JOURNAL OF MATERIALS SCIENCE **26** (1991) 216–224

Surface chemistry and suspension stability of oxide–nitride powder mixtures

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The effect of bimetallic oxide sintering aids on the colloidal stability of homogeneous (surface-coated) and heterogeneous (mechanically mixed) silicon nitride powder mixtures in aqueous solution was studied by acoustophoretic analysis. While the surface charge generation and colloidal stability of single-phase and oxide-coated silicon nitride powder mixtures may be described according to the site dissociation model of amine and hydroxyl surface groups, the surface charge observed in heterogeneous multiphase powder mixtures is associated with the adsorption of soluble metal ion hydroxocomplexes on the nitride particles. Segregation of the mixtures by heteroflocculation, which causes the formation of agglomerates and microstructural defects upon sintering, may be avoided by generation of a threshold surface potential of equal sign on all powder constituents at a pH where the metal hydroxide dissolution is subcritical.

1. Introduction

The fabrication of defect-controlled ceramic components with improved strength and high reliability of the mechanical properties essentially depends on the uniformity of the particle packing in the green compact [1, 2]. Low pore coordination numbers and small pore-size distributions were recognized to suppress defect formation upon sintering which occurs by exaggerated pore growth and differential shrinkage in the vicinity of packing inhomogeneities [3–7]. The particle arrangement during green compact formation is governed by physical and chemical particle–particle interactions which may be best controlled in a liquid suspension system [8]. Thus, colloidal processing techniques such as slip casting and filtration have become of particular importance for the formation of uniform green compacts with a high density from submicrometre ceramic powders [9–11]. By use of colloidal processing techniques, high strength and Weibull modulus could be achieved in agglomeration-free sintered compacts of titania ($\sigma = 735$ MPa, $m = 22$), silicon carbide (1087, 20), alumina (1042, 12) and yttria-stabilized zirconia (2000, 13) [12].

The particle–particle interactions in a suspension are related to the physico-chemical properties of the solid–liquid interface which is mainly dominated in aqueous suspensions by electrical surface-charge effects. Several well-established models have been developed to describe the double layer formation at the oxide–solution interface of single-phase powders, e.g. the porous-gel model [13], the site-dissociation and the site-binding models [14, 15]. They are all based on the idea of incorporating specific chemical dissociation processes at the surface and in solution into electrical double-layer theory. Usually, electrophoretic properties are measured from which the zeta potential and the conditions for colloidal stability of the dispersed phase may be evaluated for very dilute suspensions according to the DLVO theory [16]. While most of the published work on electrophoretic properties deals with single phase powders, only little information may be found on multiphase powder mixtures [11, 17, 18]. Many of the high-performance ceramics, however, contain mixtures of different powders, for example the zirconia-toughened alumina, silicon carbide whisker-toughened silicon nitride, etc. Only for silica particles dispersed in a solution containing hydrolysable cobalt ions, has an ion adsorption mechanism been proposed to explain the electrokinetic behaviour with pH as a function of the metal-ion concentration [19–21]. In the absence of any theoretical models suggested for the explanation of the electrokinetic behaviour of heteroparticulate systems, the ion-adsorption mechanism was also extended to systems containing mixtures of alumina and titania [11].

In systems containing oxide and non-oxide particles, such as silicon nitride with oxidic sintering aids, great differences in the surface chemical properties of the different powder components may occur. Even small variations in the powder surface purity, amount and distribution of the oxide phase, etc., can induce strong effects on the colloidal behaviour, for example homogeneous and heterogeneous coagulation between similar and dissimilar particles may cause inhomogeneities or specific adsorption of polyelectrolytic surfactants may become more difficult. Mg–Al and Y–Al oxide mixtures are commonly used as sintering aids to promote a liquid-phase sintering of silicon nitride [22]. After sintering high-melting oxides like $MgAl_2O_4$ or $Y_3Al_5O_{12}$ may be crystallized from the residual glass phase which results in a significant improvement of the mechanical properties at high temperatures [23].

0022–2461/91 $03.00 + .12

The object of the present investigation was to understand the influence of oxide additives on the colloidal behaviour of silicon nitride powder mixtures in aqueous suspensions. Owing to the high solids concentrations of slurries that are used in slip-casting techniques and the dependence of colloid stability on particle concentration, electrophoretic mobility measurements in dilute suspensions (<0.1 vol %) are of limited use for real systems. In particular, the surface adsorption of hydrolysis products from the solid–liquid dissolution reactions may exert a significant influence on the surface chemistry and charge generation in concentrated suspensions whereas the solubility of the solid phase plays only a minor role in very dilute suspensions. Thus, a new method, called acoustophoresis, was employed in this study which enables mobility and zeta potential values for particles in concentrated suspensions (>1 vol %) to be determined [24]. As-received silicon nitride, mechanically mixed, and surface-coated oxide–nitride powder mixtures were examined by means of acoustophoretic analysis, in order to characterize the effect of the distribution of a secondary phase on the surface chemistry and suspension stability of heterogeneous powder mixtures.

2. Experimental procedure

2.1. Powder processing

A high-purity α-Si_3N_4 powder (LC 12, H. C. Starck, Berlin, FRG) with a specific surface area (BET) of approximately $17\ m^2\,g^{-1}$ and a mean grain size of $\bar{a} = 0.45\ \mu m$ was used. The major impurities in the starting powder were carbon and oxygen with 0.19 and 1.98 wt %, and a total metal content (iron, aluminium and calcium) of 0.048 wt %. Three bimetallic oxide powder mixtures with the cation ratio Mg : 2Al, Y : Al, and Nd : Al were prepared by hydrolysis of the appropriate bimetallic alkoxides in alcoholic solution and subsequent calcination at 1000 °C for 1 h [25]. The fine size and the homogeneity of the bimetallic hydroxide precipitation particles were found to be highly suitable for attaining an intimate mixing of additives and silicon nitride powders required for sintering [26]. By *in situ* precipitation of the hydroxides in a silicon nitride suspension, coating of the particles by a sol–gel process may be achieved. After calcination, bimetallic oxides were found by X-ray diffraction: $MgAl_2O_4$ (Mg : 2Al), $Y_3Al_5O_{12} + YAlO_3$(Y : Al), and $Nd_4Al_2O_9 + NdAlO_3$ (Nd : Al). The approximation of the primary crystallite size by X-ray line-broadening measurements according to the Scherrer equation revealed an average size of 15 nm.

