

Characterization of Si₃N₄ powders in aqueous dispersions

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Abstract

α - Si₃N₄ can easily oxidize when exposed in air atmosphere or other oxidizing environment. The chemistry of Si₃N₄ particle surfaces can change by different synthesis routes and also by subsequent processing steps. To avoid this oxidation is a challenge when Si₃N₄ powder is shaped by slip casting process from aqueous suspension. This study shows the variations on Si₃N₄ powder surface after slip casting process using x-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HTEM) on the green compacts. The results show that the dispersant used during the preparation of the slurry can reduce the level of oxidation of the Si₃N₄ particles when processing in aqueous solutions.

INTRODUCTION

The combination of properties such as high strength at room temperature, low coefficient of thermal expansion, good wear resistance and low density with respect to the refractory metals has made the Si₃N₄ one of the most studied ceramic structural materials in the last 15 years. However, the correlation between Si₃N₄ powder properties and the characteristics of the resulting ceramic products is not well established. Several producers can offer high-purity Si₃N₄ powders but this is not necessarily result in materials with enhanced properties. One aspect to be considered is that the change on the powder surface during processing by different routes can affect the Si₃N₄ final properties[1-4].

Si₃N₄ powder can be easily oxidised upon exposure to air or any other oxidizing environment[4-6]. Raider et al.[5], in a X-ray photoelectron spectroscopy (XPS) study dealing with the oxidation behaviour of silicon nitride films, suggested that there is a rapid initial oxidation of its surface upon exposure to air even at room temperature. Their data revealed that there is always some amount of oxygen in the film even after chemical etching with HF.

Colloidal processing techniques are commonly accepted to provide a powerful route to improve the reability of ceramic materials. This is an attractive route to process Si₃N₄ which supply different possibilities to obtain pieces with complex shapes, for example by slip casting or pressure slip casting. Many authors have studied the colloidal behaviour of silicon nitride slips either in water or in organic media[7-10]. They have shown that similar powders behave differently depending on many processing parameters. In this sense some pretreatments strategies have been used to try to ensure that the properties of the dispersions reflect those of the powders in a pristine state or control the oxidation level on the surface of Si₃N₄ particles[8]. However the oxygen adjustment on the surface, such as silica additions or chemical and physical treatment always does not result in ceramics with equivalent properties. In other words, it is not possible avoid some oxidation effects from mixing, drying forming or other processing steps[6,11].

Slip casting has been reported elsewhere to be a suitable process to attain materials with high green densities and microstructural homogeneity[6,7]. However, to obtain a well dispersed, uniform and highly concentrated slip of a submicron Si₃N₄ powder in water with sintering aids is a particular critical step.

The aim of the present work is to investigate the Si₃N₄ powder surface during slip casting forming process. Compositions and chemical state of the atoms at the surface generated during processing are evaluated by X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HTEM) evaluate compositions and chemical state of the atoms at the surface generated during processing.

MATERIALS AND METHODS

A commercial silicon nitride powder was used (Herman C. Starck, LS 12SX, Germany). The main characteristics of starting powder are summarised in [Table I](#). The particle size distribution was measured using a laser particle size analyser (Coulter L.S. 130, USA). The specific area was calculated by single point N₂ adsorption method (Monosorb, Quantachrome, USA) and the total oxygen content by inert gas fusion technique (LECO, EF 400, USA).

Table 1. Characteristics of the Si₃N₄ powders

Impurities (wt%)	C = 0.18; O = 2.04 Fe, Ca, Al < 0.01
Specific surface area (m ² /g)	18
Mean particle size (µm)	0.7

In slip casting procedure, a powder is dispersed in a liquid medium, which is responsible for the formation of a charged double layer around the particles. This double layer controls the electrochemistry of the system and thus the stability of the suspensions. Consequently, the chemistry at the surface is strongly dependent on the dispersing conditions, i.e. the solvent and the dispersant play a key role in the charge behaviour.

The colloidal stability of the Si₃N₄ was studied in terms of zeta potential to determine the corresponding isoelectric points (i.e.p.). A laser Doppler equipment (DELSA, Coulter, USA) was used.

