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# A Surface Study on Adsorption of Lignosulphonate on Mixed $Si_3N_4$–$Y_2O_3$ Powder Dispersions

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## *Abstract*

*In the colloidal processing of high performance ceramics, knowledge of the interfacial properties is of crucial importance. Studies have accordingly been made of the surface composition and the dispersion behavior of a silicon nitride–yttrium oxide–lignosulphonate system, prior to sintering. The effect of pH on the adsorption of yttria ($Y_2O_3$) and lignosulphonate (LS) on the silicon nitride ($Si_3N_4$) powder surface is reported.*

*The samples were studied by particle size measurements, SEM, X-ray photoelectron spectroscopy (ESCA) and carbon analyses. The ESCA analyzing techniques used were (1) relative surface atomic concentrations (ACs) and (2) evaluation of the substrate coverage derived from the Tougaard background analysis.*

*It was found that the particle size distribution of the $Si_3N_4$–$Y_2O_3$ system to be strongly dependent on the pH and concentration of the lignosulphonate added in the dispersion. The ESCA results confirmed that lignosulphonate adsorbed both on the silicon nitride and yttrium oxide particles. It was also found that at pH 7 the relative amount of yttria was increased at the surface with increasing amount of lignosulphonate added in the dispersion.*

*Bei der kolloidalen Herstellung von Hochleistungskeramiken sind die Grenzflächen von besonderer Bedeutung. Die Grenzflächenchemie und das Dispersionsverhalten eines Siliziumnitrid–Yttriumoxid–Lignosulphonat-Systems wurde vor dem Sintern untersucht. Der Einfluß des pH-Werts auf die Adsorption von Yttriumoxid ($Y_2O_3$) und Lignosulphonat (LS) an der Oberfläche der Siliziumnitridpulver ($Si_3N_4$) wurde bestimmt.*

*Die Untersuchung der Proben erfolgte durch die Bestimmung der Teilchengröße, SEM, Röntgenphotoelektronenspektroskopie (ESCA) und Kohlenstoffanalyse. Bei den ESCA-Techniken handelte es sich um (1) die Bestimmung der relativen atomaren Konzentration an der Oberfläche (ACs) und (2) die Ermittlung der Substratbedeckung abgeleitet aus der Tougaard Hintergrundanalyse.*

*Es zeigte sich, daß die Teilchengrößenverteilung des $Si_3N_4$–$Y_2O_3$-Systems stark vom pH-Wert und der zur Dispersion zugegebenen Menge an Lignosulphonat abhängt. Die ESCA-Untersuchungen bestätigen, daß Lignosulphonat sowohl von Siliziumnitrid- als auch von Yttriumoxidteilchen adsorbiert wird. Weiterhin ergab sich, daß bei einem pH-Wert von 7 und bei Erhöhung des Lignosulphonatanteils an der Dispersion die relative Menge an Yttrium an der Oberfläche zunahm.*

*Dans le processus colloïdal de fabrication de céramiques hautement performantes, la connaissance des propriétés interfaciales est d'une importance cruciale. C'est pourquoi des études ont été realisées, avant frittage, sur la composition de la surface et sur le comportement à la dispersion de systèmes nitrure de silicium–oxyde d'yttrium–lignosulfonates. L'effet du pH sur l'adsorption de l'oxyde d'yttrium ($Y_2O_3$) et du lignosulfonate (LS) sur la surface d'une poudre de nitrure de silicium ($Si_3N_4$) est décrite.*

*Les échantillons ont été étudiés par sédimentométrie, MEB, spectroscopie ESCA et analyses de carbone. Les techniques d'analyse ESCA employées ont été relatives (1) aux concentrations atomiques de la surface (ACs) et (2) a l'évaluation du recouvrement de la surface à partir de l'analyse de Tougaard.*

*Nous avons trouvé que la distribution de la taille des particules du systéme $Si_3N_4$–$Y_2O_3$ est fortement dépendante du pH et de la concentration en lignosulfonate ajouté lors de la dispersion. Les résultats ESCA confirment que le lignosulfonate s'est adsorbé sur les particules de nitrure de silicium et d'oxyde*

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*d'yttrium. Il a été aussi démontré qu'à pH 7 la quantité relative d'oxyde d'yttrium a été augmentée sur la surface avec des quantités croissantes de lignosulfonates ajoutées à la dispersion.*

## 1 Introduction

Silicon nitride based ceramics are of particular interest for high-temperature, high-stress applications. In order to obtain defect-free ceramic bodies it is of importance to avoid aggregation of the dispersed powder and to be able to sinter the green body at sufficiently low temperatures.[1] These conditions are prerequisite for a dense, fine-grained microstructure. The enhanced reactivity of dispersed colloidal powders ensures the lowered sintering temperatures but introduces, on the other hand, a range of new constraints for the processing. In particular, in this so-called colloidal processing of high-performance ceramics, knowledge of the interfacial properties is of crucial importance.