The silicon nitride powder mixtures were prepared either by mechanically mixing the oxide and nitride powders or by *in situ* precipitation of the hydroxide on to the surface of the dispersed silicon nitride powder particles in alcoholic suspension (sol–gel coating, Fig. 1). Both powder mixtures contained 10 wt % oxide additives. For convenience the powders were labelled as either mechanically mixed (mm) or precipitation mixed (pm) samples. Mechanical mixing was carried out in an attrition mill with a polyamide container filled with alumina balls at 500 r.p.m. for 4 h in isopropanol. After milling, the powder mixture was dried in a rotary evaporator and sieved with 100 μm. Mixing by *in situ* precipitation of the bimetallic hydroxide in isobutyl suspension required the presence of a well-deflocculated system. To achieve deflocculation the silicon nitride powder was first ultrasonicated for 30 min. The appropriate amount of liquid alkoxide was added under intensive stirring. Subsequently, water/triethylamine solution was slowly dropped into the suspension which was stirred for 6 h to ensure complete precipitation of the hydroxides. The solute was removed under slight vacuum at room temperature in a rotary evaporator. The dried powder was calcined at 1000 °C for 1 h in air. Larger agglomerates that had been formed during calcination were destroyed by ball milling the powder mixture in isopropanol for 4 h. Finally, the pm powder was dried and sieved with 100 μm.

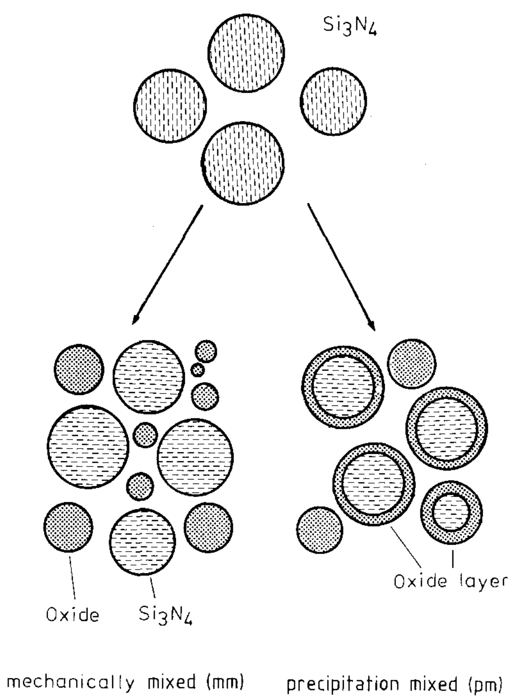


Figure 1 Schematic model of the powder microstructures prepared for the colloid stability studies.

2.2. Acoustophoretic measurements

A novel technique, called acoustophoresis, was used in this study (PEN KEM 7000, Pen Kem Inc., Bedford Hills, New York). The electric field which is generated due to charge separation between the particle and the surrounding double layer under the influence of a compressional ultrasonic wave of 200 kHz can be measured (colloid vibration potential, CVP) and transformed to a relative acoustic mobility (RAM). The RAM is analogous to the electrophoretic mobility determined in electrophoretic experiments. The RAM can be converted to an acoustic mobility (AM) on considering the particle volume fraction, ϕ, and the densities of the liquid, ρ_l, and the solid phase, ρ_s [24]

$$\mathrm{AM} = \frac{\mathrm{RAM}}{2\phi}\left(\frac{\rho_l}{\rho_s - \rho_l}\right)\frac{\gamma(\kappa a, \phi)}{\omega(\phi)} \qquad (1)$$

$\gamma(\kappa a, \phi)/\omega(\phi)$ is a complex function of the normalized electrical double layer thickness, κa, and ϕ which takes into account the particle–particle electrical and hydrodynamic interactions in real (concentrated) suspensions, based on the cell-model theory [13, 27]. For thin electrical double layers, i.e. $\kappa a \gg 1$, however, this interaction parameter can be approximated by $(1 - \phi)$, so that for decreasing particle concentrations it tends to unity. For the present measurements the powders were dispersed in aqueous solution at 25 °C with solid volume fractions of $\phi = 1$ vol %. The reciprocal Debye length, κ, is given as

$$\kappa = \left(\frac{\sum_i z_i^2 c_i F^2}{\varepsilon R T}\right)^{1/2} \tag{2}$$

where z_i and c_i are charge number and average concentration of the ions in the solution, F is the Faraday constant (9.64867×10^4 C mol^{-1}) and $\varepsilon = \varepsilon_r \varepsilon_0$ is the dielectric constant of water ($\varepsilon = 6.95 \times 10^{-10}$ C^2 J^{-1} m^{-1} at 25 °C). Thus, for an electrolyte concentration of 10^{-2} mol l^{-1} KCl a $\kappa \simeq 3.3 \times 10^8$ m^{-1} results. Taking into account the mean grain size of $a = 0.45$ µm, the normalized electrical double layer thickness of $\kappa a \simeq 148$ fulfils the assumptions mentioned above. From the acoustic mobility the zeta potential, Ψ_ζ, can be determined using similar relations as for the electrophoretic mobility [24]. For $0.2 < \kappa a < 200$ the Henry equation relates the mobility to the zeta potential [28]

$$\Psi_\zeta = \frac{3}{2} \mathrm{AM} \frac{\eta}{\varepsilon} f(\kappa a) \tag{3}$$

where η is the viscosity of water (0.89 mPa sec at 25 °C) and $f(\kappa a)$ is the "retardation" correction function which can be expressed for $\kappa a > 1$ by [29]

$$f(\kappa a) = \left[\frac{3}{2} - \frac{9}{2\kappa a} + \frac{75}{2(\kappa a)^2} - \frac{330}{(\kappa a)^3}\right]^{-1} \tag{4}$$

With $f(\kappa a) = 0.679$ for the present system ($\kappa a \simeq 148$), Equation 3 may well be approximated by the Helmholtz–Smoluchowski equation

$$\Psi_\zeta \simeq \mathrm{AM} \frac{\varepsilon}{\eta} \tag{5}$$

which therefore was used to calculate the zeta potential from the mobility data.

