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Surface Oxidation of Si_3N_4 Green Compacts: Effect of Sintering Aids

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Abstract

It is well known that the surface chemistry of Si_3N_4 *is strongly influenced by both the synthesis route and the subsequent processing steps, such as the mixing/milling vehicle, the forming procedure, etc. All these processing variables can modify not only the rheological properties of the slips, but also the formation of chemical species at the surface which are directly related to the densification and the properties of the sintered compact. In addition, the additives normally used for sintering can also influence the surface chemistry.*

The aim of the present work is to determine the possible changes in the particle surface of Si_3N_4 *green compacts prepared by different forming procedures (slip casting and isostatic pressing) with and without sintering aids (*Al_2O_3 *and* Y_2O_3*). The surface oxidation has been determined, in each case trying to separate the contribution to the oxidation induced by the processing parameters and the contribution provided by the presence of the sintering aids. X-ray photoelectron spectroscopy (XPS) is an extremely useful technique for this purpose. In this work, high resolution XPS has been applied to reveal not only the chemical changes brought about by oxidation of* Si_3N_4 *green compacts but also to quantify the extent of surface oxidation. © 1996 Elsevier Science Limited.*

Introduction

Silicon nitride has unique properties compared to other engineering ceramics. The combination of properties such as high strength at room and elevated temperature, low coefficient of thermal expansion, good wear resistance and low density with respect to refractory metals, has made the Si_3N_4 one of the most studied ceramic structural materials in the last 15 years.[1,2]

However, the correlation between Si_3N_4 powder properties and the characteristics of the resulting ceramic product is not well established. Several producers offer high-purity Si_3N_4 powders but this does 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 Si_3N_4 final properties.

Thermodynamic and kinetic studies show that Si_3N_4 powder can be easily oxidized upon exposure to air or any other oxidizing environment.[3,5] In a X-ray photoelectron spectroscopy (XPS) study dealing with the oxidation behaviour of silicon nitride films, Raider *et al.*[6] 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. In agreement with this, several bulk chemical and surface analyses of the oxygen distribution in various Si_3N_4 powders manufactured by different processing techniques showed significant differences in the oxygen content at the particle surface.[7]

In order to understand the surface chemistry of Si_3N_4 powders some researchers have used pretreatment strategies 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 Si_3N_4 particles.[8,9] The oxygen adjustment on the surface, such as silica additions or chemical and physical treatment, does not result in ceramics with equivalent properties. In other words, it is not possible to avoid some oxidation effects from mixing, drying, forming or other processing steps.

The interfacial chemistry of a ceramic powder is strongly related to its forming, rheological and casting behaviour, the extent of inhomogeneities in the green bodies and the properties of the final sintered product.[3,4] However, the influence of surface chemistry is not restricted only to the casting

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processes but any other processing treatment can also affect the surface characteristics of the Si_3N_4 powders.

The present work studies the changes on pure Si_3N_4 and Si_3N_4 with sintering aids and the oxidation behaviour of green samples prepared under different processing routes in order to evaluate the possible changes at the surface and the interactions induced during forming by slip casting and isostatic pressing, either in aqueous or in organic mixing vehicles.

Experimental

The following powders were used as starting materials: α-silicon nitride (LC12SX) provided by Hermann C. Starck (Germany), α-Al_2O_3 (HPA 0·5) from Condea (Germany) and Y_2O_3 from Mandoval (UK). The characteristics of the powders (Table 1) were taken from the manufacturers specifications except for the specific surface area, which was measured by single point BET, and the particle size which was measured using a laser-Coulter (LS 130 Coulter, USA). Pure Si_3N_4 and Si_3N_4 with 3 wt% Al_2O_3 and 3 wt% Y_2O_3 (labelled as SN and SN3A3Y, respectively) green bodies were prepared by two different routes: isostatic pressing and slip casting. For isostatic pressing a previous mixing step in a liquid medium is required. The starting powders were mixed for 2 h in an attritor mill using either an organic solvent (isopropyl alcohol) or water to compare the oxidation effect of the milling medium on the Si_3N_4 surface. The resultant homogenized mixtures were then dried at 80°C for 24 h, screened below 60 μm mesh and subsequently isopressed at 200 MPa. For comparison purposes, a third experiment was made in which the three starting powders were dry-homogenized using a plastic jar with nylon balls. In this case the oxygen contribution on the surface of the green bodies is only caused by the sintering aids and the air contamination.