Deflocculation studies on silicon nitride aqueous slip were performed testing different kinds and concentrations of deflocculants. A number of polyelectrolytes were tested, as well as strong bases, such as sodium hydroxide (NaOH) and tetramethylammonium hydroxide (TMAH) also were tested trying to stabilize the concentrated slip by means of both electrosteric and

electrostatic mechanisms.

The slips were homogenized by vigorous mechanical stirring using a high-speed mixer (Silverson L2R, UK), for 3 min. Cast green bodies were performed using aqueous slips up 65 wt% solids and slip cast onto plaster of Paris. Cylindrical bars with 5 mm diameter were prepared and furtherly dried in air for 24h.

The surface analysis of the powders was performed before and after casting using X-ray photoelectron spectroscopy (XPS). Photoelectron spectra were obtained using a Fisons ESCALAB MkII electron spectrometer employing Mg K α X-ray (photon energy, $h\nu = 1253.6$ eV), and an electron take-off angle of 45°. The base pressure of the spectrometer was typically 10^{-7} Pa. The X-ray gun was operated at 12 kV and 10 mA, corresponding to a powder of 120 W. A survey spectrum (50-1150 eV) was recorded for each sample (single scan) followed by Si2p, N1s, O1s and C1s regions where appropriate (60 scans). The analyser was operated in fixed analyser transmission (FAT) mode with a pass energy of 50 eV (survey spectrum) and 20 eV (individual peaks). Atomic percentage values were calculated from the peak areas using sensitivity factors provided with the data system and background subtraction. The accuracy of the XPS quantitative analysis, as derived for duplicate analysis, was within $\pm 4\%$. Spectra were corrected for sample charging by referencing photoelectron peaks to C-C/C-H at 284.9 eV. The precision in the binding energy of the XPS lines, obtained as average of at least two measurements, was estimated as ± 0.1 eV.

The particles were studied by transmission electronic microscopy (Jeol 2010, at 200 KeV) equipped with an ultrathin window energy dispersive X-ray detector (EDS). The particles powder were putting directly on the copper grid.

RESULTS AND DISCUSSION

The isoelectric point for starting silicon nitride powder is located at pH 8.5, which suggests a relatively low oxidation degree[12]. The electrical charges providing electrostatic stabilization in aqueous suspensions arises from surface dissolution of the particles promoting the development of a double layer. The strong surface reactions of Si₃N₄ with H⁺ and OH⁻ in water involve different kinds of interactions, such as the formation of silica and silanols, ammonia and amina-related reactions, and dissolution and readsorption of impurities. The dominant species resulting from these reactions are Si(OH)₂⁺ and Si₂NH₂⁺ for pH lower than the i.e.p. and SiO⁻ and Si₂N⁻ for pH higher than the i.e.p.[13]. The XPS analysis for the as received powder, reveals that both Si2p and N1s peaks can be split into doublets. [Figs. 1a](#) and [1b](#) show the Si2p and the N1s peaks as registered and after splitting. The location of the Si2p peak may change from 99.3 eV for Si (elemental) to 101.4 eV for Si-N bonds and 103.7 eV for Si-O bonds[14]. The location of the peaks at intermediate values of binding energy (BE) suggest that both silazane and siloxane species are present at the powder surface. [Table II](#) shows the obtained BE values and respective concentration as calculated in [15].