Pressureless sintering of silicon nitride requires addition of sintering agents to ensure a densification by liquefied phase sintering. Since relatively little is known about the distribution of the sintering agent in the matrix, it was considered of importance to investigate the distribution of yttrium oxide $Y_2O_3$ in $Si_3N_4$, prior to sintering. The dispersability of the powder(s) was enhanced by adding a small amount of lignosulphonate (LS) to the dispersions. The authors report on the effect of pH and the lignosulphonate addition on the adsorption of $Y_2O_3$ on the silicon nitride surface.

The powders were studied by X-ray photoelectron spectroscopy (ESCA), particle size measurements, scanning electron microscopy (SEM) and carbon analysis. In the ESCA investigations both relative elemental surface concentrations[2] and in-depth analysis based on the relative increase of inelastic background after a photoelectron peak (qualitative Tougaard analysis[3]) were used.

In a later paper the wet characteristics of the dispersed particles, e.g. electrokinetic potential measurements and surface charge titrations, will be reported.

## 2 Experimental

### 2.1 Raw materials

The silicon nitride powder (SN E-10) used in this study was supplied by UBE Industries, Yamaguchi, Japan. According to the manufacturer the specific surface area was 10 $m^2/g$ and the particle size ~0·4 $\mu m$. The yttrium oxide powder (grade fine) was supplied by H. C. Starck, Berlin, Germany. The BET specific surface area according to the manufacturer was 13·7 $m^2/g$. The particle size distribution was given to be $X_{90} < 2{\cdot}5\ \mu m$, $X_{50} < 0{\cdot}8\ \mu m$ and $X_{10} < 0{\cdot}35\ \mu m$. The lignosulphonate used was Wargonin extra (calcium–sodium lignosulphonate) supplied by Lignotech, Sweden. The elemental composition of lignosulphonate powder was checked with SEM/EDS and found to be approximately 90·6 wt% C, 2·1 wt% Ca, 2·3 wt% S and 5·0 wt% Na. According to the manufacturer the molecular weight distribution of lignosulphonate is 70% < 5000, 10% 5000–10 000, 6% 10 000–20 000, 14% > 20 000. In general it has been found that lignosulphonates in the molecular weight range of 5000–40000 g/mol act as dispersants, while higher molecular weight lignosulphonates exhibit flocculating properties by causing interparticle bridging.[4] The lignosulphonate is soluble in water within the concentrations used. The powders were used without further purification. The water used was distilled and purified with a Milli Q system to obtain a minimum resistivity of 18 MΩ/cm.

### 2.2 Sample preparation

The list of samples is given in Table 1. The samples contained silicon nitride, yttrium oxide and lignosulphonate. The amount of the sintering agent, $Y_2O_3$, was kept at a constant level of 5 wt% and the concentration of the dispersing agent added in the solution was 0·05, 0·5 or 2·0 wt%. Percentage additives are calculated for the dry content of the slurry.

All samples were prepared by first adding the lignosulphonate powder (when used) in water, then adding $Y_2O_3$ (when used) and finally $Si_3N_4$. The concentration of each slurry was about 20 wt%.

After the preliminary testing in the pH range 2–10, the pH values 7 and 10 were selected for further investigations. pH 7 was chosen in order to obtain counter-charged particle surfaces, thus ensuring an electrostatic adsorption of $Y_2O_3$ on $Si_3N_4$ surface.[5] This pH is also close to the natural pH of the slurry. pH 9–10 is typically used in processing of silicon nitride powders.[6] The pH of the respective slurries was adjusted using 0·1 M HCl or NaOH (Merck titrisols).

**Table 1.** List of the samples used (all samples except pure lignosulphonate specimen were treated in solutions of pH 7 and pH 10)

| |
|---|
| $Si_3N_4$ |
| $Y_2O_3$ |
| Lignosulphonate (LS) |
| $Si_3N_4$ + 5 wt% $Y_2O_3$ |
| $Si_3N_4$ + 5 wt% $Y_2O_3$ + 0·05 wt% lignosulphonate |
| $Si_3N_4$ + 5 wt% $Y_2O_3$ + 0·5 wt% lignosulphonate |
| $Si_3N_4$ + 5 wt% $Y_2O_3$ + 2·0 wt% lignosulphonate |

The dispersions were processed in ultrasonic stirrer and thereafter the pH of the dispersion was readjusted. The dispersion was allowed to equilibrate for 24 h before the measurements under stirring to ensure a sufficient conditioning time. Prior to the measurements the pH values of the dispersions were readjusted once more to the respective correct pH value. The dispersion was centrifuged (3000 rpm, 30 min) prior to each measurement and separated from the supernatant.