On the other hand, the initial mixture of powders was slip cast in water onto plaster of Paris molds. Aqueous slips of silicon nitride and silicon nitride plus sintering aids with solid loadings up to 65 wt% were prepared using tetramethylammonium hydroxide (TMAH) as dispersant. In order to compare the extent of the surface oxidation, non-aqueous slips were also prepared using isopropyl alcohol and TMAH. Both the aqueous and the organic slips were homogenized by vigorous mechanical stirring using a high-speed mixer (Silverson L2R, UK) for 3 min. Bubbles were removed after 30 min by low-speed stirring. The cast green bodies were dried in air for 24 h. Cylindrical bars of 5 mm diameter were prepared for all forming procedures and conditions. The surface analyses of the green compacts were performed on fracture surfaces.

XPS spectra of Si_3N_4 with and without Al_2O_3 and Y_2O_3 obtained by isostatic pressing and slip casting in different conditions have been recorded. Photoelectron spectra with a spatial resolution of a few nanometres were obtained using a Fisons ESCALAB Mk II electron spectrometer using Mg*Kα* X-rays (photon energy, hν = 1253·6 eV), and an electron take-off angle of 45°. The base pressure of the spectrometer was typically 10^{-9} mbar. The X-ray gun was operated at 12 kV and 10 mA, corresponding to a power 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). For samples with additives the Y3d and A12p core level spectra have been also recorded. The analyzer was operated in fixed analyzer transmission (FAT) mode with a pass energy of 50 eV (survey spectrum) and 20 eV (individual peaks). Data analysis was performed on a VGS 5000 data system based on the DEC PDP11 computer. The methodology employed for peak fitting of the peak envelopes has been described in detail.[10] Typically 1·8–2·0 eV line widths and a Gaussian/Lorentzian mix with a Lorentzian contribution of 30% were employed for the components of N1s and Si2p envelopes. Atomic percentages values were calculated from the peak areas using sensitivity factors provided with the data system and background subtraction. The accuracy in the binding energy of the XPS lines, obtained as average of at least two measurements, was estimated as ± 0·1 eV. The accuracy of the XPS quantitative analysis, as derived for duplicate analysis, was within ± 4%. Spectra were corrected for sample charging by referencing photoelectron peaks to C–C/C–H at 284·9 eV.

Table 1. Characteristics of the starting powders: Si_3N_4 (LC12SX-Starck); Al_2O_3 (HPA 0·5-Condea); Y_2O_3 (Mandoval)

	Si_3N_4	Al_2O_3	Y_2O_3
Main impurities (wt%)	C = 0·18; O = 2·04; Fe, Ca, Al <0·01	<0·01	<0·01
Specific surface area (m^2/g)	18·0	9·5	6·9
Mean particle size (μm)	0·8	0·4	3·5

The total oxygen contents of the powder and green compacts were analyzed by the inert gas fusion technique using a LECO EF-400 instrument. At least three measurements of each sample were performed. The precision of the analysis was within ± 5%. The standard deviation of different measurements for one sample was within ± 1%.

Results

XPS spectra of the green bodies of Si_3N_4 with Al_2O_3 and Y_2O_3 (SN3A3Y) obtained by isostatic pressing and slip casting in different conditions were recorded. The XPS spectra for pure Si_3N_4 green compacts (without sintering aids) have been previously reported.[11] Figure 1 displays the survey spectrum of the as-received Si_3N_4 material and its 3A3Y-doped counterpart. These spectra show the characteristic N1s, Si2p and O1s core levels and the complementary X-ray-induced O_{KLL} and N_{KLL} Auger emissions. A C1s peak is always present due to environment contamination. For the SN3A3Y sample, the Al2p and the Y3d peaks can be also discerned in the survey spectrum. However, as these additives are present in very low proportions, the observation of these elements becomes easier upon *Y*-axis expansion. This is illustrated in the inset of Fig. 1, which enlarges the 1050–1200 eV kinetic energy region. As denoted by arrows, the principal Si2p and Si2s peaks are accompanied by small peaks at 1093 eV (Y3d), and 1120 (Al2s) and 1178 eV (Al2p). Both position and peak areas of these peaks have been accurately measured by scanning each spectral window many times.

The binding energy of the Si2p peak may change from 99·3 eV for Si (metallic), to 101·4 eV for Si_3N_4 and 103·4 eV for SiO_2. However, in most cases more than one species is present on the surface and asymmetric peaks are observed. In the Si_3N_4 powder used in this study the peaks Si2p and N1s show asymmetrical line profiles. By applying peak synthesis procedures two contributions have been identified in these peaks. Their binding energies and peak areas have been precisely quantified. In all cases the major Si2p and N1s components placed at low binding energies are associated to Si_3N_4 while the corresponding high energy peaks are related to an intermediate state between silicon oxynitride (Si2p = 101·9 eV) and silica (Si2p = 103·4 eV), in good agreement with other literature reports.[12,13] Also the high binding energy component of N1s is slightly higher than expected for the silicon oxynitride.