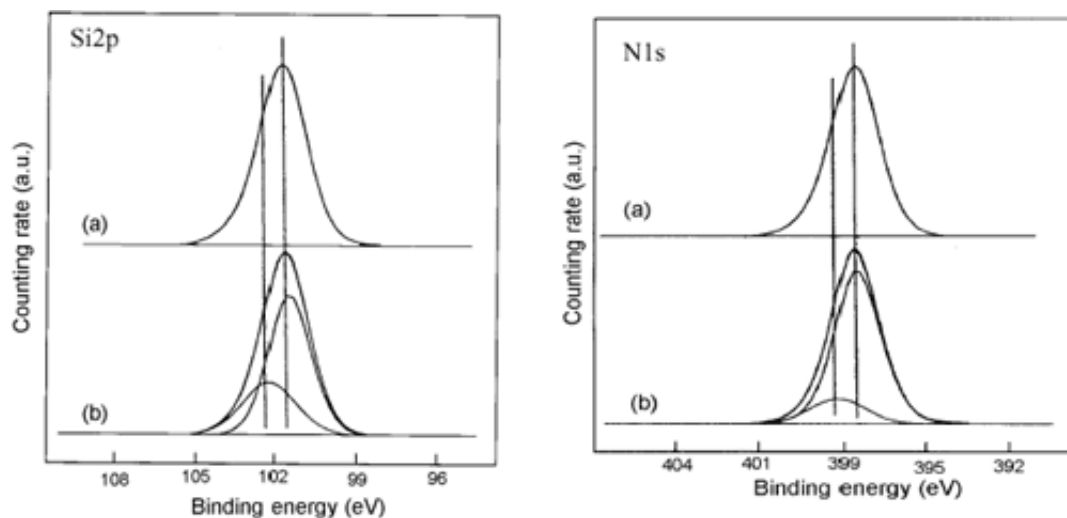


Figure 1: Core level spectra for the Si₃N₄ powder as registered and after curve fitting to two components (nitride and oxynitride) for Si2p peak (a) and N1s peak (b).

Table II: Assignment of the XPS peaks of silicon nitride and surface concentration of the elements.

Peak	BE (eV)	Percentage	Species	Atomic Ratio
Si2p	101.6	72	Si ₃ N ₄	28
Si2p	102.6	28	SiO _x N _y	11
N1s	397.6	80	Si ₃ N ₄	41
N1s	398.6	20	SiON(H)	10
O1s	532.7		SiON(H)	

The results show that the powder has around 10 at% of anionic oxidizing on surface in good agreement with the determined i.e.p.

Different commercial polyelectrolytes were tested in order to provide electrosteric stabilization to the slip. [Table III](#) summarizes in a qualitative way the aspect of the corresponding slips, as well as that of slip prepared with strong bases (NaOH and TMAH). As observed in the Table, some electrolytes could be used for the preparation of stable slips with solid content up to 50 wt%. However, for casting operations, higher solid loads are desirable. Stable slips with solids loading of 65wt% can only prepared using strong bases, that is by means of a pure electrostatic stabilizing mechanism. As reported below, the optimum conditions for preparation of the aqueous slips are a high pH value by action of a strong base. TMAH and NaOH have been considered although the introduction of Na⁺ is not convenient because it forms low viscosity liquids during sintering. However, the rheological behaviour is also good for casting.

Table III: Dispersion behaviour of Si₃N₄ with different dispersants.

<i>Dispersant</i>	<i>Concentration</i> (wt.%)	<i>Suspending</i> <i>Liquid</i>	<i>PH</i>	<i>Maximum</i> <i>Solids (wt%)</i>	<i>Stimated</i> <i>Viscosity</i>	<i>Obs.</i>
<i>DOLAPIX</i>	1	H ₂ O	8.4	33.2	High	After 3h
<i>PC - 33*</i>	2	H ₂ O	9.4	33.5	Very high	Mixing
<i>DARVAN</i>	1	H ₂ O	7.5	48	High	—
<i>C #</i>	2	H ₂ O	9	45	Very high	—
<i>KV5080*</i>	0.5	H ₂ O	7.2	28.1	High	—
<i>KV5088*</i>	0.5	H ₂ O	10	44.8	High	—
<i>KV9021*</i>	2	Ethanol	—	50	Very high	12 hours
<i>KV9027*</i>	2	Ethanol	—	50	Very high	ball milling
<i>TMAH</i> □	1	H ₂ O	11-12.5	70	Very low	—
<i>NaOH</i>	—	H ₂ O	11	70	Very low	—

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In previous works[15], it has been stated using the XPS analysis that green bodies obtained by aqueous slip casting using TMAH as deflocculant had not a higher oxidation degree than other samples prepared by isostatic pressing using alcohol as homogenizing media. The objective here is to compare the surface state behaviour of silicon nitride bodies processed in water using either TMAH or NaOH as dispersing agents.