### 2.3 Particle size measurements

The particle size analyses of the samples were carried out using light-scattering equipments (Malvern 4700C, Malvern Instruments). The concentration of the electrolyte used was 1 mmol/liter, and 7 mg of the sample was added in 500 $cm^3$ electrolyte. The particle sizes reported at pH 7 are interpolated results from several measurements, due to the strong dependence of particle size on pH in this region. The measured values ranged from pH 6·7 to 7·8.

### 2.4 SEM/EDS

A Cambridge S200 scanning electron microscope with a Link AN10 000 energy dispersive analyzer was used both in X-ray microanalysis of the lignosulphonate and in surface topographical analysis of the dried dispersions via secondary electron imaging.

For the X-ray microanalysis the pure lignosulphonate was spread on a clean molybdenum substrate, dried and coated with carbon. Samples for imaging were coated with a thin layer of gold, using a SEM coating unit (PS3, Agar Aids) prior to the measurement.

### 2.5 ESCA

A Perkin-Elmer Small Spot PHI 5400 ESCA system with unmonochromatized $MgK_\alpha$ radiation was used in all measurements, using 0·5 eV step and 89 eV analyzer energy. The sample area analyzed was a spot of ~1 mm in diameter. The base pressure in the spectrometer was $7{\cdot}0 \times 10^{-7}$ Pa and the pressure during the measurements was typically $2{\cdot}0 \times 10^{-6}$ Pa.

The samples were prepared as follows: after the treatment the dispersion was centrifuged and the wet powder, separated from the supernatant, was spread on a clean molybdenum plate. All samples were dried at 50°C for about 1 h.

A 1 h survey spectrum ranging from 0 eV to 1100 eV (binding energy) was recorded of each sample. With the acquisition parameters used the detection limit for light elements is better than 0·5 at.% within the analysis depth of 2–6 nm.

For the surface compositional analysis, elastic photoelectron peaks of the survey spectra were analyzed, using tabulated sensitivity factors.[7] For a qualitative in-depth analysis within the first few nanometres, increases in the background intensity on the low kinetic energy sides of Y 3*p* and Si 2*p* photoelectron peaks were investigated.[2,8] The two independent ESCA analyses were performed on the same measured spectra.

### 2.6 Carbon analysis

The carbon analyses were carried out using a carbon analyzer model Leco EC-12. Each sample was dried at 60°C for 4 h prior to the analysis.

## 3 Results and Discussion

The $Si_3N_4$–$Y_2O_3$ dispersions were adjusted to pH 7 or 10 and varying amounts of lignosulphonate (LS) added. In order to study the changes induced by the addition of LS, the samples of $Si_3N_4$, $Y_2O_3$ and $Si_3N_4$–$Y_2O_3$ were also pH treated.

### 3.1 Particle size measurements

#### 3.1.1 *The influence of lignosulphonate addition on the pure components*

The measured particle sizes of the one-component systems were compared with the values reported by the manufacturers.