Figures 2A and B show the Si2p core level spectra for all different processing conditions. The corresponding binding energies are shown in Table 2. In all cases the O1s spectra display a single peak located at 532·6 ± 0·1 eV corresponding to Si–O bonds. Similarly, Fig. 3A and B display the N1s core level spectra for the same samples obtained under different processing conditions. The as-received material exhibits an asymmetric N1s profile which can be split into two components at

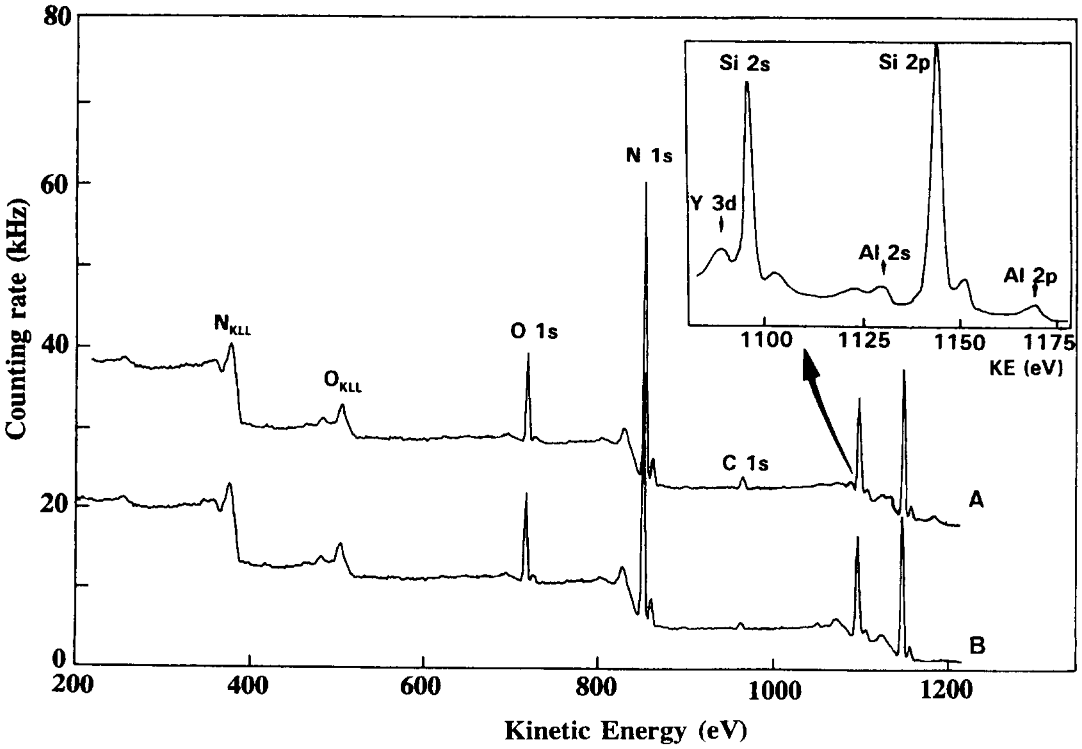


Fig. 1. Survey XPS spectra of the silicon nitride green compacts, (A) SN3A3Y-d-PI, (B) SN-d-PI. [SN: Si_3N_4; SN3A3Y: Si_3N_4 + 3 wt% Al_2O_3 + 3 wt% Y_2O_3; d: dry; IP: isostatic pressing].

