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Changes in Surface Characteristics of Silicon Nitride Prepared for Extrusion

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Abstract

The preparation step for extrusion (with binders) of Si_3N_4 powder, as well as the extrusion process itself, modify the original properties of the powder so that its recovery and subsequent rework are not possible.

X-ray photoelectron spectroscopy (XPS), X-ray diffraction, infra-red spectroscopy, potentiometric titrations and zeta potential determinations have been used to identify the surface modifications in Si_3N_4 due to addition of binders, and to examine powders after elimination of the binders by extraction with organic solvents and heat treatment.

The original Si_3N_4 with binders showed a shift in zeta potential and point of zero charge (PZC) to lower pH, indicating the adsorption of organic compounds on the Si_3N_4 surface at this step. The appearance of one O_{ls} peak at 532·3 eV in the XPS spectrum showed the presence of Si_2N_2O. After extraction with organic solvents the PZC value was close to that of the Si_3N_4 + binders (pH = 3·2), indicating incomplete removal of organics; this was confirmed by XPS determination (C_{ls} intensity data) and chemical analysis. The presence of Si_2N_2O was not modified as shown by XPS and the value of the isoelectric point. Heat treatment removes the organics completely but produces an oxidation of Si_3N_4 to SiO_2 as evidenced by a shift in the binding energy of the O_{ls} photopeak to 534·0 eV. © 1996 Elsevier Science Limited.

La mélange du Si_3N_4 en poudre avec des liants organiques et son postérieur processus d'extrusion, produit des modifications dans les propriétés originelles du Si_3N_4 qui ne permettent pas sa récupération et subsequent réutilisation. L'identification des modifications superficielles du Si_3N_4 avec des liants et après élimination des liants par extraction par solvents organiques et traitement thermique, ont été suivis par ESCA, DRX IR, titrages potenciomètriques et potentiel zèta.

Le Si_3N_4 avec liants a montré une diminution de la valeur du potentiel zèta et du point de zero charge (PZC), par rapport au Si_3N_4, ce qui indique l'existence d'adsorptions organiques superficielles. Le spectre ESCA, avec une pic à 532·4 eV (O_{ls}) démontre la présence du Si_2N_2O. Après l'extraction par solvents organiques, la valeur du PZC, près du Si_3N_4 + binders (pH = 3.2), marque la disparition partiel des liants organiques, aussi bien que les donnés d'intensité du C_{ls} et des analises chimiqués. L'ESCA et la valeur de IEP ont montré aussi la présence du Si_2N_2O. Le traitement thermique élimine completement les liants organiques mais produit l'oxidation du Si_3N_4 à SiO_2 comme montré l'apparition d'un pic a 534·0 eV du O_{ls}.

Introduction

The processing of silicon nitride powders to produce ceramics and the characteristics of the ceramics have been widely studied and reported.[1] Properties such as high fracture strength and decomposition point, and good wear, oxidation and thermal shock resistances make silicon nitride ceramics attractive for application in high-temperature machine parts.

The main forming process is injection (or extrusion) moulding; binders are mixed with Si_3N_4 powder and the forming process is similar to those used for plastics. Different and at times complex shapes, which are required by machine parts, can be achieved using this method. However, the binders (15–25%) must be removed before sintering. When a hot isostatic press (1000–3000 kg cm^{-2}, 500–2000°C) is employed, the application of binders is not necessary. In this case, the powder is formed and sintered in one step, but this is a high-cost process and complexity of the part shape is a limiting factor. In consequence, extrusion and the subsequent sintering process are used extensively.

Obviously, after the sintering temperature has been applied to the brown body and a material with high fracture strength obtained, recovery and subsequent rework of the powder is not possible. Therefore, the silicon nitride will be wasted if the shape or other properties of the final product do not satisfy the requirements.

Although recovery of the powder with its original properties from the brown body might be feasible, it has not been achieved to date.[2] Binders can be adsorbed with no subsequent elimination, modifying the surface properties of the silicon nitride powder and hindering its recovery not only after extrusion but also after thermal treatment for 1 week at 500°C. Thick, immobile, adsorbed layers of silane coupling agents have been reported[3] to be responsible for the creation of defects during binder removal. Consequently, study of the surface properties of Si_3N_4 powder, as well as those of brown bodies, is very important for exploring the possibility of powder recovery before sintering.