#### 3.1.2 $Si_3N_4$

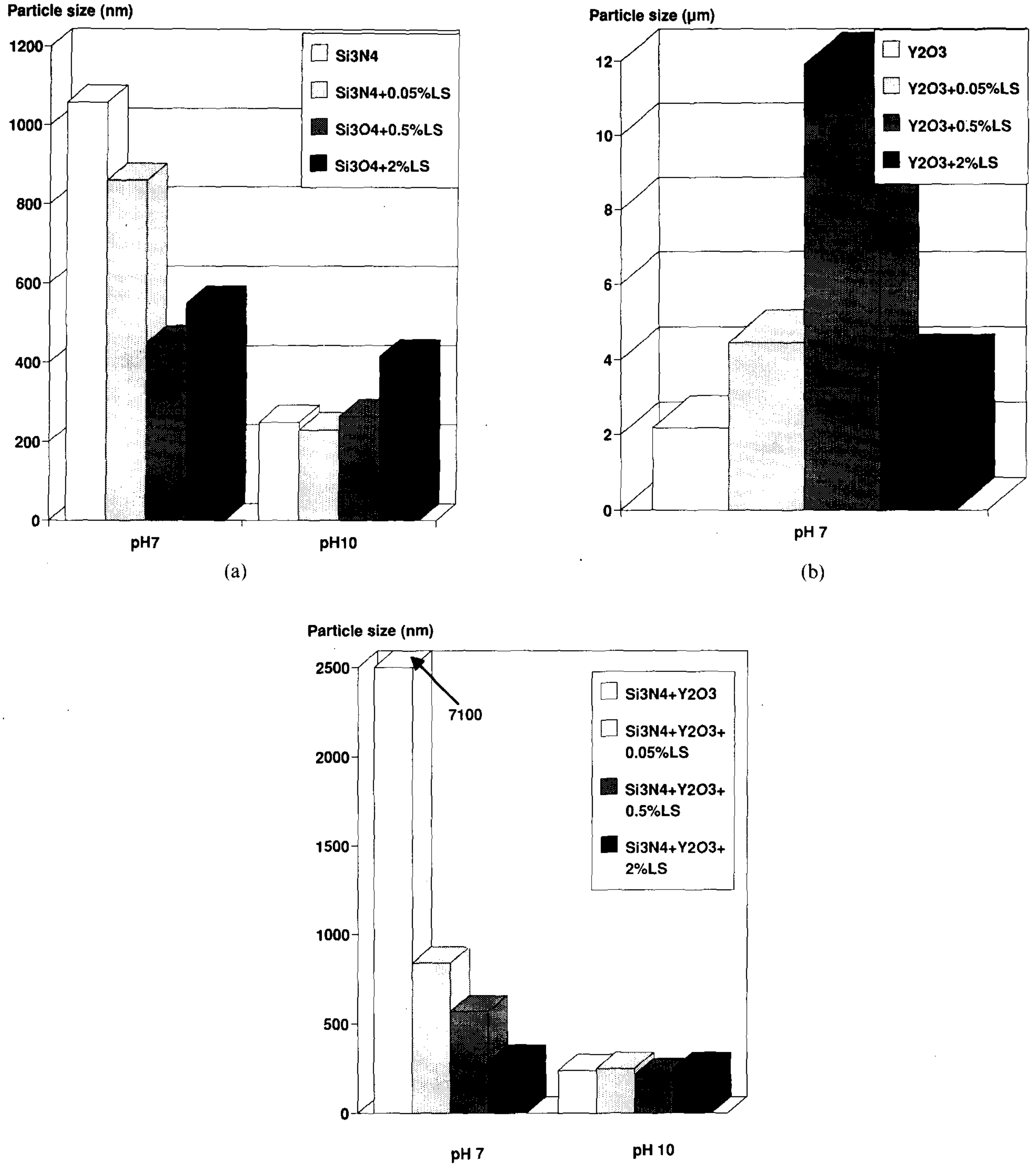
The measured particle size of pure $Si_3N_4$ at pH 10 was around 0·2 μm, which is in fair agreement with that reported by the manufacturer, indicating that the $Si_3N_4$ powder was well dispersed. At pH 7 the measured particle size was around 1 μm, indicating aggregation.

The LS added in the $Si_3N_4$ dispersion at pH 7 caused a decrease in the mean particle size, indicating that LS was functioning as a dispersant, see Fig. 1(a). This is due to the electrostatic repulsion, as LS is known to increase the negative surface charge of silicon nitride.[6,9]

#### 3.1.3 $Y_2O_3$

The measured particle size of the pure $Y_2O_3$ dispersion conditioned at pH 7 was around 2 μm, indicating aggregation of yttria, since the average particle size reported by the manufacturer was around 0·8 μm. Due to the strong buffering capacity of yttria, the authors were not able to measure the particle size of $Y_2O_3$ at pH 10.

Small additions of LS in the $Y_2O_3$ dispersion at pH 7 caused further aggregation of $Y_2O_3$, whereas 2 wt% addition of LS dispersed yttria totally, see Fig. 1(b). At pH 7 yttria has a posi-



(a)

(b)

(c)

**Fig. 1.** Results from the particle size analysis. (a) $Si_3N_4$ and lignosulphonate (at pH 7 and pH 10); (b) $Y_2O_3$ and lignosulphonate (pH 7); (c) $Si_3N_4$–$Y_2O_3$ and lignosulphonate (at pH 7 and pH 10).

tively charged surface. Small additions of LS adsorbing on yttria perform as a charge neutralizer, enhancing further the aggregation of yttria particles. However, at the highest concentration of LS addition the yttria surfaces become negative (due to the adsorbed LS) and thus LS is functioning as a dispersant.