The XPS analysis of green cast samples obtained from slips dispersed with one of these mentioned dispersants reveals noticeable differences between them. [Figs. 2](#) and [3](#) show the Si2p and N1s peaks of XPS analysis made on the greens prepared with TMAH and NaOH, just as registered and after deconvolution. In the samples deflocculated with TMAH a major contribution of Si-N bonds and smaller peaks for the oxydized species are found. However, the signals obtained for slip cast samples deflocculated with NaOH are inverted, showing a higher contribution of the oxydized form.

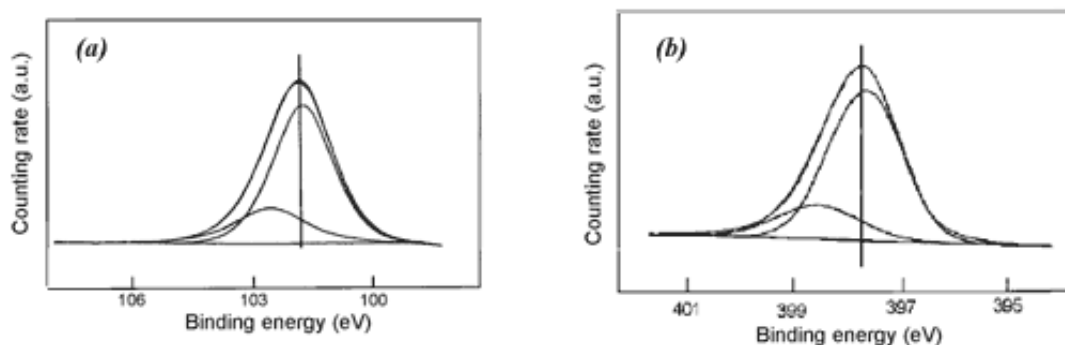


Figure 2. (a) Si2p and (b) the N1s peaks of Si₃N₄ samples after slipped from TMAH deflocculated..

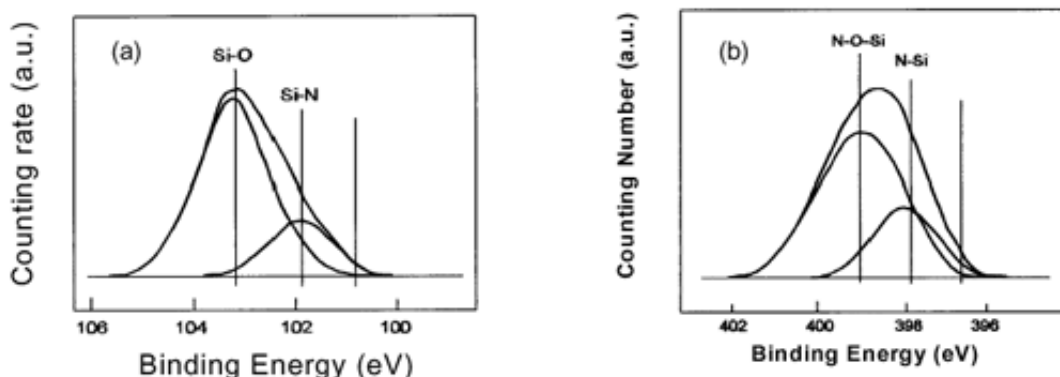


Figure 3. (a) Si₂p and (b) the N₁s splitting peaks Si₃N₄ powder after slip casting from NaOH dispersed.

The location in the spectra of the different contributions of the Si₂p and N₁s peaks for both samples is reported in [Table IV](#). This surprising result suggests that aqueous slip casting promotes a rapid oxidation of silicon nitride, as usually thought. The use of TMAH protects the particle surface and impedes a progressive oxidation. In order to demonstrate the protective screen effect of TMAH, the surface of the starting powder and that of the powder obtained from a slip deflocculated with TMAH were analyzed by high resolution transmission electron microscopy (HRTEM).

Table IV: Binding energy of Si₂p and N₁s peaks of TMAH-treated and NaOH-treated samples in the XPS spectra.

Sample	Si ₂ p (eV) ^a	N ₁ s (eV) ^a
TMAH-treated	101.6 (65)	397.5 (87)
	102.3 (35)	398.5 (13)
NaOH-treated	101.9 (29)	397.6 (26)
	103.2 (71)	398.6 (74)

^a Percentages are given in brackets.