It is well known that surface composition influences the colloidal dispersion behaviour of silicon nitride powders in aqueous suspensions. This has a strong influence on the physical properties of the final sintered product.[4–8] Measurements of the surface charge by means of titration techniques have been used to characterize as-received and treated silicon nitride powders. Minor differences in powder surface compositions lead to changes in the point of zero charge (PZC) as determined by surface titration. In this way, depending on the source of the material, the PZC of silicon nitride powder has been found in the pH range 3–9.[5] X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that has been used to analyse the surface layer composition of several commercial silicon nitride powders.[9] Even when these powders are just exposed to ambient conditions, different proportions of silica and silicon oxynitride compounds have been identified. Consequently, these alterations in surface layer composition and structure would influence the behaviour of binders during steps in the formation of green and brown bodies.

This research is aimed at gaining an understanding of the transformations undergone by silicon nitride powder as a consequence of (1) the addition of binders and (2) their later elimination, by heat treatment or organic solvent extraction. Changes in surface composition have been studied by XPS and measurement of the surface charge by potentiometric titration and microelectrophoresis, whereas X-ray diffraction (XRD) and infra-red (IR) spectroscopy were used to monitor changes in the bulk sample.

Experimental

Materials

A commercial α-Si_3N_4 (95%) powder from Ube (SN-E10), with a particle size (80%) <0·8 μm and specific surface area of 9–13 $m^2\ g^{-1}$ (manufacturer's specifications), was selected for this research. The brown bodies, prepared from this powder, were kindly supplied by the Industrial Research Institute Aichi Prefectural Government. The binders utilized were polypropylene, polystyrene, propyl methacrylate, stearic acid and dioctylphtalate, in a ratio of binders/Si_3N_4 close to 20%.

Binder elimination methods

Binder elimination from brown bodies was carried out by heat treatment. The sample was milled by hand and heated at 500°C for 1 week. Heat treatment is the usual method employed in the industrial processing of silicon nitride powders. In the second method, not used in manufacturing processes, the binders were eliminated by extraction with organic solvents. In these experiments, the sample was treated with concentrated nitric acid followed by slow drying at 100°C, washed with water until neutral pH and washed again with ethanol. After this first treatment was completed, the residue was consecutively Soxhlet extracted and solvent washed with toluene (3 h), chloroform (4 h) and ethanol (1 h), heated in the presence of H_2O_2 to dryness and finally washed several times with distilled water.

Characterization techniques

X-ray diffractograms were obtained on a Philips PW 1140 diffractometer using CuK_α radiation and an Ni filter. The working conditions were 40 kV and 20 mA. Samples were analysed by means of the powder mounting technique.

Infra-red spectra of samples were obtained on KBr pellets (1% sample/KBr) using a Perkin–Elmer 577 spectrometer. The spectra were recorded on absorbance.

XPS analyses were performed in an ESCA Shimadzu 750 spectrometer with an Escapac 750 system. An Mg anode (1253 eV) operating at 30 mA and 8 mV was used as excitation source in a residual vacuum of 10^{-5} Pa. An energy correction was made to account for sample charging based on the C_{1s}, peak at 285 eV. The XPS spectra were normalized, the area of the peaks integrated and the full width at half-maximum (FWHM) measured.

Potentiometric titration experiments were carried out by first dispersing 5 g of sample in 90 ml of 0·1 or 0·001 M KCl supporting electrolyte. These dispersions were then titrated in nitrogen atmosphere with 0·1 M HCl or KOH solutions by adding a fixed volume of titrant every 15 min.[10] For each experiment, the relative adsorption of proton or hydroxyl ions by the solid, reported as $\mu C\ g^{-1}$, was plotted as a function of the dispersion pH. The common intersection point in the potentiometric curves obtained at different electrolyte concentrations was considered as the point of zero charge (PZC) of the sample. Samples were washed with water and ultracentrifuged before potentiometric titration was carried out.