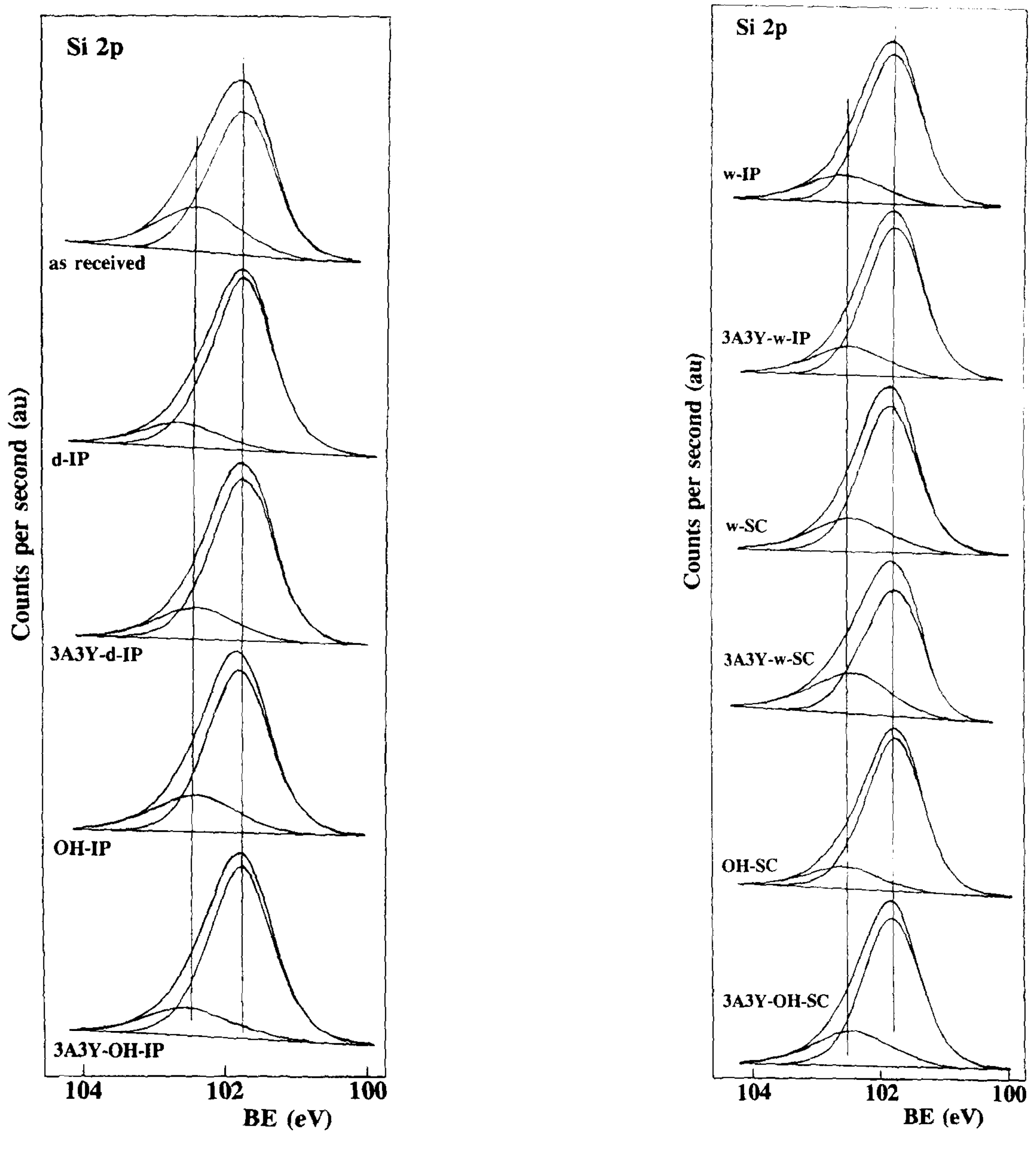


Fig. 2. (A) and (B), Si2p core level spectra for as-received Si_3N_4, and Si_3N_4 samples after the different processing techniques. [SN: Si_3N_4; SN3A3Y: Si_3N_4 + 3 wt% Al_2O_3 + 3 wt% Y_2O_3; d: dry; OH: isopropyl alcohol; w: water; IP: isostatic pressing; SC: slip casting].

binding energies from 397·6 to 398·6 eV. The same behaviour is observed for all the slip cast samples, either Si_3N_4 pure or with sintering aids, prepared in water or in organic solvent. However, the isopressed samples display a symmetric peak located at 397·7 eV except in the case of aqueous milling of the powder with additives. This difference is important since it reflects that the N1s peak may be a single or a doublet depending on the process, rather than the composition. Slip casting gives place to both nitride and oxynitride forms, whereas in the case of isopressed bodies the nitrogen is associated only to silicon nitride. This behaviour has been also observed in the Si2p peaks for the pressed samples in which the high-energy contribution tends to higher values than those corresponding to cast samples. In the isopressed samples it seems that the oxidation progresses to silica form. This fact is directly related to the absence of the high-energy contribution in the N1s peak, since the oxynitride form has been completely oxidized to silica.

The Si2p peaks are always asymmetric with two contributions. The low-energy peak is located at 101·7 ± 0·1 eV, corresponding to Si2p core levels from Si_3N_4. However, the high-energy contribution shows larger differences depending on the processing conditions. In general, it can be also observed that isopressed samples of pure Si_3N_4 gives higher values of BE for the oxynitride species than cast ones. This tendency is also observed when sintering aids (Al_2O_3 and Y_2O_3) are introduced. However, the effect of these additives is to shift down slightly the high-energy contribution.