[Figs. 4](#) and [5](#) show the microstructure, the X-ray microanalysis and the selected area diffraction spectra obtained from the powder as received and the powder obtained from the slip deflocculated with TMAH samples, respectively. In the starting powder, the existence of a layer surrounding the particle surface can be observed. The EDS in this area reveals the presence of O, N, and Si, that is, oxidized species, which is in good agreement with the XPS analysis. In the case of the powder suspended in TMAH this layer is not appreciable and the EDS only detects the presence of N and Si. This demonstrates the lower oxidation degree of the TMAH-treated powder.

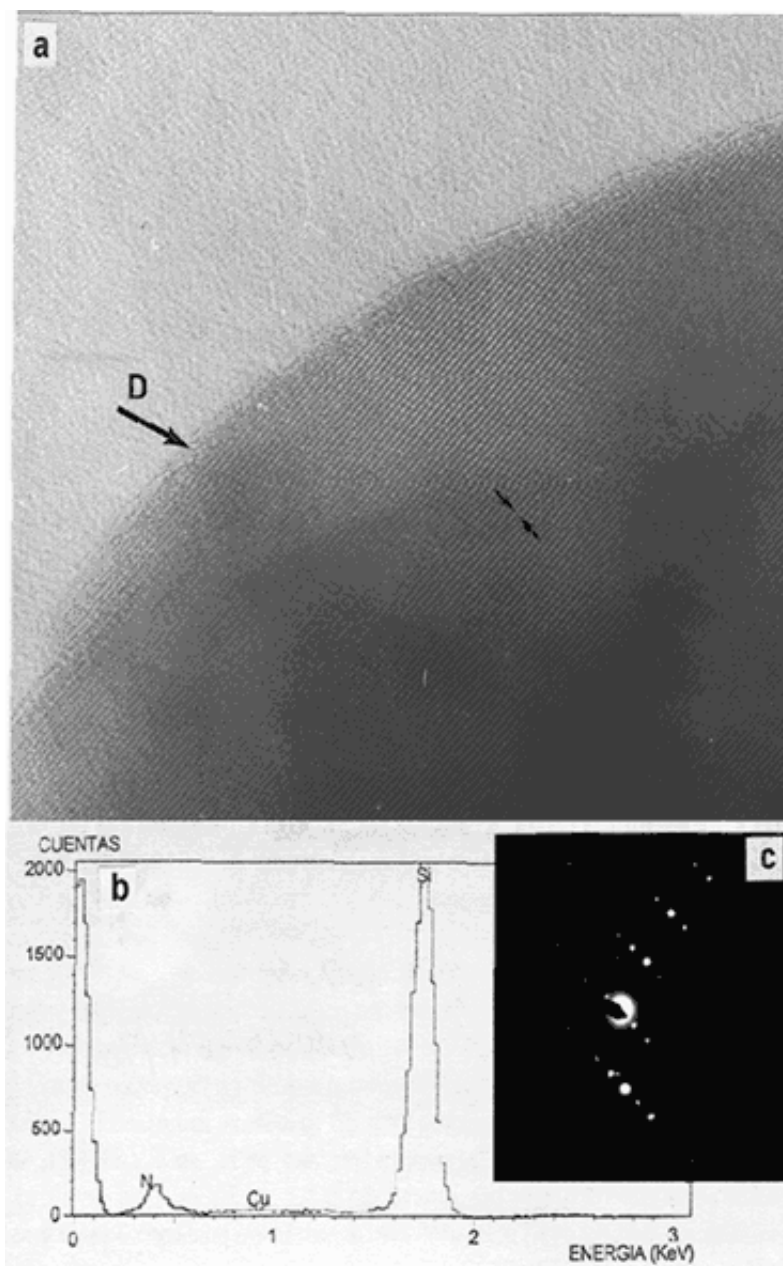


Figure 4 - Microstructure (a) and microanalysis by EDX (b), SAD (c), in the region D, obtained by HRTEM from as received powder. (interplanar distance, [001] 6,7 Å).

