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Aqueous Processing of Carbothermally Prepared Ca-α-SiAlON and β-SiAlON Powders: Powder and Suspension Characterisation

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Abstract

Properties of carbothermally prepared Ca-α-SiAlON and β-SiAlON powders and aqueous suspensions thereof were determined. The isoelectric points of Ca-α-SiAlON and β-SiAlON were 3·4 and 4·6. After addition of deflocculant, Dolapix CE64, the behaviour of both suspensions is nearly identical. The isoelectric points become 5·5 and 5·3, respectively. Despite differences in bulk composition, grain size distribution, grain size and shape, both SiAlON suspensions show a similar dependence of a zeta potential on pH. Optimum slip casting properties, i.e. lowest viscosity values (below 10 mPa s), the highest absolute zeta potential values, the smallest floc size and sediment volume were found between pH 10–11 for both powders. The potentials of the different suspension characterisation techniques were compared and zeta potential and viscosity measurements were found the most convenient. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: sialon, suspensions, slip casting, carbothermal synthesis, aqueous processing.

1 Introduction

Fastly developing technology requests introduction of new materials as well as improvement of existing ones. One of the well known high performance engineering materials is the Si_3N_4 ceramic which has very good mechanical properties at high temperatures. Simultaneous equivalent substitution of Si–N by Al–O in the Si_3N_4 lattice results in the compound called SiAlON.[1] SiAlON possesses two different structural modifications α and β as being derived from the Si_3N_4 structure. Much work has been devoted to α/β composite materials with a varying ratio between α ($Me_{m/\mathrm{val}}Si_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, where m stands for the replacement of (Si–N) by (Al–N) and n stands for the replacement of (Si–N) by (Al–O), val stands for the valency of the metal ion 'Me') and β ($Si_{6-z}Al_zO_zN_{8-z}$, $z = 0-4{\cdot}2$).[1] These composites provide attractive possibilities to tailor their properties. Complex shaped products, for example single parts applied in gas turbines, should be made with fully densified, highly reliable and low-costs ceramics. Controlling the microstructure of green and final products, which are strongly related to powder characteristics, compaction processes and sintering conditions will only attain excellent properties.

In this work a carbothermal reduction and nitridation of oxides is used, which is relatively inexpensive. Further, slip casting is used, which has been reported as a suitable, relatively cheap process to attain materials with high green densities and microstructural homogeneity, even for complex geometry.[2–5] Such materials are obtained if a good slip is prepared. Preparation of the slip is a particularly critical step.[5,6] The slip needs to meet a number of commonly known requirements.[7] It has to be stable, well-dispersed, uniform and highly

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concentrated. In colloidal processing the surface chemistry of a powder is of a fundamental importance.[8] Different preparation methods of nitride powders result in change of surface characteristics (a wide range of the pH of isoelectric point, $pH_{iep} = 2{\cdot}5-8^9$) strongly influencing the colloidal behaviour of the suspensions. In order to understand and manipulate the behaviour of slips, different techniques like measurement of the zeta potential, either measured conventionally or by Electrokinetic Sonic Amplitude (ESA), floc size measurement, rheometry and sedimentation measurements can be performed. Slight variations of the dispersion of the slurries, caused by the changes in solid loading (quantity and characteristics), slurry pH, dispersant dosage and surface characteristics may result in green bodies with non-optimal properties.[10,11] Certain similarities in surface characteristics[12] and so in processing by slip casting can be expected between Si_3N_3 and SiAlON powders. β-SiAlON was already successfully processed by aqueous slip casting[13,14] under similar conditions as Si_3N_3.[3]

Relatively inexpensive and single phase Sialon powders were produced here. Comparison and understanding of suspension behaviour of Ca-α-SiAlON and β-SiAlON with and without deflocculant were the main purposes of this work. The parallel studies of Ca-α-SiAlON and β-SiAlON powders are performed to perceive the readiness and traps while using the slip casting procedure for the composite mixtures of these powders aimed at.

A comparison between the used techniques to characterise behaviour of slips with respect to both their reliability and convenience is discussed. An attempt is made to establish a fast and reliable route of suspension characterisation in order to supply a good background for evaluation of deflocculation degree of the slurry, as one of the most important parameters. It can be related to and will result in a better and more homogeneously densified green product. The latter aspect will be evaluated in the future.