A titration burette (ABU 93, Radiometer, Copenhagen, Denmark) was used to change the pH continuously in the range 2 to 12 by adding KOH or HCl (1 mol l^{-1}), respectively. Prior to taking the measurements, the suspensions were ultrasonicated and magnetically stirred under vacuum to ensure that only single particles were measured.

3. Results and discussion

3.1. Zeta potential and surface chemistry

3.1.1. Single-phase silicon nitride powder

The RAM–pH isotherms for the as-received single-phase silicon nitride powder are given in Fig. 2. The aqueous suspension contained a solid-phase volume ratio of 5% (= 15.7 wt %). The curves for the three different KCl concentrations of 0.01, 0.027 and 0.045 mol l^{-1} all intersect at the same isoelectric point (iep), at pH 7.4 (at the iep RAM = $\Psi_\zeta = 0$). The common iep indicates that the background electrolyte KCl is not potential-determining but only the H$^+$ and OH$^-$ ions [29].

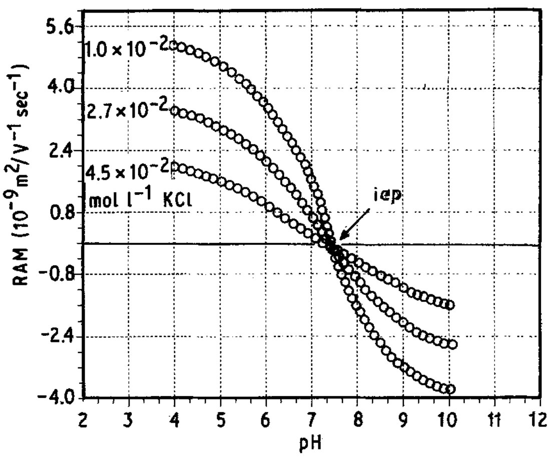


Figure 2 RAM–pH isotherms of single-phase Si_3N_4 powder in aqueous suspension (5 vol %) at various KCl concentrations.

Earlier studies [30, 31] suggest a hydrolysis at room temperature of silicon nitride to form silica and ammonia

$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3. \tag{6}$$

A high pH could facilitate this reaction by dissolution of SiO_2 so that new Si_3N_4 surface is made available. The hydrolysis reaction can be written by use of surface groups instead of molecules [32]

$$\left[\begin{array}{l}\mathrm{Si}\\ \mathrm{Si}\end{array}\!\!>\mathrm{N{-}Si}\right] + 2H_2O \rightarrow [\mathrm{Si{-}NH_2}] + 2[\mathrm{Si{-}OH}] \tag{7a}$$

$$[\mathrm{Si{-}NH_2}] + H_2O \rightarrow [\mathrm{Si{-}OH}] + NH_3 \tag{7b}$$

Surface charging of the silicon nitride particles in water is, therefore, related to the pH-dependent dissociation of silanol groups, SiOH, on the particle surface

$$[\mathrm{SiOH_2}]^+ \xleftarrow{H^+} [\mathrm{SiOH}] \xrightarrow{OH^-} [\mathrm{SiO}]^- + H_2O \tag{8a}$$

which is essentially equivalent to the specific adsorption of protons or hydroxyls. The ionization of surface groups is commonly observed with oxide as well as amine surfaces [29]. A similar dissociation mechanism is assumed to account for the charge formation on the surface of nitride particles where amino-derived surface groups, silazane Si_2NH and silylamine $SiNH_2$, may form positively and negatively charged surface groups

$$[\mathrm{Si_2NH_2}]^+ \xleftarrow{H^+} [\mathrm{Si_2NH}] \xrightarrow{OH^-} [\mathrm{Si_2N}]^- + H_2O \tag{8b}$$

$$[\mathrm{SiNH_3}]^+ \xleftarrow{H^+} [\mathrm{SiNH_2}] \xrightarrow{OH^-} [\mathrm{SiNH}]^- + H_2O \tag{8c}$$

It has been shown that the number of amino groups could be increased by leaching the silicon nitride powder in an alkaline solution [33]. Leaching in acidic solution, however, resulted in a decrease of surface amino groups and an increase of silanol site density on the surface [34]. Depending on the fractional site occupancy of the various surface groups, ν_i, ($\nu_i = n_i/N$ where n_i is the number of surface groups i, N is to the total number of dissociating surface groups, and $\Sigma_i \nu_i = 1$) and their pH-dependent dissociation a wide variation of the iep can be observed in silicon nitride powders [32, 35–37]. From long-term ageing experiments, however, a constant value for the iep at $\text{pH} = 6.8 \pm 0.3$ was found which was interpreted as the equilibrium iep for silicon nitride in aqueous suspension [32]. A lower iep at pH 4 to 6 may be attributed to a silanol-rich surface. An iep at pH 6.5 to 8 may be explained by the dominance of silazane and silylamine groups, as it was found, for example, in laser-synthesized highly pure silicon nitride powder [38].