### *3.1.4. $Si_3N_4$–$Y_2O_3$ system*

At pH 7 the mean particle size of the $Si_3N_4$–$Y_2O_3$ system was increased dramatically, as compared with that of the pure $Si_3N_4$, see Fig. 1(c). The phenomenon was also verified by the secondary electron images, where agglomerates consisting of 0·2–0·4 µm particles could be seen, see Fig. 2(a). This can be explained by heterocoagulation of the particles due to electrostatic attraction.

At pH 10, the particle size of $Y_2O_3$–$Si_3N_4$ system was similar to that of pure $Si_3N_4$. However, the observed particle size was only about half of the original particle size of $Si_3N_4$ reported by the manufacturer. This was also confirmed by the SEM imaging, indicating that conditioning at pH 10 results in splitting of the primary particles.

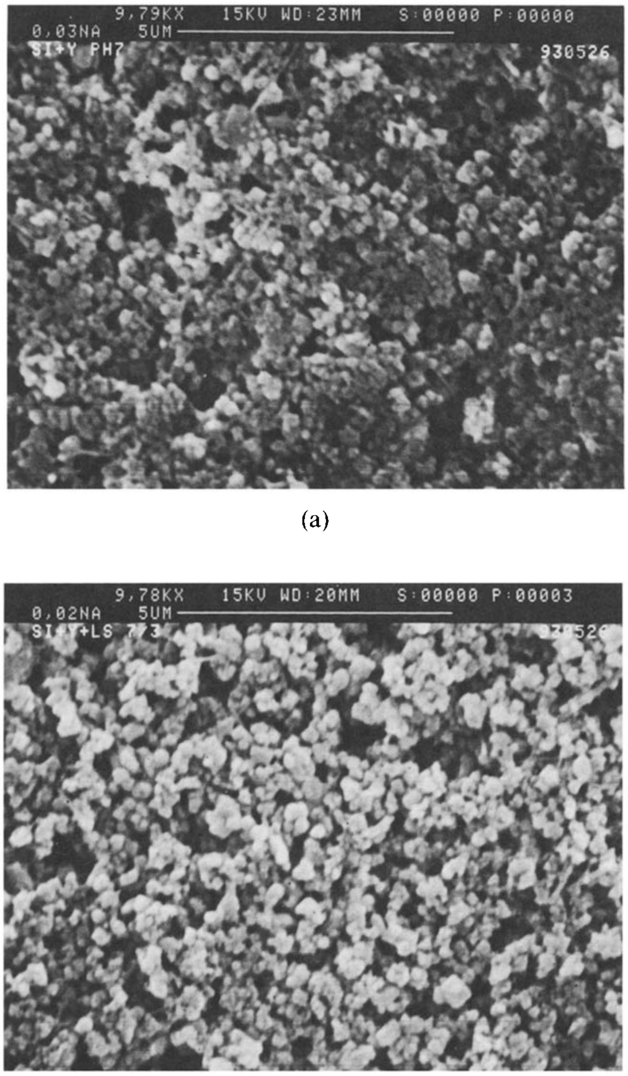


**Fig. 2.** Secondary electron images of (a) the $Si_3N_4$ + 5 wt% $Y_2O_3$ sample, and (b) the $Si_3N_4$ + 5 wt% $Y_2O_3$ + 2 wt% lignosulphonate sample, treated in aqueous solutions at pH 7.

### *3.1.5 Influence of lignosulphonate addition on $Si_3N_4$–$Y_2O_3$ system*

At pH 7 the particle size of the $Si_3N_4$–$Y_2O_3$ dispersion decreased with increasing addition of LS, see Fig. 1(c). The LS added in the dispersion is clearly functioning as a dispersant via a consequent break up of the agglomerates, causing the measured particle size to diminish. The decrease in particle size of the $Si_3N_4$–$Y_2O_3$ system is possible as the amount of yttria added in the dispersion is only 5 wt% and is consequently not visible as an independent size fraction. The results were further verified by the secondary electron images in which the agglomerates of the $Si_3N_4$– $Y_2O_3$ system were no longer detected (see Fig. 2(b) with 2% LS addition).

At pH 10 the LS addition had no effect on the particle sizes, indicating that the presence of sintering agent $Y_2O_3$ had facilitated the dispersion of the $Si_3N_4$ particles, prior to the addition of LS. This is due to the fact that all the particles in the dispersion are strongly negatively charged. Thus, at pH 10, LS is acting as an optimum dispersing agent in the dispersion. The measured particle size has reached the minimum, due to the electrostatic depletion of the particles.