Electrokinetic potentials of samples were determined using a Laser Zee Meter 501. The electrophoretic mobilities were converted into zeta potentials according to the Smoluchowski equation. For each determination, 0·05–0·1 g of sample was dispersed in 100 ml of 0·01 M KCl solution and the slurry stirred magnetically for at least 18–24 h before the measurements were carried out. To generate zeta potential versus pH curves and from them the isoelectric point (IEP), the pH of the slurry was adjusted using dilute HCl and KOH solutions followed by magnetic stirring to equilibrium.

Results and Discussion

Bulk characterization

Comparison of the XRD pattern of original silicon nitride (Si_3N_4) with those corresponding to samples obtained after binder addition (Si_3N_4 + binders) and subsequent removal by organic extraction (Si_3N_4 + binders/organic) or heat treatment (Si_3N_4 + binders/500°C), shown in Fig. 1, does not reveal any differences in number or in position of the peaks between the samples. These results indicate that the introduction and later elimination of the binders, by both organic extraction and heat treatment, do not lead to modifications of the crystalline species of the silicon nitride powder.

The IR spectra of the samples are illustrated in Fig. 2. The spectrum of Si_3N_4 + binders (spectrum b) shows bands at 1380, 1460, 2850, 2930 and 2970 cm^{-1} and at 1730 cm^{-1} which correspond to aliphatic C–H bonds and carbonyl (C=O) groups, respectively, of the organic compounds used as binders. These bands disappear after the sample has been treated to eliminate the binders (spectra c and d) and the spectra are similar to that obtained from original silicon nitride powder (spectrum a). The addition of binders followed by their removal does not introduce changes in the structure of the silicon nitride powder detectable by IR. However, a residual carbon content of 0·75% has been determined chemically in the Si_3N_4 + binders/organic sample No carbon was found in the Si_3N_4 + binders/500°C sample. The organic carbon concentration of the Si_3N_4 + binders sample was 18·2%.

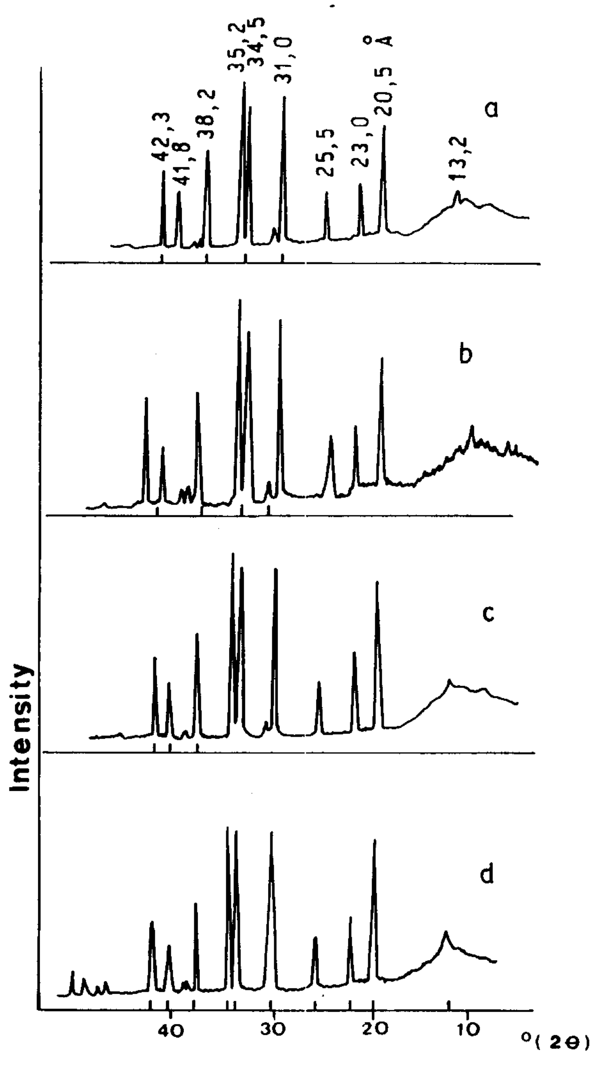

Fig. 1. XRD patterns of samples: (a) Si_3N_4, (b) Si_3N_4 + binders, (c) Si_3N_4 + binders/organic and (d) Si_3N_4 + binders/500°C.