The zeta potential data may be quantitatively analysed in terms of electrical double-layer theory by relating the total double-layer potential, Ψ_0, to the pH by a modified Nernst equation [15]

$$\Psi_0 = 2.303\frac{kT}{e}\left(\text{pH}_{\text{pzc}} - \text{pH} - \frac{1}{2}\log\Omega\right) \quad (9)$$

where pH_{pzc} is the pH at the point of zero charge and Ω is given by the concentration ratio of all positively and negatively charged surface groups at a given pH, according to

$$\Omega = \prod_i \left[\frac{(\text{M}_i\text{H}_2)^+}{(\text{M}_i)^-}\right]^{\nu_i} \quad (10)$$

with $\text{M}_i = \text{SiO}^-$, Si_2N^-, and SiNH^-, respectively. In the absence of specific adsorption from the background electrolyte as indicated by Fig. 1, the pzc equals the iep, and the double-layer potential, Ψ_0, may be approximated by the measurable zeta potential, Ψ_ζ. Using the concept of surface dissociation constants, K, [39] for the hydroxide dissociation reactions according to Equations 8 with

$$K_a = \frac{[\text{MH}_2^+]}{[\text{MH}][\text{H}^+]} \quad (11a)$$

$$K_b = \frac{[M^-][\text{H}_2\text{O}]}{[\text{MH}][\text{OH}]} = \frac{1[\text{M}^-][\text{H}^+]}{K_w[\text{MH}]} \quad (11b)$$

(a: acid, b: base, w: water)
Ω may be expressed as

$$\Omega = \prod_i \left[\frac{K_{ai}(\text{H}^+)_s^2}{K_{bi}K_w}\right]^{\nu_i} \quad (12)$$

The surface proton concentration $(\text{H}^+)_s$ is related to the bulk concentration $(\text{H}^+)_b$ by [29]

$$(\text{H}^+)_s = (\text{H}^+)_b\exp\left(-\frac{F\Psi_0}{RT}\right) \quad (13)$$

At the iep the zeta potential equals zero and $(\text{H}^+)_s = (\text{H}^+)_b$ so that from Equations 9 and 12

$$\text{pH}_{\text{iep}} = 7 + \frac{\sum_i \nu_i \text{p}K_{bi} - \sum_i \nu_i \text{p}K_{ai}}{2}$$
$$= 7 + \frac{1}{2}\sum_i \nu_i \Delta\text{p}K_i \quad (14)$$

with $\Delta\text{p}K = \text{p}K_b - \text{p}K_a$. Equation 14 shows that for $\Sigma\,\nu_i\text{p}K_{ai} = \Sigma\,\nu_i\text{p}K_{bi}$ a pH_{iep} of 7 is calculated resulting in a symmetrical Ψ_ζ–pH isotherm, whereas the asymmetry increases with increasing difference between $\Sigma\,\nu_i\text{p}K_{ai}$ and $\Sigma\,\nu_i\text{p}K_{bi}$. Using the dissociation constant for H_4SiO_4, Table I, a $\text{pH}_{\text{iep}} \simeq 4.5$ is estimated from Equation 14. Such low values were found in preoxidized silicon nitride powders where a 1.5 to 2 nm thick silica layer on the surface governs the surface charge generation [40]. Extending the above approximation to ammonia-derived surface groups and taking for Si_2NH a $\text{p}K_b \simeq 9$ as it is characteristic for aromatic amines a $\text{pH}_{\text{iep}} \geqslant 9$ would be calculated for the case of primary and secondary amine surface groups dominating the surface chemistry. Suggesting that at equilibrium both the silanol and silazane surface groups contribute to the generation of an average surface charge, $\nu_{\text{SiOH}} = \nu_{\text{Si}_2\text{NH}} = 0.5$, Equation 14 yields a mean pH_{iep} of approximately 7. This estimated value coincides with experimentally determined pH_{iep} for aqueous silicon nitride suspensions in equilibrium [32]. Although the dissociation of surface-bonded silanol or silazane groups may differ from that of the corresponding acid or base in aqueous solution and the surface composition may be much more complex than assumed, this estimation clearly shows the influence of surface composition on the pzc (and iep) and the sign of the surface charge on silicon nitride powders suspended in water.

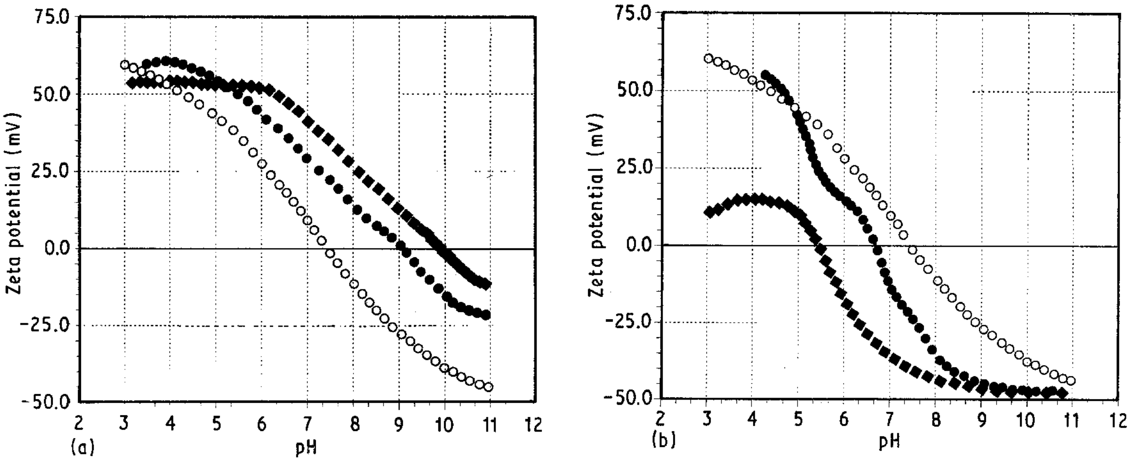
TABLE I Base constants and solubility products of metal hydroxides at 25 °C [53].

Metal hydroxide	$\text{p}K_b$	$\Delta\text{p}K$	pH_{iep}	K_s
Mg(OH)_2	2.59	−8.8	2.6	1.8×10^{-11}
Y(OH)_3	5.66	−2.6	5.7	8×10^{-23}
Nd(OH)_3	5.5	−3	5.5	3.2×10^{22}
Al(OH)_3	8.99	4.0	9.0	1.3×10^{-33}
Si(OH)_4	4.49	−5.0	4.5	
aromatic amines	>9	>5	9.5	

$K_s = (\text{M}^{n+})(\text{OH}^-)^n(\text{mol}\,\text{l}^{-1})^n$.