## 3.2 Surface composition

The surface composition of the dried $Si_3N_4$–$Y_2O_3$(–LS) dispersions were investigated using ESCA elastic peak analysis (relative surface elemental concentrations[2]), ESCA peak shape analysis (Tougaard background analysis[3]) and carbon analysis.

### *3.2.1 Elemental analysis*

According to the measured ESCA spectra of the outermost surface of the $Si_3N_4$–$Y_2O_3$(–LS) systems, this consisted mainly of silicon, nitrogen, yttrium, oxygen and carbon. In addition to these elements small amounts of calcium, sodium, sulphur, molybdenum and fluorine were detected. The ESCA atomic concentrations are shown in Table 2. According to these results the carbon contamination level in the $Si_3N_4$–$Y_2O_3$ system was about 3–4 at%. Calcium, sodium and sulphur, as well as small amount of nitrogen, were detected in the spectrum of LS. The molybdenum signal originated from the substrate plate and the fluorine signal probably originated from the magnetic stirrer coated with PTFE. The pH adjustment with NaOH caused an increase in the sodium level of the sample surface, detected especially at pH 10.

No effort was made to wash the samples from the leached ionic species, in order to relate the dried sample surface to the sample surface of the real slurry. Sodium and other ionic species, leached

**Table 2.** ESCA relative atomic concentrations of the sample surfaces

| *Sample* | *pH* | *Si* | *N* | *Y* | *O* | *C* | *Na* |
|---|---|---|---|---|---|---|---|
| $Si_3N_4$ | 7 | 33·9 | 40·0 | — | 20·4 | 5·7 | — |
| $Y_2O_3$ | 7 | — | — | 20·3 | 60·6 | 19·1 | — |
| $Si_3N_4$ + $Y_2O_3$ | 7 | 33·3 | 39·4 | 1·6 | 22·1 | 3·6 | — |
| $Si_3N_4$ + $Y_2O_3$ + 0·05 wt%LS | 7 | 33·1 | 40·1 | 1·9 | 20·7 | 4·0 | 0·1 |
| $Si_3N_4$ + $Y_2O_3$ + 0·5 wt%LS | 7 | 29·0 | 33·5 | 2·5 | 23·9 | 10·5 | 0·6 |
| $Si_3N_4$ + $Y_2O_3$ + 2 wt%LS | 7 | 23·4 | 26·2 | 2·8 | 26·9 | 19·7 | 0·7 |
| $Si_3N_4$ | 10 | 32·4 | 38·2 | — | 20·2 | 6·8 | 2·5 |
| $Y_2O_3$ | 10 | — | — | 15·0 | 48·3 | 36·7 | — |
| $Si_3N_4$ + $Y_2O_3$ | 10 | 33·2 | 41·0 | 1·7 | 21·0 | 3·2 | — |
| $Si_3N_4$ + $Y_2O_3$ + 0·05 wt%LS | 10 | 31·5 | 37·9 | 2·6 | 22·6 | 2·5 | 2·9 |
| $Si_3N_4$ + $Y_2O_3$ + 0·5 wt%LS | 10 | 32·5 | 39·5 | 1·7 | 22·0 | 2·7 | 1·5 |
| $Si_3N_4$ + $Y_2O_3$ + 2 wt%LS | 10 | 31·0 | 36·6 | 2·3 | 24·4 | 4·0 | 1·3 |