Table 2. Binding energies (eV) of core electrons for silicon nitride and silicon nitride plus sintering aids subjected to different processing conditions

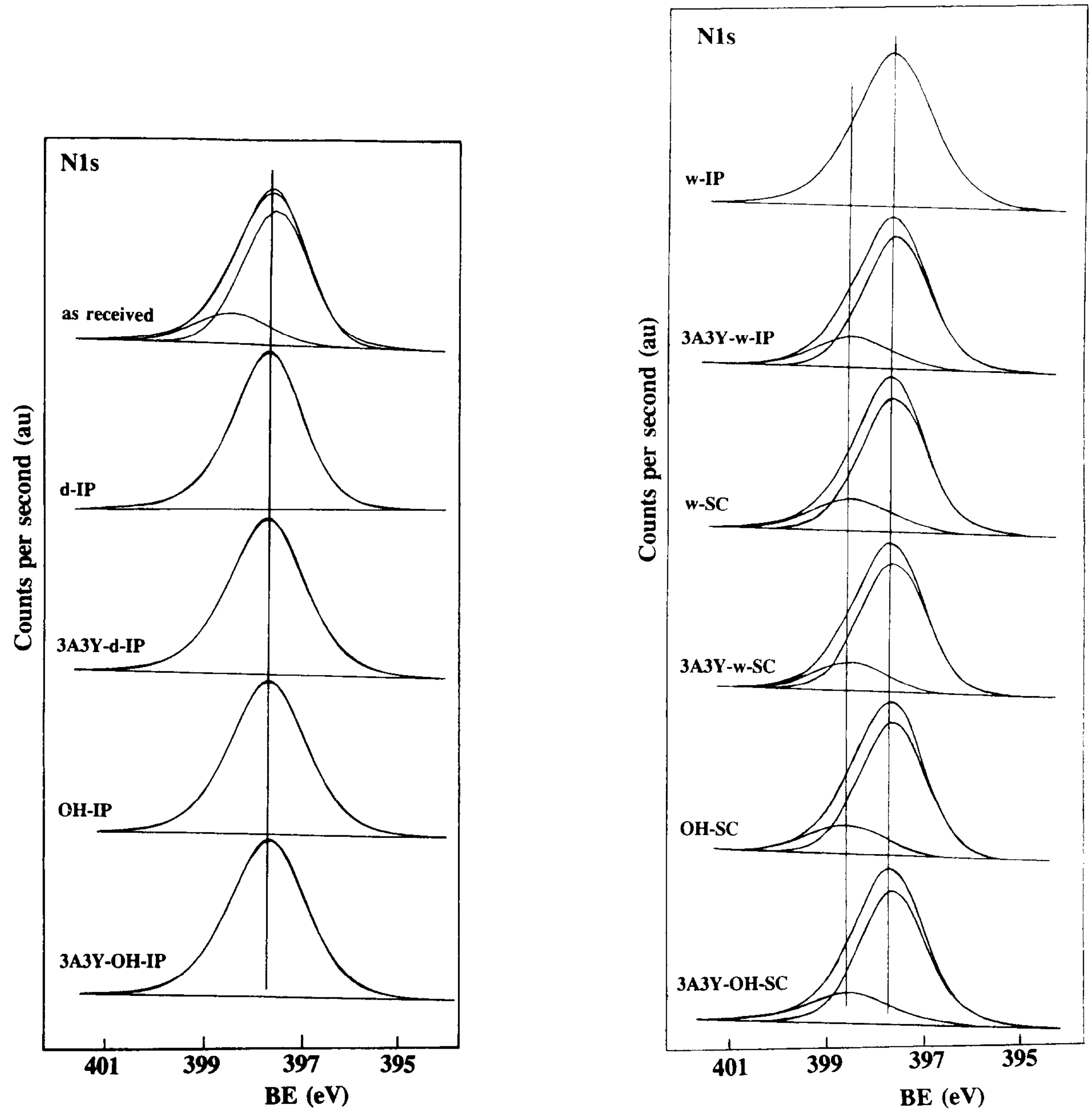
Samples	*O1s*	*N1s*	*Si2p*	*Al2p*	*Y3d*
SN as-received	532·7	397·6 (80%) 398·6 (20%)	101·6 (72%) 102·6 (28%)	—	—
SN-d-IP	532·7	397·7	101·7 (88%) 103·2 (12%)	—	—
SN3A3Y-d-IP	532·7	397·7	101·8 (84%) 103·0 (16%)	74·8	158·2
SN-OH-IP	532·7	397·7	101·7 (79%) 103·0 (21%)	—	—
SN3A3Y-OH-IP	532·6	397·6	101·7 (84%) 102·8 (16%)	74·8	158·4
SN-w-IP	532·6	397·7	101·8 (83%) 103·0 (17%)	—	—
SN3A3Y-w-IP	532·5	397·6 (82%) 398·5 (18%)	101·7 (83%) 102·8 (17%)	74·7	158·9
SN-w-SC	532·6	397·5 (82%) 398·3 (18%)	101·6 (77%) 102·6 (23%)	—	—
SN3A3Y-w-SC	532·5	397·5 (87%) 398·5 (13%)	101·6 (65%) 102·3 (35%)	74·8	158·8
SN-OH-SC	532·5	397·7 (88%) 398·7 (12%)	101·7 (86%) 102·8 (14%)	—	—
SN3A3Y-OH-SC	532·5	397·5 (84%) 398·5 (16%)	101·5 (75%) 102·4 (25%)	74·9	158·9