3.1.2. Oxide-coated silicon nitride powder (pm)

The zeta potential of the silicon nitride–oxide powder mixtures at a constant ion strength of 0.01 mol l^{-1} KCl are given in Fig. 3a to c. Significant differences may be seen between the single-phase silicon nitride and the oxide-coated multiphase powder mixtures. While the single-phase silicon nitride powder exhibits an iep at pH = 7.4, the Mg–Al-oxide containing samples show the iep at pH = 10 Fig. 2a. In contrast to the single-phase silicon nitride, the pm powder shows a high positive zeta potential at intermediate and low pH but only a small negative value above the iep. Thus, between pH 7.4 and 10 a potential reversal occurred from the nitride to the oxide-coated powder. Similar differences between the single-phase silicon nitride and the Y-Al- and Nd–Al-oxide containing samples, but with a shift of the iep to lower pH, are shown in Fig. 3b and c.



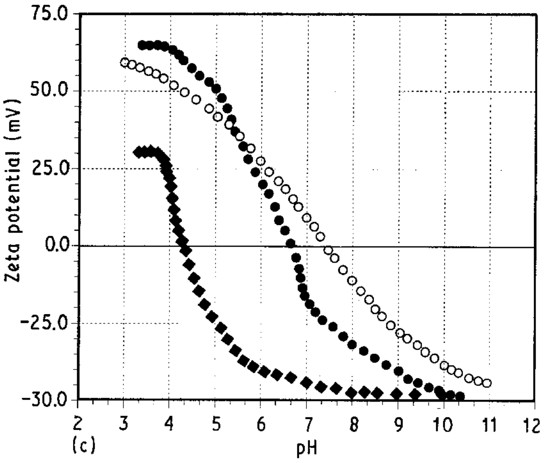


Figure 3 Ψ_ζ-pH isotherms of (a) $MgAl_2O_4$, (b) $Y_3Al_5O_{12}$ and (c) $NdAlO_3$ containing powder mixtures (1 vol %). (●) Mechanical mixture and (◆) surface coated (precipitation mixed) powders, (○) single-phase Si_3N_4.

With increasing occupancy of the silicon nitride surface by the precipitated oxide phase, the pH-dependent dissociation and solubility of the hydrolysed surface groups on the outer oxide/liquid surface will increasingly influence the surface charge generation in the powder mixture. According to the hydrolysed metal ion adsorption model [19–21], low concentrations of hydrolysed metal ions in the solution may induce a charge reversal on the matrix powder due to specific adsorption of charged metal hydroxo-complexes which can result in the occurrence of more than one pzc (and iep) [41]. Above a certain thickness of the precipitated oxide layer on the matrix powder surface, however, surface charge generation will be dominated by the oxide phase only. For oxides with low solubility, Table I, a surface layer thickness of only a few nanometres would be sufficient for a total screening of the silicon nitride powder surface [42]. The coated multiphase silicon nitride powder mixture will behave like a single-phase oxide powder which exhibits significant differences in sign and magnitude of the zeta potential compared to the single-phase silicon nitride powder, Fig. 3a to c. Expressing the iep of the oxide-coated powder mixtures in terms of the ΔpK values of the corresponding metal hydroxides, according to Equation 14, results in pH values of 2.6 (MgO), 5.7 (Y_2O_3), 5.5 (Nd_2O_3) and 9.0 (Al_2O_3) for monometallic and 6.9 ($MgAl_2O_4$), 7.3 ($Y_3Al_5O_{12}$) and 7.2 ($NdAlO_3$) for bimetallic oxide coatings. A comparison of the estimated pH values for the iep with the measured values from Fig. 3a to c shows that the measured values of $pH_{iep} = 9.8$ ($MgAl_2O_4$), 5.5 ($Y_3Al_5O_{12}$) and 4.4 ($NdAlO_3$) cannot be explained by the bimetallic oxide surface compositions. While the $MgAl_2O_4$-coated Si_3N_4 powder exhibits a high pH_{iep} which is characteristic for aluminium hydroxide, the charge generation on the $Y_3Al_5O_{12}$- and $NdAlO_3$-coated particles seems to be dominated by the yttrium– and neodymium–hydroxide dissociation resulting in a significant decrease of the pH_{iep}.

Equilibrium between the suspended powder and the suspension medium requires that the oxide surface coating must dissolve until the solution composition corresponds to the solubility conditions, K_s,

$$K_s = (M^{n+})(OH^-)^n \qquad (15)$$

for the dissolution reaction $M^{n+}(OH)_n \rightarrow M^{n+}$-aqu. + nOH^-. While for silicon nitride and some oxides, notably α-alumina, the dissolution kinetics are so slow that they may be regarded as essentially "insoluble" in water, the ageing may become important for the systems at present under consideration. Preferential dissolution of the metal hydroxides with the highest solubility may significantly influence the surface composition and structure of the aged powder. Owing to the solubility at equilibrium conditions, Table I

$$K_s^{Mg(OH)_2} > K_s^{Nd(OH)_3} > K_s^{Y(OH)_3} > K_s^{Al(OH)_3}$$

an enrichment of aluminium hydroxide on the surface of the oxide-coated silicon nitride may be possible at low pH. The change of the surface composition due to leaching may become even more important with decreasing grain size where the solubility increases. In-particular the small primary crystallite size of sol–gel derived surface coatings on the nanometre scale may cause significant ageing effects such as pH change and destabilization with time, resulting in spontaneous flocculation and agglomeration of the oxide-coated silicon nitride powder.

3.1.3. Mechanically mixed silicon nitride–oxide powder mixture (mm)

While the generation of the electric double layer in a suspension containing only particles of the same phase may be explained by a well-established surface site dissociation model [29], the situation in suspensions containing more than one solid phase is more complex. Two different surfaces, that of the nitride and that of the oxide particles, now interact with the aqueous solution and with each other. According to the ion adsorption model [19–21], hydrolysed metal ion complexes from the oxide phase may be specifically adsorbed on the nitride surface either by chemical or physical interaction. While physically adsorbed counterions only result in a reduction of the zeta potential, chemically adsorbed ions result in a shift of the pH_{iep}. For this reason, the effect of pH on the zeta potential of silicon nitride and oxide mixtures in aqueous suspensions cannot be explained solely in terms of the total surface area of each powder present [11] but has to consider the presence of hydrolysed metal ions which may alter the zeta potential by specific adsorption processes. Thus, with increasing particle concentration, the pH-dependent solubility of the different powder components will exert an increasing influence on the zeta potential behaviour of the major powder component.

