Si_3N_4 ceramics observed in our investigation. However, further investigations have taken to explore the mechanism responsible for the high reliability of this material.

4. Conclusions

Surface modification of silicon nitride powder, i.e. coating the powder with its Y–Al oxide sintering aids and oxidation of the coated powder, obviously increases the dispersability of the powder in aqueous media, because the surface of the treated powder is similar to that of oxides, which exhibit good dispersion in aqueous solution. The coating process and proper scheme of oxidation ultimately improve the bending strength and reliability of silicon nitride ceramics fabricated by gelcasting and GPS. CIP of gel-cast green bodies from coated and oxidised Si_3N_4 powder and an optimised scheme of GPS further improves the properties of the material. Silicon nitride ceramics with three-point bending strength and two-parameter Weibull modulus as high as 944.7 ± 29.5 MPa and 33.9 were prepared with the optimal processing strategy combining (i) coating of the starting Si_3N_4 powder with sintering aids, (ii) oxidation of the coated powder with a proper scheme, (iii) gelcasting the surface-modified powder, (iv) CIP of the gel-cast green bodies after binder burnout and (v) optimised GPS.

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