2 Experimental Procedures

2.1 Powder preparation and characterisation

The fine powders: Al_2O_3 (grade 'C', $\gamma + \delta$ Al_2O_3), $CaSiO_3$ (Wollastonite SG, Reinsche Kalksteinwerke), SiO_2 (Aerosil OX50, Degussa) and carbon black C (Elftex 125, Cabot) as starting materials for the carbothermal synthesis of Ca-α-SiAlON, and kaolin (Monarch, Cyprus Industrial Minerals Company) and carbon C (Elftex 125, Cabot) were used for the carbothermal synthesis of β-SiAlON powders. The starting materials were weighed out in the appropriate amounts according to eqn (1) for Ca-α-SiAlON ($m = 1{\cdot}6, n = 1{\cdot}2$) and to eqn (2) for β-SiAlON ($z = 3$):

$$\begin{aligned} &0{\cdot}8CaSiO_3 + 8{\cdot}4SiO_2 + 1{\cdot}4Al_2O_3 + 22{\cdot}2C \\ &\quad + 7{\cdot}4N_2 \\ &\quad \Rightarrow\ Ca_{0{\cdot}8}Si_{9{\cdot}2}Al_{2{\cdot}8}O_{1{\cdot}2}N_{14{\cdot}8} + 22{\cdot}2CO \qquad (1) \end{aligned}$$

$$\begin{aligned} &3(2SiO_2{\cdot}Al_2O_3{\cdot}2H_2O) + 15C + 5N_2 \\ &\quad \Rightarrow\ 2Si_3Al_3O_3N_5 + 15CO + 6H_2O \qquad (2) \end{aligned}$$

The choice of materials and the detailed preparation procedures were the same as previously discussed for Ca-α-SiAlON[15] and β-SiAlON.[16,17] The stoichiometric mixtures were tumbled with water in an Eirich mixer (Labormischer RO2). Afterwards, the pellets were dried in air at 100°C for 24 h. The pellets (5–10 mm) were placed in alumina tubes with an inner diameter of 25 mm for Ca-α-SiAlON and of 50 mm for β-SiAlON using a packed bed of approximately 200 mm in length. The packed bed was formed using alumina fibre material as a plug. Usage of a smaller diameter tube inside the 50 mm diameter tube was necessary for the preparation of Ca-α-SiAlON in order to prevent the furnace tube failure due to formation of unknown corrosive liquid phases during synthesising the powder. During the synthesis nitrogen gas (containing less than 20 ppm O_2 and H_2O) flowed through the tube at a controlled flow rate of 35 l h^{-1} (measured at normal pressure and temperature). The powders were synthesised by simultaneous carbothermal reduction-nitridation in a horizontal tube furnace with a hot-zone length of approximately 400 mm (High Temperature Horizontal Furnace, Carbolite, Sheffield, UK). A maximum temperature of 1500°C was retained for 55 h in the case of Ca-α-SiAlON[15] and for 29 h in the case of β-SiAlON.[16,17] The heating and cooling rates were 2°C min^{-1}.

The phase formation of the Ca-α-SiAlON powders was examined by powder X-ray diffraction (XRD), which was carried out on a Philips diffractometer, type PW 1120, with Cu $K\alpha$ radiation. The samples were measured between 10° and 97° 2θ with a counting time of 5 s per $0{\cdot}01°$ 2θ.

The unit cell dimensions were calculated using the following reflections: (311), (203), (222), (213), (321), (303), (411), (004), (322), (204), (330) and (421). For accurate determination of the lattice parameters high diffraction angles ($2\theta > 50°$) and the step scan mode (as mentioned) were used for all synthesised batches. The unit cell dimensions were used to calculate the m and n values, thus obtaining the chemical composition of the produced Ca-α-SiAlON powders. The general formula for Ca-α-SiAlON is $Ca_{m/2}Si_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$, and the following equations developed by Hintzen *et al.*[18,19] were applied:

$$a(\mathring{A}) = 7{\cdot}749 + 0{\cdot}0673{\cdot}m + 0{\cdot}0023{\cdot}n \quad (3)$$

$$c(\mathring{A}) = 5{\cdot}632 + 0{\cdot}0550{\cdot}m - 0{\cdot}0054{\cdot}n \quad (4)$$