The main effect of $MgAl_2O_4$ in the mm-powder mixture, Fig. 3a, may by attributed to a cation chemisorption onto the silicon nitride surface which results in a shift of the pH_{iep} to higher values, combined with a distinct reduction of the highly negative zeta potential at $pH > pH_{iep}$

$$Mg(OH)_2 \xrightarrow{H_2O} Mg(H_2O)_{4+x}(OH)_{2-x}^{x+} + xOH^- \tag{16}$$

The positively charged metal hydroxo complex may be specifically adsorbed on the negatively charged silicon nitride surface via hydrogen bridges

$$[Si{-}O]^- + Mg(H_2O)_{4+x}(OH)_{2-x}^{x+} \rightarrow [Si{-}O{-}H{-}O{-}Mg(H_2O)_{4+x}(OH)_{1-x}]^{(x-1)+} \tag{17}$$

resulting in a charge reversal at pH values above the iep and where the hydroxide is partly or fully dissociated. According to Equation 16, the concentration of cation hydroxo complexes will decrease with increasing pH, as defined by the solubility of the metal hydroxide in aqueous solution, Table I. Hence, at very high pH where the cation concentration becomes negligible, the net surface charge on the silicon nitride becomes negative (at $pH > pH_{iep} = 9.2$).

In the Y-Al- and Nd-Al-oxide containing mm-samples, however, a chemical adsorption of anions has to be concluded from Fig. 3b and c which results in a shift of the pH_{iep} to lower values and a reduction of the positive zeta potential at $pH < pH_{iep}$

$$(Y, Nd)(OH)_3 \xrightarrow{H_2O} (Y, Nd)(H_2O)_{3-x}(OH)_{3+x}^{x-} + xH_3O^+ \tag{18}$$

The negatively charged metal hydroxo complexes are suggested to be chemically adsorbed on the surface of positively charged silicon nitride at a pH below the pH_{iep}

$$[Si{-}OH_2]^+ + (Y, Nd)(H_2O)_{3-x}(OH)_{3+x}^{x-} \rightarrow [Si{-}O{-}H{-}O{-}(Y, Nd)(H_2O)_{3-x}(OH)_{2+x}]^{(x-1)-} + H_2O \tag{19}$$

At very low pH the concentration of negatively charged metal hydroxo complexes decreases so that the silicon nitride will again become positively charged.

3.2. Suspension stability

Stable suspensions are only obtained when the particles repel each other, and they flocculate when the interaction between particles is mainly attractive. For homogeneous dispersions like single-phase or completely oxide-coated silicon nitride powder, all particles bear the same charge so that electrostatic particle–particle interaction is always repulsive. For multiphase mixtures of oxides and nitride, however, they can be partly attractive, which may have great practical implications for the rheological properties of multiphase slurries. The net interaction between two suspended particles is additionally influenced by van der Waals forces which are always attractive. The energy of attractive interaction for two spheres of radius, r, is given as

$$V_{att} = -\frac{rA}{12s} \tag{20}$$

where A is the Hamaker constant and s is the distance of closest approach between the particles. Table II lists the Hamaker constants for the phases under consideration, found in the literature and estimated from Tabor–Winterton approximation [43] (see Appendix). The energy of repulsion, V_{rep}, may be approximated by [44]

$$V_{rep} = 2\pi\varepsilon r\left(\frac{4RT\Upsilon}{zF}\right)^2 e^{-\kappa s} \simeq 2\pi\varepsilon r\Psi_d^2 e^{-\kappa s} \tag{21}$$

where for diffuse double layer without the simplifying assumption of low potentials the complex potential parameter Υ is defined by

$$\Upsilon = \tanh(zF\Psi_d/4RT) \tag{22}$$

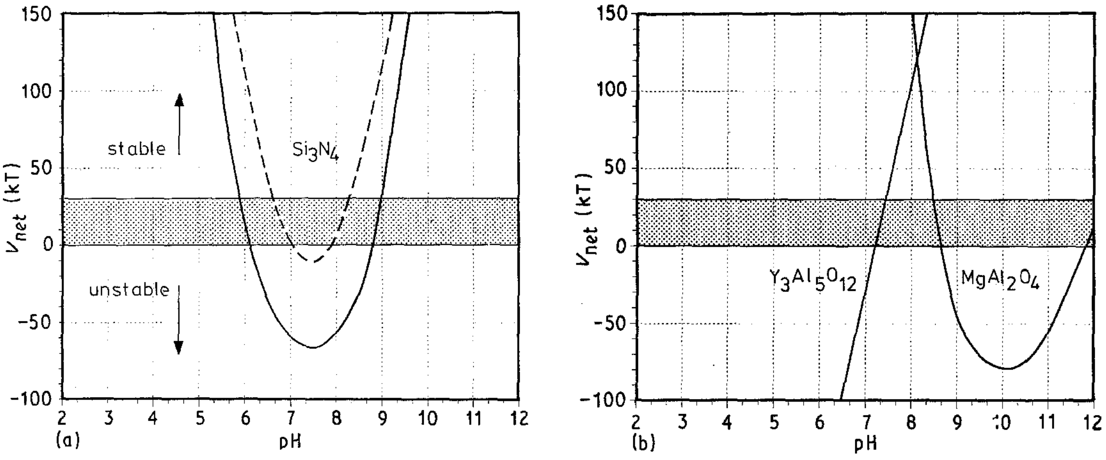
according to the Gouy–Chapman theory, with z the charge number of counterions [45]. With

$$\Psi_d \simeq \left[\frac{4RT\Upsilon}{zF}\right] \tag{23}$$

TABLE II Hamaker constants $A_{\alpha\beta\alpha}$ calculated according to the Tabor–Winterton approximation, (Equation A1) from the refractive index, n, and the dielectric constant, ε

α	Structure	ε	n	$A_{\alpha\beta\alpha}$	A(lit.)	(kT)
Si_3N_4	phenacite	8	2.1	24.3	14.8	[51]
SiO_2	quartz	4	1.46	3.6	0.55	[45]
$MgAl_2O_4$	spinel	7.5	1.72	9.3		
$Y_3Al_5O_{12}$	garnet	5	2.2	36.2		

β: $\varepsilon(H_2O) = 78.5$ and $n(H_2O) = 1.333$ at 25 °C.