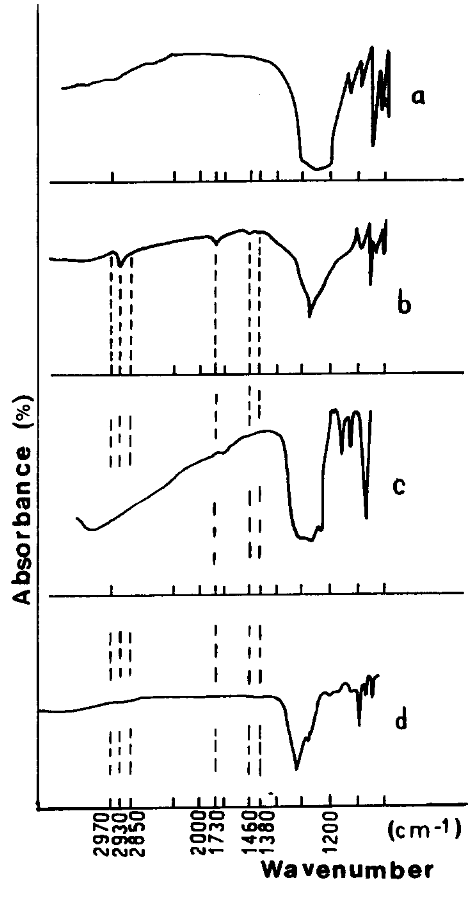

Fig. 2. IR spectra of samples: (a) Si_3N_4, (b) Si_3N_4 + binders, (c) Si_3N_4binders/organic and (d) Si_3N_4 = binders/500°C.

Table 1. Area (a.u.) and FWHM (eV) measured for C_{1s}, N_{1s}, O_{1s} and Si_{2p} peaks in the XPS spectra of samples

	Si_3N_4 + *binders*	Si_3N_4 + *binders/organic*	Si_2N_4 + *binders/500°C*
Peak area			
C_{1s}	70113	31436	24023
N_{1s}	3411	7102	29630
O_{1s}	23085	25487	61106
Si_{2p}	4320	4638	18576
FWHM			
C_{1s}	2·2	2·1	3·0
N_{1s}	1·8	1·9	2·0
O_{1s}	2·7	2·9	2·5
Si_{2p}	2·3	2·2	2·4

Surface characterization

Table 1 shows values of the area and FWHM for peaks in the XPS spectra of Si_3N_4 + binders, Si_3N_4 + binders/organic and Si_3N_4 + binders/500°C. The N_{1s} and Si_{2p} peaks were symmetrical and could not be deconvoluted, their FWHM values being similar to those obtained by Bergstrom and Pugh[7] for three silicon nitride powders of different origin (N_{1s} = 2·1 ± 0·07 eV and Si_{2p}= 2·4 ± 0·04 eV). As expected, the removal of organic compounds led to a decrease in the C_{1s} peak area. In the case of the Si_3N_4 + binders/organic sample, the area decrease was less sharp. This result agrees with the residual carbon content that was chemically determined in this sample as mentioned above. Unlike carbon, oxygen content at the surface increases upon elimination of binders, this being especially remarkable for the Si_3N_4 + binders/500°C sample Thus compared with those of Si_3N_4 + binders and Si_3N_4 + binders/organic, the area of the O_{1s}, peak for Si_3N_4 + binders/500°C is more than doubled. These results suggest the oxidation of the sample surface during binder elimination mainly by heat treatment. The increase of N_{1s} and Si_{2p} areas could be due to organic screen elimination.