The β-SiAlON phase composition was examined using XRD techniques (Rigaku, with Cu $K\alpha$ radiation). The unit cell dimension were calculated using the following reflections: (110), (200), (101), (210), (111), (300), (201), (220), (310), (301), (221) and (311). The general formula for β-SiAlON is $Si_{6-z}Al_zO_zN_{8-z}$ ($z = 0$–$4{\cdot}2$).[1,16] The equations, developed by Ekström *et al.*,[20] relating the z value to the cell dimensions are:

$$a(\mathring{A}) = 7{\cdot}603 + 0{\cdot}0296{\cdot}z \quad (5)$$

$$c(\mathring{A}) = 2{\cdot}907 + 0{\cdot}0255{\cdot}z \quad (6)$$

The reproducibility of the phase formation of β-SiAlON powder was previously studied and reported in literature.[16,17] The possibility to obtain a single phase Ca-α-SiAlON powder with the chosen composition was previously reported.[15] During this investigation the reproducibility was checked by producing a number of batches. Both powders were heated in air up to 750°C and retained at this temperature for 8 h in order to remove any residual coal.

2.2 Suspension preparation and characterisation

In order to prepare the synthesised β-SiAlON powder for attrition milling the pellets were first dry milled in a hammer crusher (Retsch Mulhle, Retsch) to breakdown hard agglomerates. The Ca-α-SiAlON pellets had only weak agglomerates and did not need such a pre-treatment. The suspension of Ca-α-SiAlON was prepared following the previously optimised procedure of β-SiAlON.[17] Both powders were attrition milled (HD 01, Union Process) at a speed of 400 rpm in 200 g ultra pure water (AlphaQ, Millipore) using a 750 ml tefzel (teflon) coated tank and 900 g Si_3N_3 milling balls (7 mm diameter). If used a surfactant, Dolapix CE64 Zschimmer and Schwartz (ammonium salt of ionic polyacrylic acid) powder was added (0·3 wt%). The resulting suspensions were sieved over a screen with openings of 33 μm. After sieving the suspension had an initial solid content of about 60 wt%. Lower solid contents (necessary for different suspension characterisation techniques) were obtained by dilution with water to the required percentage and were subsequently aged for 24 h on a roller bench. Samples of the suspensions adjusted to different pHs were prepared with 0·1 M and 0·4 M HNO_3 or 0·1 M NH_4OH and were subsequently left for 24 h on a roller bench. The examined pH range was from 3 to 12 unless narrowed by technique's restrictions.

The following characteristics, of the used powder and suspensions, were determined: particle size, particle size distribution, degree of agglomeration, surface area, zeta potential, sedimentation (i.e. packing density) and viscosity.

The *particle size* distribution was analysed by the *sedimentation method* (Sedigraph 5100, Micromeritics). The Sedigraph was also used to study the influence of pH change on the agglomeration behaviour.

The *specific surface area* of the SiAlON powder after attrition milling was measured. After drying the suspension for 24 h at 100°C the specific surface was determined by means of the *BET method* (Flowsorb II 2300, Micromeritics, nitrogen gas adsorption technique).

The *grain size and grain shape* were also observed with *Scanning Electron Microscopy* (SEM JOEL 840). The SEM samples were prepared by drying drops of diluted suspensions of Ca-α-SiAlON and β-SiAlON powders on graphite or brass holders which were subsequently coated with gold.

The *zeta potential and particle size distribution* were measured by the Delsa 440 system based on *Electrophoretic Light Scattering* (ELS). Suspensions with a pH ranging from 3 to 12 containing 5 wt% solid loading were used for both Ca-α-SiAlON and β-SiAlON powders. Part of the 5 wt% suspensions with different pH were pressure filtered through 0·25 μm filters. Subsequently, a drop of the 5 wt% unfiltered suspension was added to the obtained supernatant and such prepared sample was examined. So the solid content for zeta potential measurements is about 1 wt%.

The measured *zeta potential* values were compared with the *Electrokinetic Sonic Amplitude* (ESA) *potential* obtained with the Matec ESA system (ESA-8000) equipment. The ESA potential was used to determine values of the isoelectric point of a powder in high solid loading suspensions. While using the titration cell the electro-acoustic signal, electrical conductivity and temperature as a function of pH are registered. A stirring speed of 400 rpm was applied to prevent settling. The change of polarity of a suspension is reflected in change of phase angle. The generated signal is a mirror image of true data across the line of zero ESA. The measurements were performed with 25 wt% suspensions of Ca-α-SiAlON and β-SiAlON powders, whereas the titration was carried out with 0·1 M NaOH and 0·1 M HCl.