SN: Si_3N_4; SN3A3Y: Si_3N_4 + 3 wt% Al_2O_3 + 3 wt% Y_2O_3; d: dry; OH: isopropyl alcohol; w: water; IP: isostatic pressing; SC: slip casting.

Table 3 shows the surface atomic ratios for all the processing conditions studied. Obviously, for any processing procedure, the presence of Al_2O_3 and Y_2O_3 increases the O/Si ratio. But the extent of the oxidation is very different for the cast samples with respect to the pressed ones. The O/Si ratio increases from 0·33 to 0·38 when oxides are cast in water and from 0·31 to 0·38 in alcohol. In the pressed samples obtained by dry milling the O/Si ratio is 0·41 and increases in wet milling. Alcohol does not promote a high oxidation degree (O/Si = 0·44), but milling in water increases the O/Si ratio up to a value of 0·57, very high when compared with slip casting samples, either in water or in alcohol. It can be seen that dry milling and pressing increases the O/Si ratio and decreases the N/Si. This is in good agreement with the observations made by Bergström *et al.*[12] The same effect is also observed for wet-milled powders. The highest N/Si ratio and the lowest O/Si ratio are obtained for non-aqueous slip-cast Si_3N_4 samples. When the additives (Al_2O_3 and Y_2O_3) are introduced the picture is more complicated. The XPS analyses have been made on samples including oxides as sintering aids prepared under the same conditions, thus allowing separation of the different contributions to the surface oxidation, that due to the processing conditions and that due to the sintering aids. However, in the presence of the additives, the tendencies are the same as for pure Si_3N_4 samples.

All these values must be also related to the other columns in Table 3, where the Al/Si and the Y/Si ratios are shown. Once more, there is a big difference between the pressed and the slip-cast samples. The pressed samples show Al/Si ratios of 0·026 (dry), 0·020 (alcohol) and 0·021 (water) and Y/Si ratios of 0·024 (dry), 0·022 (alcohol) and 0·001 (water). This very low Y/Si ratio in the sample prepared in water indicates that during milling in water and drying some agglomerates of Y_2O_3 are being formed or that some diffusion of Y_2O_3 into the bulk can take place. In the case of slip-cast samples, the Al/Si ratios are similar for aqueous slips (Al/Si = 0·020) but in the case of organic slips this value strongly decreases to 0·007. A similar behaviour is observed for the Y/Si ratio, being 0·026 for aqueous slips and <0·001 for organic ones. This fact is probably due to the low stability of the organic slips where the oxides may precipitate, especially the coarse Y_2O_3 starting powder. The values obtained for aqueous slip casting are very similar to those obtained for pressed samples.

The different contributions to the total surface oxidation are shown in Table 4 for Si_3N_4 samples



(A) (B)

Fig. 3. (A) and (B), N1s core level spectra for as-received Si_3N_4, and Si_3N_4 samples subjected to different processing techniques. [SN: Si_3N_4; SN3A3Y: Si_3N_4 + 3 wt% Al_2O_3 + 3 wt% Y_2O_3; d: dry; OH: isopropyl alcohol; w: water; IP: isostatic pressing; SC: slip casting].