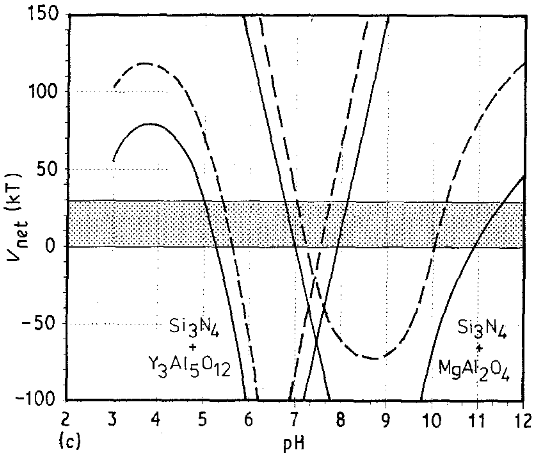


Figure 4 V_{net}–pH isotherms calculated according to Equation 24 for (a) the single-phase, (b) oxide-coated and (c) mechanically mixed Si_3N_4 powder. The van der Waals attraction term was calculated using two different Hamaker constants: (---) $A_{SiO_2/H_2O/metal\ hydroxide}$ and (——) $A_{Si_3N_4/H_2O/metal\ hydroxide}$ to account for an oxide and nitride-dominated Si_3N_4 particle surface.

where Ψ_d is the potential at the outer Helmholtz plane of the electrical double layer [14], the net interaction energy for the case of symmetrical electrolytes is given as

$$V_{net} = r\left[2\pi\varepsilon\Psi_d^2 e^{-\kappa s} - \frac{A}{12s}\right] \qquad (24)$$

It is generally assumed that Ψ_d may be approximated by the experimentally determined zeta potential, Ψ_ζ. Fig. 4a to c show V_{net} plotted against pH for single-phase silicon nitride, pm, and mm powders at $s = 1/\kappa$. If the magnitude of Ψ_ζ is high enough, the van der Waals force will be overcompensated and the particles will remain stably dispersed in solution.

Although the calculation of the total interaction energy according to Equation 24 is quite sensitive to the estimation of κ and A, the curves given in Fig. 4a to c show general trends of the stability behaviour. When the net interaction energy, V_{net}, is highly positive (10 to 30 kT), the colloidal suspension can be considered as stable [44]. Two positive branches of the interaction energy curve of single-phase silicon nitride indicate the possibility of stabilizing silicon nitride either at high (> 8 to 9) or low pH (< 5 to 6). The oxide-coated powders, however, may only be stabilized at low pH (<6 to 7) in the case of $MgAl_2O_4$ and high pH (>6 to 8) for $Y_3Al_5O_{12}$- and $NdAlO_3$-coated powders. Thus, the pH above which stability of the suspension may be achieved under given experimental conditions (solids concentration, grain-size distribution, flow, etc.) may be referred to as the critical pH value for stabilization [46].

The stability of multiphase, mechanically mixed powder mixtures is strongly influenced by the adsorption of counterions on the charged silicon nitride surface. Equations 2 and 23 show that the addition of counterions by dissociation of metal hydroxides, according to Equation 16, will reduce the repulsion via compression of the double layer ($\kappa \sim zc^{1/2}$) and via decrease of the surface potential ($\Psi \sim \Upsilon/z$). For the transition between stable and unstable behaviour, a critical flocculation concentration (cfc), can be defined according to the Schulze–Hardy rule which is proportional, for small double layer potentials near the iep, to Ψ^4/A^2z^2 [47]. For the cfcs, concentrations of 0.01 to 0.1 $mmol\,l^{-1}$ have been reported with trivalent counterions [40, 48]. The conditions for stability in the presence of dissociated cations may then be found by comparing the pH-dependent cation concentration, as defined by the solubility product of the hydroxide, with the critical flocculation concentration. Thus, flocculation will be prevented by using only such additives which show, under given conditions, a cation concentration less than the cfc. For multiphase mechanically mixed silicon nitride slip formation at high pH, the Al^{3+} concentration is negligible due to the very low solubility product ($K_s = 1.3 \times 10^{-33}\,(mol\,l^{-1})^4$) whereas Mg^{2+}- and Y^{3+}, Nd^{3+}-cation concentrations ($K_s = 1.8 \times 10^{-11}\,(mol\,l^{-1})^3$ and $K_s = 8 \times 10^{-23}$ and $3.2 \times 10^{-22}\,(mol\,l^{-1})^4$) dominate the flocculation behaviour of the nitride particles. Either the pH has to be kept above a value of approximately 8 to 9 (depending on the basicity of the silicon nitride surface), or double oxides which show lower activities of the metal ions like $MgAl_2O_4$ or $Y_3Al_5O_{12}$ have to be used in order to decrease the counterion concentration in solution.

The colloidal stability of multiphase powder mixtures will be significantly influenced by the grain sizes of the various powder constituents. While with decreasing grain size the solubility of small oxide particles increases, the amount of the net interaction potential decreases (Equation 24), and hence the stability of the powder mixture against flocculation will be reduced. Generally, the electrostatic stabilization of fine-grained powder mixtures in aqueous solution will become more and more difficult with increasing solid-phase concentration so that electrosteric or steric stabilization mechanisms may become more favourable for these complex systems. Although the specific adsorption behaviour of surface-active deflocculants is also influenced by the electric charge on the particle surface, polyelectrolytic surfactants may provide sufficient steric and electric repulsion between particles of different surface composition. Future work will therefore be focused on the surface modification of multiphase powder mixtures by multifunctional surfactants to achieve colloidal stabilization independent from the specific particle surface chemistry.