The measured binding energies (BE) of N_{1s}, O_{1s} and Si_{2p} electron levels from XPS spectra of Si_3N_4 + binders, Si_3N_4 + binders/organic and Si_3N_4 + binders/500°C are given in Table 2, together (for comparison) with binding energies for Si_3N_4, SiO_2 and Si_2N_2O previously reported by other authors.[7–9,11,12] The addition of binders to silicon nitride powder does not modify the binding energies of the N_{1s} and Si_{2p} electron levels. However, a signal appears at 532·5eV which can be ascribed to O_{1s} from Si_2N_2O. The peaks corresponding to N_{1s} and Si_{2p} are shifted to higher energies after the removal of binders. In addition, for Si_3N_4 + binders/500°C, the energy increase of the Si_{2p} level is higher and approaches that of SiO_2. The energies of Si_{2p} and O_{1s} for the Si_3N_4 + binders/organic sample are comparable to those of Si_2N_2O. When the Si–N bond is converted to Si–O by surface oxidation, the charge on Si atoms will increase. Consequently, the binding energy of Si_{2p} will be higher. The Pauling charge on Si atoms for samples have been estimated based on a linear relationship established by Brown and Pantano[6,11] between average charge on Si atoms and binding energy of Si_{2p} level for several silicon compounds. Average charges on Si atoms of 1·67, 1·89 and 2·30 eV for Si_3N_4 + binders, Si_3N_4 + binders/organic and Si_3N_4 + binders/500°C, respectively, have been obtained. Values of 1·56, 1·81 and 2·34 eV were previously determined on Si atoms for Si_3N_4, Si_2N_2O and SiO_2. These results suggest that the outer surfaces of the brown bodies studied are on the whole silica-like when heat treatment is applied, whereas the predominant compound in the solvent extracted samples seems to be oxynitride-like.

The titration curves of silicon nitride, silicon nitride with binders and those samples obtained after binder removal are illustrated in Fig. 3. The PZC of silicon nitride occurs at pH 6·2 [Fig. 3(a)]. This result is in agreement with that previously reported for this powder.[5] The presence of binders shifts the PZC value of silicon nitride to pH 2·8 [Figure 3(b)] and the subsequent extraction with organic solvents to pH 3·2 [Fig. 3(c)]. This result shows the presence of acidic groups after addition of binders. The PZC for Si_3N_4 + binders/500°C at pH = 5·5 [Fig. 3(d)] is close to that of the original silicon nitride powder [Fig. 3(a)]. It seems that removal of binders by heat treatment partly restores the original titrated surface groups of silicon nitride powder, but the charge density does not attain the original Si_3N_4 value (e.g. at pH 7 for Si_3N_4 the charge density was

Table 2. Binding energies (BE in eV) of N_{1s}, O_{1s} and Si_{2p} in the XPS spectra of samples and those of silica, silicon nitride and silicon oxynitride[7–9,11,12]

Sample	N_{1s}	O_{1s}	Si_{2p}
Si_3N_4	397·3–397·7	–	101·4–101·7
Si_3N_4 + binders	397·9	532·5	101·7
Si_3N_4 + binders/organic	398·2	532·6	102·1
Si_3N_4 + binders/500°C	399·0	534·0	103·0
Si_2N_2O	397·7–397·9	532·6	101·9–103·1
SiO_2	–	533·6	103·6

10 × 10^6 μC g^{-1} and for Si_3N_4 + binders/500°C was 0·5 × 10^6 μC g^{-1}). The oxidation of Si_3N_4 to Si_2N_2O or SiO_2, detected by XPS results, is not evidenced by titration curves.

An isoelectric point (IEP) at pH range 6–7 has been reported for the silicon nitride powder employed in this work.[4,12] As shown in Table 3, the addition of binders to silicon nitride to form the brown body shifts the IEP value to lower pHs. Si_3N_4 + binders shows an IEP at pH = 2·1. In addition, the removal of binders does not lead to the recovery of the original IEP at pH range 6–7. The IEP has been reported to provide an estimate of the acidity of the solid surface, which increases as the IEP is shifted to lower pHs. Based on this, the addition of binders to silicon nitride powder clearly increases its acidity. These results suggest that the surface of silicon nitride was oxidized during the first step of processing, in agreement with XPS results, as a consequence of binder addition. Therefore, their subsequent elimination will result in changes in surface composition but the oxidized surface groups will remain or even increase in concentration, depending on the binder removal method used. The IEP differences between solvent extracted (IEP at pH 2·2) and heat-treated (IEP at pH 3·3) samples may be due to the remaining organic compounds adsorbed on the surface of the former. The difference between the IEP and PZC values (pH = 5·5 and 3·3, respectively) for the Si_3N_4 +binders/500°C sample indicates the surface adsorption of a compound of lower PZC such as SiO_2 (PZC of SiO_2 pH = 2 to 2.5[14]).