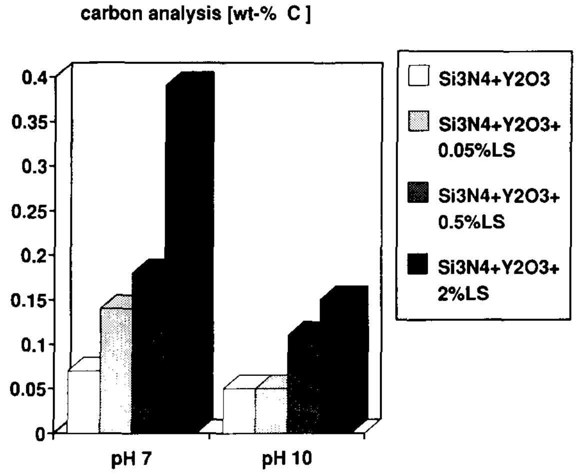


**Fig. 3.** Results from the carbon analysis.

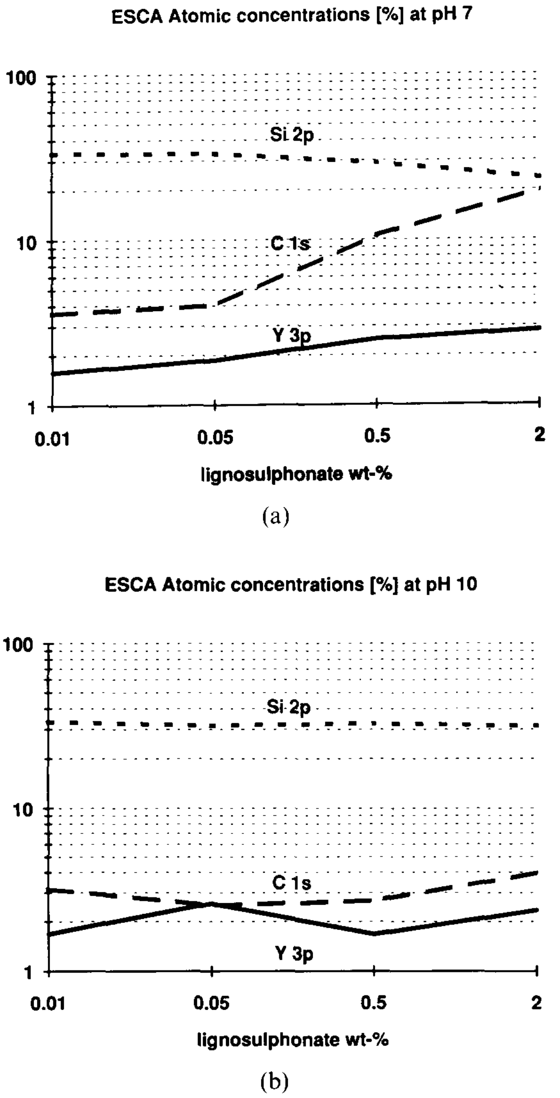
from the solid in the dispersion, will evidently be present as they are dried on the sample surface during the slip casting and sintering.

### *3.2.2 Lignosulphonate adsorption*

The carbon analysis showed that the LS was adsorbed into the $Si_3N_4$–$Y_2O_3$ system more at pH 7 than at pH 10, see Fig. 3. According to the ESCA analysis based on C 1*s*, Y 3*p* and Si 2*p* elastic peaks, at pH 7 the carbon and yttria contents at the surface increased, while the silicon content decreased with increasing addition of LS in the dispersion (see Fig. 4(a)) indicating that LS was adsorbed on the $Si_3N_4$ particles.

However, at pH 10, there was no variation in the carbon, yttrium or silicon contents of the surface and the amount of LS added, despite the increased amount of carbon detected in the carbon analysis (see Figs 3 and 4(b)).

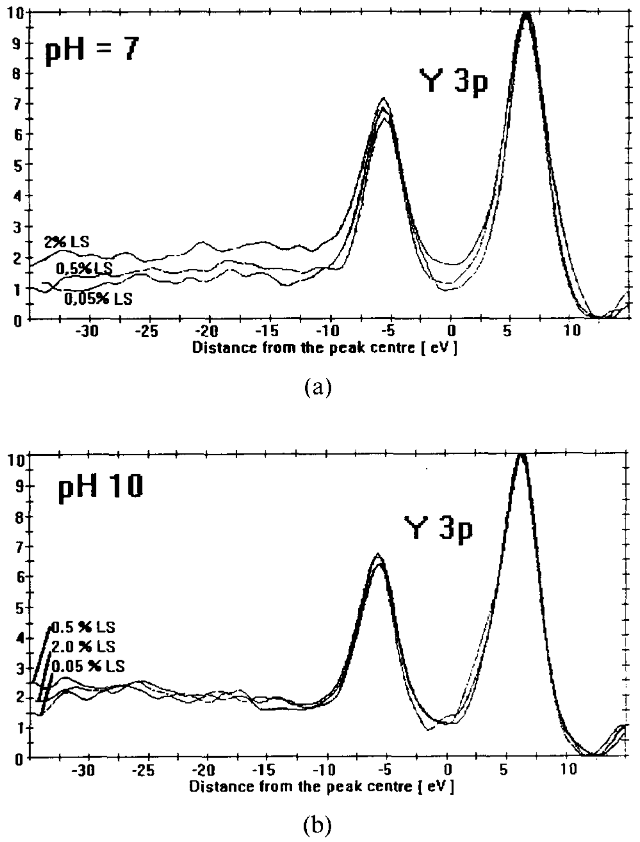
To evaluate further the adsorption of LS, the background tailing yttrium 3*p* and silicon 2*p* peaks were investigated. (The increase in the background intensity relative to the respective peak is indicative of increased coverage of the element.[3,10]) According to these results, for samples prepared at pH 7, the coverages of both yttrium and silicon were increased with increasing concentration of LS added into the dispersion, whereas there were no detectable changes in the relative background intensities at pH 10 (see Fig. 5 for yttrium). This indicates that although some LS is adsorbed by the $Si_3N_4$–$Y_2O_3$ powder system at pH 10 upon drying (c.f. carbon analysis), it does not cover the particles as at pH 7, where an adsorption occurred naturally in the dispersion.