Sedimentation experiments with 16 wt% diluted suspensions were used to determine the *packing density* for pH values ranging from 3 to 12. The degree of suspension deflocculation was correlated to the slurry behaviour via sediment volume.

The *rheological measurements* were performed using a TA Instruments Weissenberg Rheogoniometer, fitted with a Mooney geometry (combined concentric cylinder and a cone/plate). The measurements were performed at 20°C at shear rates of 1–200 s^{-1}. The data were also analysed by TA Instruments Rheology Solution Software using the Bingham model. Viscosities given in the figures are differential viscosities (slope in Bingham model). Note that the Bingham model is only an approximation. Ideally flow curves should be straight lines to allow the Bingham model to be applied. In reality all flow curves were slightly curved (see Fig. 8 as an example). We also attempted to use the yield values as a measure of the state of aggregation. The viscosities were also calculated at single point at shear rate of 100 s^{-1}. They were found to correlate well with the differential viscosities so the latter are discussed here. *Viscosities* of Ca-α-SiAlON suspensions of different solid loading (60, 50, 30, and 5 wt%) and of β-SiAlON suspension of 60 wt% solid loading were determined.

3 Results

3.1 Powder preparation and characterisation

All synthesised Ca-α-SiAlON batches resulted in a single phase material with no indication of amorphous or secondary phases (Fig. 1). A very good reproducibility of the synthesis of Ca-α-SiAlON powders was indicated by small scatter in calculated unit cell parameters. Average values for 22 batches are: $a = 7{\cdot}843 \pm 0{\cdot}040$ Å and $c = 5{\cdot}707 \pm 0{\cdot}040$ Å. These values are in a good agreement with the results found by Rutten *et al.*[15] ($a = 7{\cdot}84$ Å, $c = 5{\cdot}68$Å) as well as with the chosen composition and the reference values in the JCPDS card ($a = 7{\cdot}852$ Å, $c = 5{\cdot}709$ Å).[19] Using eqns (3) and (4) the average m value for all Ca-α-SiAlON batches was about $1{\cdot}4 \pm 0{\cdot}3$ which does not differ significantly from the expected $m = 1{\cdot}6$. The n value cannot be calculated reliably and therefore is not used.[18]

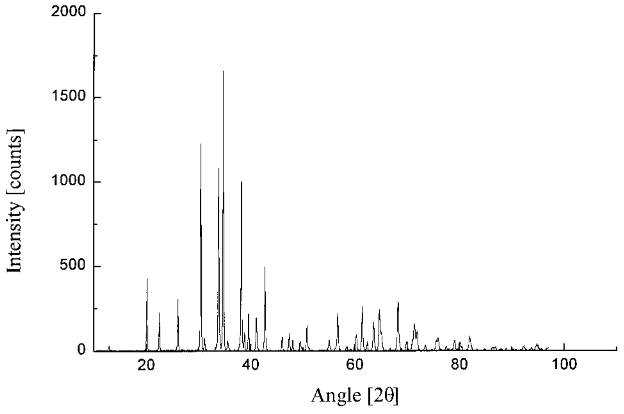


Fig. 1. X-ray diffraction pattern of Ca-α-SiAlON powder. All reflections can be attributed to the Ca-α-SiAlON.

The β-SiAlON batches contained typically 90 wt% of the β-phase and 10 wt% 15-R phase (Fig. 2). The unit cell parameters of β-SiAlON powder with eqns (5) and (6) were $a = 7{\cdot}68$ Å, $c = 2{\cdot}97$ Å resulting in $z = 2{\cdot}5 \pm 0{\cdot}1$. The reproducibility of the β-SiAlON powder synthesis used in this work was reported previously.[17] After removal of the residual coal in air at 750°C for 8 h the noise of the X-ray diffraction pattern is reduced while the full width at half maximum (FWHM) of the peaks is slightly decreased. The weight loss after carbon removal was less than 0·001 mg per few grams indicating that most of the used carbon had reacted during the synthesis itself.