Table 3. IEPs of samples from zeta potential versus pH curves and that of silicon nitride[5,13]

Samples	*pH_{IEP}*
Si_3N_4	6–7
Si_3N_4 + binders	2·1
Si_3N_4 + binders/organic	2·2
Si_3N_4 + binders/500°C	3·3

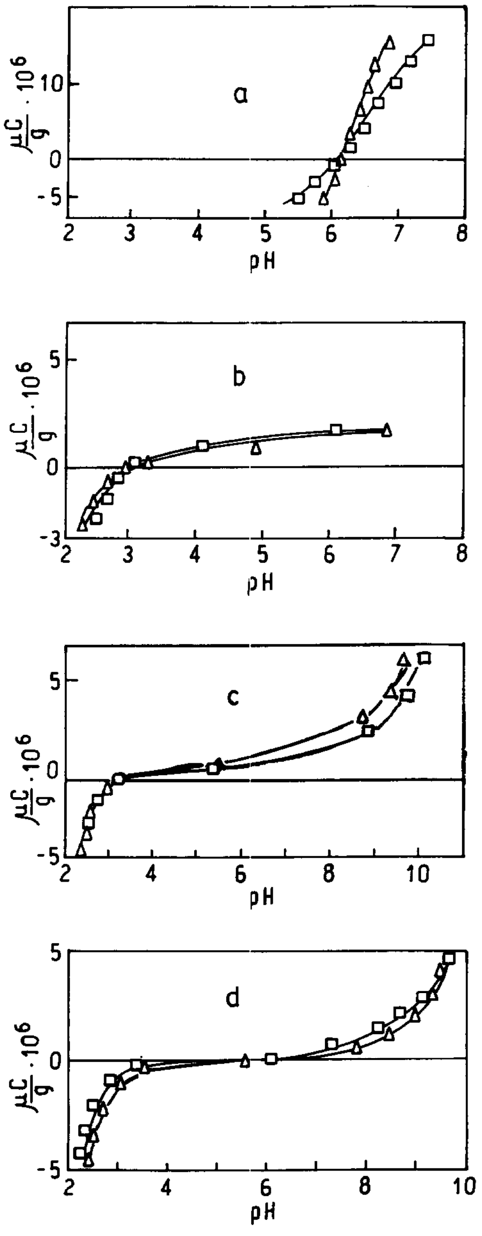

Fig. 3. Titration curves of samples: (a) Si_3N_4, (b) Si_3N_4 + binders, (c) Si_3N_4 + binders/organic and (d) Si_3N_4 + binders /500°C. In KCl supporting electrolyte: (□) 10^{-1} and (△) 10^{-3} M.

The surface oxygen content has been found to have a clear influence on the pH of the IEP of silicon nitride powders. In fact, a linear relationship between the surface oxygen content and the pH of the IEP was established for these compounds.[9] For example, by applying this equation the to the IEP value of the Si_3N_4 + binders/500°C sample, a surface oxygen content of 0·10 g/cm^{-2} was estimated, whereas the oxygen content of the original silicon nitride powder was 0·04 g/cm^{-2}. This surface oxygen increase of more than twice in Si_3N_4 + binders/500°C is assigned to SiO_2 in agreement with XPS results, and corroborates the difference observed between IEP and PZC values.

Conclusion

The addition of binders to Si_3N_4 powders, for extrusion, leads to surface changes which hinder its recovery from the brown body step and after extraction by organic solvents or heat treatments.

Binder addition results in adsorption of organic compounds on the Si_3N_4 surface, evidenced by an abrupt decrease in the pH values of IEP and PZC from 6·2 and 6–7 to 2·1 and 2·8, respectively. A surface oxidation to Si_2N_2O was revealed by the appearance of an O_{1s}, photopeak, in the XPS spectra, at 532·3 eV.

Binder extraction by treatment with organic solvents produces an intense but not total elimination of organic adsorption as shown by the decrease of C_{1s}

peak area from 70 113 to 31 436 (a.u.) and by chemical analysis. The similar IEP and PZC values obtained for samples Si_3N_4 + binders and Si_3N_4 + binders/organic indicate that surface modifications remain unaltered.

Heat treatment eliminates the surface organic adsorption and produces Si_3N_4 oxidation to SiO_2, as revealed by the more than two-fold increase in the O_{1s} photopeak area and the difference between IEP and PZC values.

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