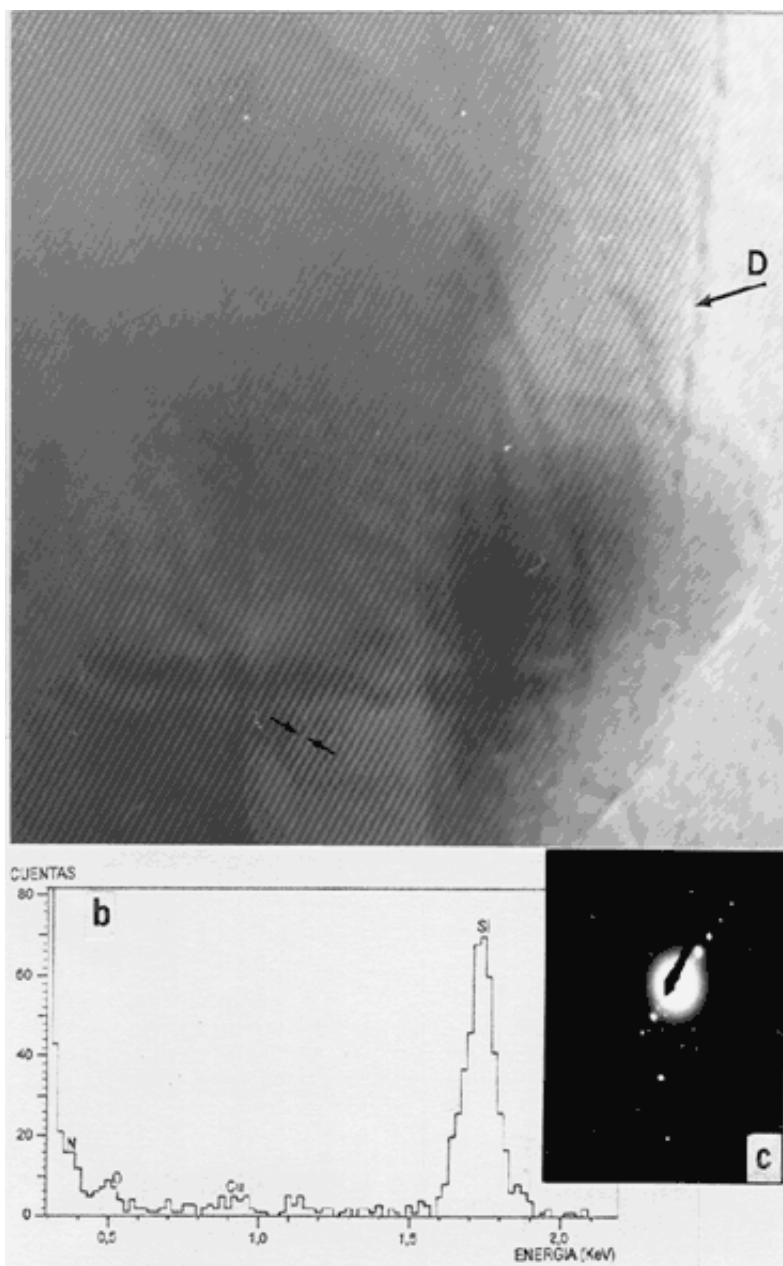


Figure 5: Microstructure (a) and microanalysis by EDX (b), SAD (c), in the region D, obtained by HRTEM from TMAH-treated Si₃N₄ sample . (interplanar distance, [001] 6,7 Å).

From XPS data and the HRTEM observations it can be concluded that TMAH forms a partially oxidized layer in which oxynitrides are present. However, this layer acts as protective screen avoiding further oxidation to silica, as it was suggested in previous works[14,15]. This can explain the unexpected low oxidation of slip cast samples in comparison with those obtained by other non-aqueous processing routes, as isostatic pressing of powders previously homogenised in alcohol, in which the oxygen content at the surface was expected to be markedly lower. This provides also founded expectations to obtain dense silicon nitride parts by a simple processing route as slip casting in water, without increased surface oxidation.

CONCLUSION

The results obtained in the present investigation have shown that aqueous suspensions of Si₃N₄ can be prepared at solid content of 65-70% maintaining a good stability and very low viscosity for casting. The use of normal bases contributes significantly to the surface oxidation. In this work it is stated that TMAH is useful because it forms a partially oxidize layer with Si-O-N species which acts as a protective screen onto the silicon nitride particles thins, difficulting a

further oxidation.

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