with and without additives. The total oxidation is calculated from the difference between the O/Si ratio obtained after each processing treatment and in the starting powder according to the values reported in Table 3. A first contribution to the oxidation is due to the processing procedure, including the homogenizing medium (dry, water, alcohol) and the forming method (isostatic pressing, slip casting). The oxidation due to the processing steps for SN3A3Y samples is obtained by subtracting the [O/Si] contribution of the oxides to the total calculated oxygen. A second contribution to the oxidation is that due to the presence of the oxides. The presence of Al_2O_3 and Y_2O_3 on the surface should increase the O/Si ratio by a factor (f) of:

$$f = \left(\frac{\mathrm{Al}}{\mathrm{Si}} + \frac{\mathrm{Y}}{\mathrm{Si}}\right) \times \frac{3}{2}$$

The contribution of the sintering additives to the oxidation is in the range of f = 0·06–0·08 for pressing after dry or alcohol milling and for aqueous slip casting. In the case of aqueous milling and pressing there is a very high oxidation and in the alcoholic casting ones the Al/Si and the Y/Si ratios are very low.

All these measurements have been made on bulk surfaces. However, it has been observed that the zone of the aqueous slip-cast greens in contact with the plaster mould presents very high values of both the Al/Si and the Y/Si ratios. During

Table 3. Atomic ratios of silicon nitride and silicon nitride plus sintering additives subjected to different processing conditions

Samples	*N/Si*	*O/Si*	*Al/Si*	*Y/Si*
SN as-received	1·350	0·281	—	—
SN-d-IP	1·265	0·334	—	—
SN3A3Y-d-IP	1·295	0·409	0·026	0·024
SN-OH-IP	1·306	0·336	—	—
SN3A3Y-OH-IP	1·294	0·442	0·020	0·022
SN-w-IP	1·217	0·562	—	—
SN3A3Y-w-IP	1·330	0·570	0·021	0·001
SN-w-SC	1·270	0·334	—	—
SN3A3Y-w-SC	1·340	0·384	0·020	0·026
SN-OH-SC	1·390	0·310	—	—
SN3A3Y-OH-SC	1·420	0·380	0·007	<0·001

Legends as Table 2.

casting, a rapid diffusion of the oxides towards the mould is observed. There is also an attack from the mould. Some experiments have been conducted on the external part of the cast bodies, that is, the cast wall in contact with the plaster mould. The presence of Ca^{2+} in the wall in contact with plaster has been detected for both water and organic slips. Figure 4 displays the survey spectrum of samples prepared by slip casting in water. For the sake of clarity the kinetic energy region 890–910 eV has been enlarged in the inset of this figure in order to visualize the observation of Ca2p peaks arising from calcium contamination. However, in the case of organic slips, there are no differences between the Al/Si and Y/Si ratios in the external surface and in the bulk.

The results shown above demonstrate that aqueous slip casting of Si_3N_4 does not promote an enhanced particle surface oxidation, as usually thought. However, there is some contamination due to the contact with the plaster mould, only affecting a few atomic layers. The results obtained for pure Si_3N_4 green compacts after different processing routes are confirmed when the additives

Table 4. Contributions to the oxidation expressed as O/Si ratio (at%) by XPS from samples obtained by different conditions process

Samples	*SN*	*SN3A3Y*		
Process	*Total (Processing steps)*	*Total*	*Additives 3(Al/Si + Y/Si)/2*	*Processing steps (Total − additives)*
d-IP	0·053	0·128	0·075	0·053
OH-IP	0·055	0·161	0·063	0·098
w-IP	0·281	0·289	0·034	0·255
w-SC	0·053	0·103	0·069	0·034
OH-SC	0·029	0·099	0·011	0·088

Legends as Table 2.