4. Conclusions

The Ψ_ζ-pH relationship implies that small amounts of ionic admixtures have a profound influence on the interaction between the suspended powder particles. These admixtures are inadvertently present in the system as a result of leaching from all constituents in the multiphase powder mixture suspension. Position and type of the charge reversals observed (positive to negative or negative to positive) depend on the particular system and the concentrations of metal ions present in solution. The basic types of charge reversal that can occur are associated with: (i) the iep of the particles in the absence of metal ions (single-phase silicon nitride); (ii) the iep of a hydroxide precipitate of the soluble ion due to coating of the particles with the hydroxide (sol–gel-coated powder); and (iii) a change in adsorption of soluble ions on the particles as a result of altering pH (two-phase nitride–oxide mechanical mixture).

In heterogeneous multiphase powder mixtures segregation of the mixture by heteroflocculation may become a problem when the ieps of the phases are located at significantly different pH values. In the case of $MgAl_2O_4$–silicon nitride powder mixtures, separate flocculation of the oxide phase may occur at $pH > 9$ where silicon nitride powders usually are stabilized. The flocculation phase may form agglomerates which will cause the generation of microstructural defects upon consolidation (shaping and sintering). Segregation of silicon nitride–oxide powder mixtures may only be avoided by coating the nitride powder with the oxide which results in a single-phase behaviour of the multiphase powder mixtures. According to the results, the $MgAl_2O_4$-coated silicon nitride mixture can be processed in aqueous solution at $pH < 8$ whereas the yttrium- and neodymium–aluminate coated powder was successfully processed at $pH > 7$.

Steric stabilization mechanisms based on the surface adsorption of macromolecular surfactants may allow stabilization of the multiphase suspension at critical pH values. Most of the highly effective deflocculants, however, exhibit a polyelectrolytic behaviour with acidic/basic functional surface groups such as $-COOH$, $-SO_3H$, or $-OPO_3H_2$ which are preferentially adsorbed on negatively charged surfaces. Thus, stabilization via polyelectrolytic surfactants also requires the control of the surface charge formation of each constituent in the multiphase powder mixture.

Acknowledgement

This work was financially supported by the Deutsche Forschungsgemeinschaft under Project no. Gr 961/1-1.

Appendix

The stability of a colloidal suspension against flocculation is strongly restricted by Van der Waals attraction between two solid particles. The Van der Waals attraction force, Equation 20, is dominated by the Hamaker molecular interaction constant A, which is related to the electromagnetic interaction between fluctuating dipoles in the different phases [49] and obtains values in the range of 1 to 100 kT for most ceramic materials. Various methods for computation of the Hamaker constant have been developed, based on the optical dispersion characteristics of the phases [50]. An example of an accurate calculation of the Hamaker constants of silica and alumina using the oscillator strengths and relaxation frequencies is given by Clarke [51]. Owing to the lack of optical constants for the bimetallic oxides used in this work, a simple procedure based on the Tabor–Winterton approximation [43, 52] was applied to estimate the Hamaker constants from the refractive index, n, and the dielectric constant, ε, of the solid phase α dispersed in the liquid phase β

$$A_{\alpha\beta\alpha} = \frac{3}{4}kT\left[\frac{\varepsilon_\alpha - \varepsilon_\beta}{\varepsilon_\alpha + \varepsilon_\beta}\right]^2 + \frac{3}{8}\frac{\pi\hbar\nu}{2^{1/2}}\frac{(n_\alpha^2 - n_\beta^2)^2}{(n_\alpha^2 + n_\beta^2)^{3/2}} \tag{A1}$$

Table II shows the literature data for n and ε from which the Hamaker constants were estimated which were used to calculate the net interaction potential, Equation 24. Comparison with literature data shows a sufficient coincidence.

A modification of the Van der Waals attraction results when two different solid phases are involved, i.e. the nitride and the oxide particles in the mechanical mixtures. Two different flocculation processes may be considered, i.e. homo- and heteroflocculation between similar and dissimilar particles. The Hamaker constant for the interaction between two dissimilar solid phases α and γ separated by the liquid phase β were approximated by [45]

$$A_{\alpha\beta\gamma} = (A_{\gamma\gamma}^{1/2} - A_{\beta\beta}^{1/2})(A_{\alpha\alpha}^{1/2} - A_{\beta\beta}^{1/2}) \tag{A2}$$

With

$$A_{\alpha\alpha} = (A_{\beta\beta}^{1/2} - A_{\alpha\beta\alpha}^{1/2})^2 \quad \text{and} \quad A_{\gamma\gamma} = (A_{\beta\beta}^{1/2} - A_{\gamma\alpha\gamma}^{1/2})^2 \tag{A3}$$

Equation (A1) may be rewritten

$$A_{\alpha\beta\gamma} = (A_{\alpha\beta\alpha}A_{\gamma\beta\gamma})^{1/2} \tag{A4}$$

Using the $A_{\alpha\beta\alpha}$ values given in Table II, the Hamaker constants for the interaction between two dissimilar phases $A_{\alpha\beta\gamma}$ were calculated, Table AI, which were used to estimate the interaction potentials drawn in

TABLE AI Hamaker constants $A_{\alpha\beta\gamma}$ for the interaction of two different solid phases α and γ separated by the liquid phase β calculated according to Equation A4

αβγ	$A_{\alpha\beta\gamma}$(kT)
$Si_3N_4/H_2O/MgAl_2O_4$	7.0
$Si_3N_4/H_2O/Y_3Al_5O_{12}$	4.5
$SiO_2/H_2O/MgA_2O_4$	1.3
$SiO_2/H_2O/Y_3Al_5O_{12}$	0.9

Fig. 3c. To account for the oxygen content on the surface of the silicon nitride particles, either Si_3N_4 or SiO_2 was taken as the effective nitride particle surface composition.

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Received 4 September 1989
and accepted 19 February 1990