(a)

(b)

**Fig. 4.** Relative ESCA atomic concentrations of silicon (Si 2*p*), yttrium (Y 3*p*) and carbon (C 1*s*) of the dried samples treated in a solution at (a) pH 7 and (b) pH 10.



(a)

(b)

**Fig. 5.** The yttrium 3*p* spectra for $Si_3N_4$–$Y_2O_3$(–LS) samples treated at (a) pH 7 and (b) pH 10. All spectra have been rescaled to unit peak heights of Y $3p_{3/2}$.

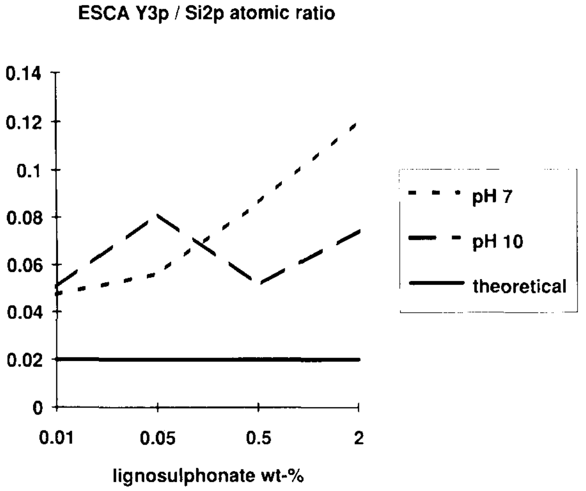


**Fig. 6.** Y/Si ratios for the $Si_3N_4$–$Y_2O_3$(–LS) system calculated from ESCA atomic concentrations.

### *3.2.3 Deposition of yttrium*

For a homogeneous $Si_3N_4$–$Y_2O_3$ system with 5 wt% $Y_2O_3$ the calculated Y/Si atomic ratio is 0·02. The Y/Si ratios calculated from ESCA atomic concentrations for the $Si_3N_4$–$Y_2O_3$(–LS) system varied from 0·05 to 0·12, indicating only a slight enrichment of yttrium on the surface. For the samples treated at pH 7, the Y/Si ratio increased with the increasing addition of lignosulphonate (see Fig. 6). At pH 10 the ratio remained fairly constant. The ESCA background analysis of Si 2*p* showed no difference between the $Si_3N_4$ and $Si_3N_4$–$Y_2O_3$ samples.

Since $Y_2O_3$ was added in the LS-containing solution prior to $Si_3N_4$ and since it has a surface charge opposite to LS, the LS adsorbs more on the yttrium surface. However, at pH 7, both the Y/Si ratios and the coverage of yttrium increased with increasing addition of LS (Figs 4(a) and 5). If yttria was covering the silicon nitride particles colloidally, the ESCA results should show a substantial yttria enrichment on the surface.

These results showed that most of the yttria did not cover the $Si_3N_4$ particles colloidally. However, the measured mean particle size at pH 7 indicates splitting of the primary yttria particles (from 0·8 $\mu$m to 0·3 $\mu$m), proposing that even colloidal particles exist in the system. This is assumed to be an explanation for the increase in the Y/Si ratio with the increasing addition of LS. According to Lidén *et al.*,[11] at pH 7, an addition of increasing amount of $Y_2O_3$ decreases the negative charge of the $Si_3N_4$ particles and finally countercharges the particles when more than 3 wt% $Y_2O_3$ is added. An adsorption of 2 wt% of $Y_2O_3$ on the $Si_3N_4$ occurs at a total of 5 wt% $Y_2O_3$ added in the dispersion.

## 4 Conclusions

It was found that the particle size of the $Si_3N_4$–$Y_2O_3$ system was strongly dependent on the pH and concentration of the lignosulphonate added in the dispersion. The ESCA results confirmed that lignosulphonate adsorbed both on the silicon nitride and yttrium oxide particles. It was also found that at pH 7 the relative amount of yttrium was increased at the surface with increasing amount of lignosulphonate added in the dispersion, suggesting an enhanced adsorption of yttria on silicon particles, due to the electrostatic attraction.

In the authors' next work further investigations on the electrokinetic potential measurements will be reported.

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