The SEM photographs [Fig. 3(a) and (b)] show grains of both as-prepared Ca-α-SiAlON and β-SiAlON powders, respectively. They both revealed sintered agglomerates of primary particles with different grain size and shape. Crystal facets for Ca-α-SiAlON are observable. Primary equiaxed particles are estimated to have a size below 3 μm on the average while the sintered agglomerates are larger than 10 μm. In case of the β-SiAlON powder the primary particles are needle like and of submicron meter size while the agglomerates are of the size of few micrometers. The significant difference in morphology between Ca-α-SiAlON and β-SiAlON powders after carbothermal synthesis can be due to differences in processing parameters (as starting powders), different crystal growth

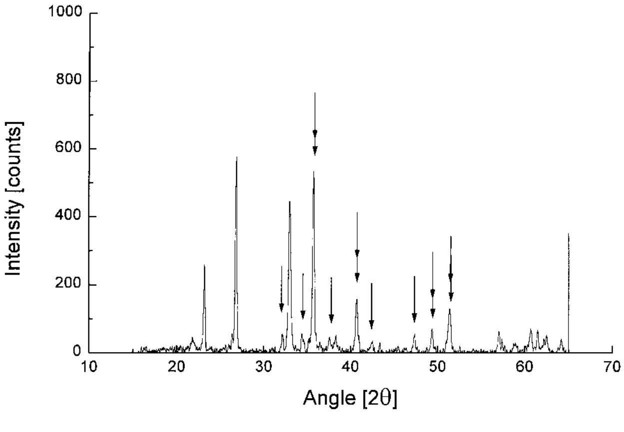
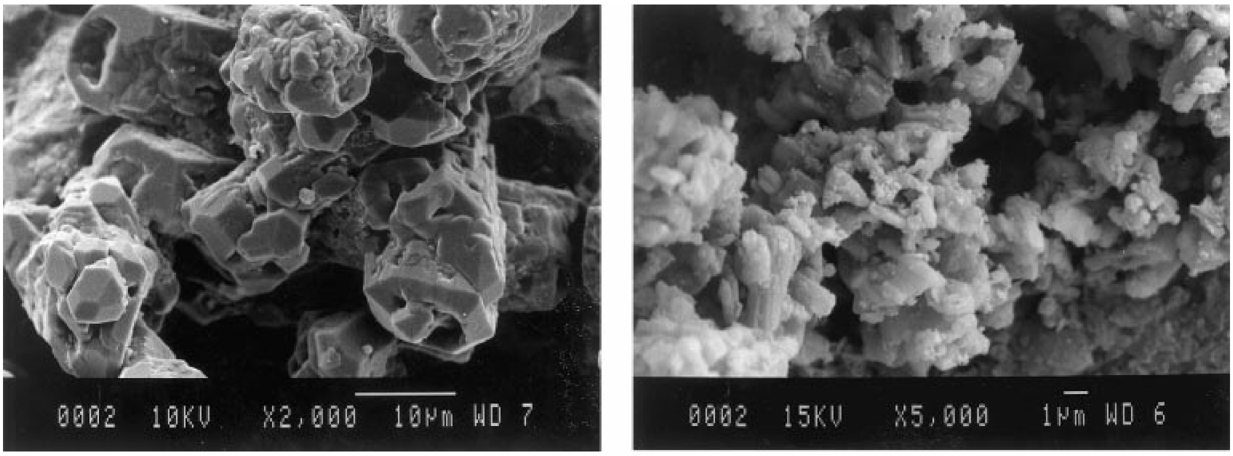


Fig. 2. X-ray diffraction pattern of β-SiAlON powder, where all reflections but single arrowed are assigned to β-SiAlON phase. Single arrows indicate reflections, which can be ascribed only to the 15-R phase, double arrows to both phases.



(a) (b)

Fig. 3. (a) SEM photograph of as-prepared Ca-α-SiAlON powder; (b) SEM photograph of as-prepared β-sialon powder.

mechanism or influence of liquid phase in case of Ca-α-SiAlON.