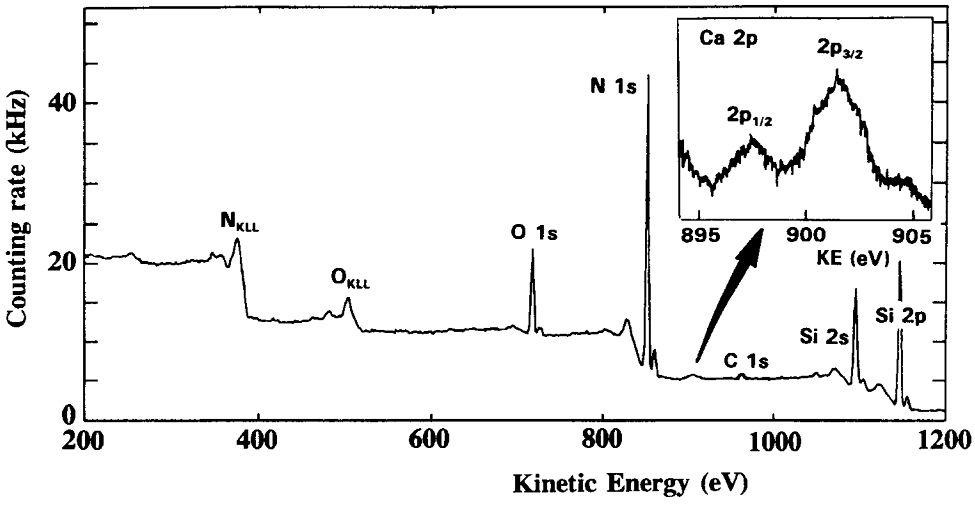


Fig. 4. Survey XPS spectrum of the SN3A3Y-w-SC samples, with enlarged Ca2p peaks. [SN3A3Y: Si_3N_4 + 3 wt% Al_2O_3 + 3 wt% Y_2O_3; w: water; SC: slip casting].

Table 5. Oxygen content determined by LECO from samples obtained by different process conditions, expressed as O_2 wt%

	Bulk O_2 (wt%)		*Process contamination (wt%)*	
Samples / *Process*	*SN*	*SN3A3Y*	*SN*	*SN3A3Y*
As-received	1·7		—	—
d-IP	1·93	3·65	0·23	0
OH-IP	2·12	4·0	0·42	0·35
w-IP	2·67	4·0	0·97	0·35
w-SC	2·29	3·73	0·59	0·08
OH-SC		3·7	—	0·05

Legends as Table 2.

are introduced in similar processing conditions. The XPS quantitative analysis is capable of reflecting the tendencies reported in this work since the differences observed in the samples are higher than the possible errors in the measurements.

In order to provide some additional data in this sense, an oxygen analysis by Leco has been performed for all the samples studied. The analyses of the bulk oxygen contents are reported in Table 5 for samples of pure Si_3N_4 and Si_3N_4 with additives. The oxygen content in the bulk increases for water treatments in pure Si_3N_4 samples. When the dopant oxides are present the total oxygen content increases, as expected. Taking into account that the sintering aids have been added in a concentration of 3 wt% each, the theoretical oxygen contribution due to the additives is 2·05 wt%, so the total contribution for SN3A3Y is 3·05 wt% (0·94 × 1·7 + 2·05). Thus, it is possible to calculate the oxygen contamination due to the process from the measured oxygen contents in each sample without and with oxides.

In Table 5 very similar values of total oxygen content are shown. The error of the technique is within ± 5%, very similar to the differences obtained in this work. However, some trends can be observed. For example, water tends to increase the oxygen content in the pure samples. In the presence of oxides, the oxidation due to the process is much lower than the oxygen content introduced with the additives. For the pressed samples a higher oxygen content is clearly obtained, thus confirming the XPS results. In this case the oxidation effect is so high that the Leco analysis can detect it. In the other samples much more precision is required for the analysis, as that provided by the XPS quantitative analysis.

Conclusions

The oxygen contamination of Si_3N_4 green compacts is strongly dependent on the processing conditions. The X-ray photoelectron spectroscopy technique (XPS) is a powerful tool to determine the formation of different species on the Si_3N_4 surface and allows analysis of possible contributions to the oxidation. According with this, the two different sources for the oxidation, relating to the presence of oxides used as sintering aids and the contamination during processing treatments, have been separated. The tendencies in oxidation behaviour have been determined for green compacts of pure Si_3N_4 and Si_3N_4 including sintering additives (Al_2O_3 and Y_2O_3) prepared by slip casting and isostatic pressing. The analysis of both compositions reveals that the surface oxidation is related to the process rather than the composition. Any processing treatment introduces some oxygen contamination. Processing with alcohol does not produce an important surface oxidation to the samples, as recognized elsewhere. In the case of aqueous treatments very high differences have been found between slip casting and isostatic pressing. Aqueous milling for pressing produces a very high oxidation effect, whereas in the case of slip casting the oxidation effect is much more limited, being comparable to that obtained in alcohol. This effect must be related to the dispersant used to stabilize the slips (TMAH) which is an ammonium compound with anchors to the particle surfaces providing a protective screen to further oxidation. In fact, it has been observed that the slip-cast samples give place to both nitride and oxynitride contributions but the isopressed samples give only one single N1s peak corresponding to a more oxidized form. This is confirmed by the Si2p peaks that can be fitted into doublets in all the samples, but the higher-energy contribution shifts up in the pressed ones.

However, some contamination is observed up to a very small depth in the walls in contact with plaster. This contaminated external layer can be avoided by using protective coatings on the mould walls.

Acknowledgements

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