3.2 Suspension preparation and characterisation

3.2.1 Ca-α-SiAlON suspension

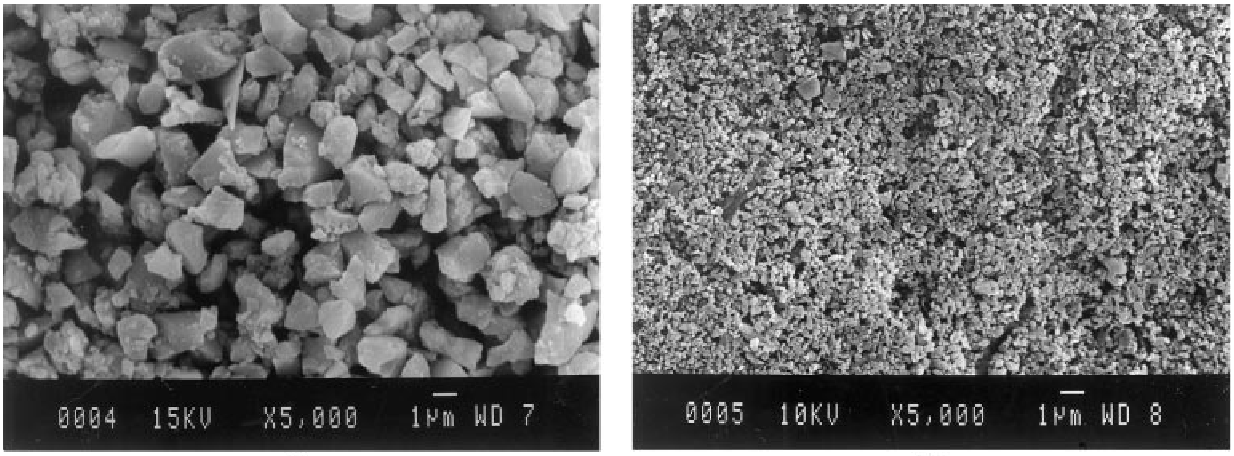
The SEM micrograph of the attrition milled Ca-α-SiAlON powder [Fig. 4(a)] revealed non-uniform grains, which sizes were estimated starting from submicron meter to 3 μm. The milling procedure produced very small equiaxed particles ground-off- or chopped-down-like from bigger particles but still leaving some significantly bigger ones ($>1\mu$m). The specific surface area was 3·7 m^2 g^{-1}, which corresponds to a calculated spherical particle size of about 0·5 μm.

The large primary particle, hardness and sintered agglomerates strength of Ca-α-SiAlON probably caused the extensive attrition milling time needed for this powder. It took 8 h to obtain a median grain size (d_{50}) of 2·3 μm ($d_{10} = 0{\cdot}6\mu$m, $d_{90} = 5{\cdot}1\mu$m) as determined by Sedigraph. The mass loss of the Si_3N_3 milling balls was about 0·32 wt%.

Figure 5(a) shows the zeta potential of Ca-α-SiAlON measured in diluted suspensions with and without deflocculant. The isoelectric point was found at pH 3·4 and the highest absolute zeta potential values above pH 10. After addition of Dolapix the pH_{iep} shifted to more basic pH (5·5). The highest zeta potential values were again found between pH 10 and 11. Above pH 8 the absolute zeta values of suspensions with and without Dolapix did not differ significantly. The viscosity measurements on high solid loading suspensions without added deflocculant were very difficult at pH ranges close to pH_{iep}. However, at pH 10–11 the viscosity decreased after addition of Dolapix from about 0·1 Pa s to below 10 mPa s.

Since the addition of the deflocculant improved the stability and brought the properties of α- and a β-suspensions close together (see Section 3.2.2). Further experiments were performed with addition of 0·3 wt% of Dolapix.

In order to check whether the same pH_{iep} as obtained with the zeta potential also holds for high solids contents, ESA measurements were performed



(a) (b)

Fig. 4. (a) SEM photograph of Ca-α-SiAlON powder after attrition milling; (b) SEM photograph of β-SiAlON powder after attrition milling.

for 25 wt% suspension The pH corresponding with the zero ESA signal was indeed 5·3. The particle size measurement with the Sedigraph also revealed a small, but significantly increased particle size near pH_{iep} with a maximum at 4·9.

The increased flocculation at pH_{iep} was confirmed by measurement of the sediment volumes. The highest sediment volume and the clearest supernatant were found between pH 5 and 6 [Fig. 6(a)]. In contrast the lowest sediment volume with a misty supernatant is observed at about pH 10–11 as an indication of the best dispersion that would lead to the highest packing density for Ca-α-SiAlON suspension.

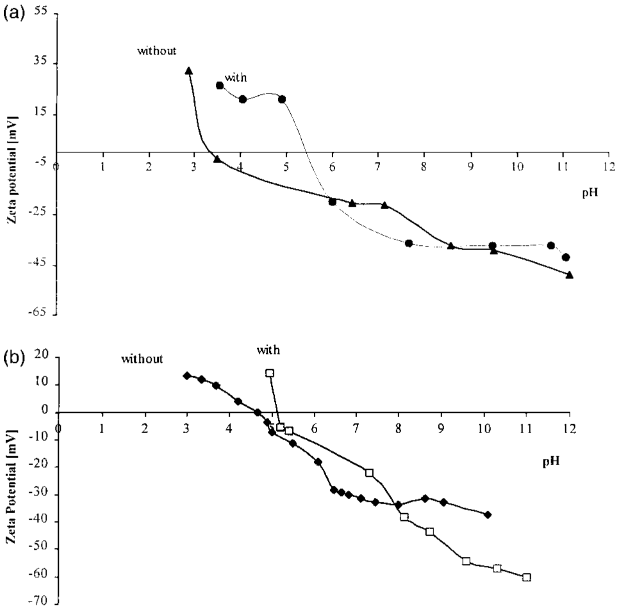


Fig. 5. (a) Zeta potential of Ca-α-SiAlON with and without deflocculant (0·3 wt%); (b) zeta potential of β-SiAlON with and without deflocculant (0·3 wt%).

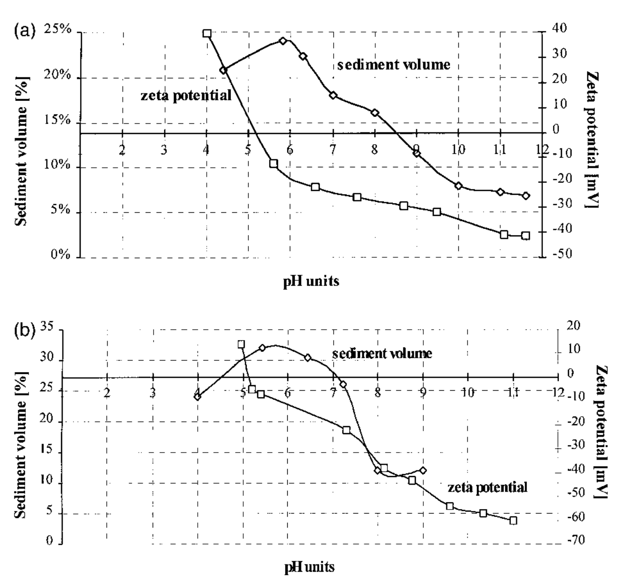


Fig. 6. (a) Zeta potential and sediment volume of Ca-α-SiAlON suspensions with 0·3 wt% deflocculant as a function of the pH; (b) zeta potential and sediment volume of β-SiAlON suspensions with 0·3 wt% deflocculant as a function of the pH.

All studied Ca-α-SiAlON suspensions show shear thinning behaviour with a yield stress and approaching constant viscosities at high shear rates. They are analysed with the Bingham (plastic behaviour) model with yield values as shown in Table 1. The highest yield value (1·7 Pa) was found at about pH 5 where the highest viscosity was also measured (28 mPa s). The lowest yield value (0·02 Pa) was found at pH 10–11 together with the lowest viscosity (below 10 mPa s). As an example of the rheological data, the result for a 60 wt% Ca-α-SiAlON suspension at pH $\approx$8·1 is shown in Fig. 7(a). The effect of the solids loading on the viscosity is presented in Fig. 8(a), the viscosity versus pH of the 50 and 60 wt% suspension is given as example. The minimum viscosity values were obtained at pH 10–11 and the maximum values at about pH 5. The only exception observed was for the 60 wt% sample suggesting a second local maximum, which was reproducible. It did not appear in the other viscosity curves (neither for 50, 30 and 5 wt%). No other results obtained with other techniques suggested reasons for such a viscosity maximum. The anticipated difference in the maximum value of plastic viscosities due to dilution between 50 and 60 wt% suspensions was about 15 mPa s [Fig. 8(a)] that is a factor 2.

3.2.2 β-SiAlON suspension

The SEM micrograph of the attrition milled β-SiAlON powder presented in Fig. 4(b) revealed a quite uniform grain size of less than 1 μm. Milling down to the grain size (d_{50}) of 1·3 μm ($d_{10}=0{\cdot}4$ μm, $d_{90}=3{\cdot}7$ μm) as determined by Sedigraph took only 4 hours of attrition milling. The mass loss of Si_3N_3 milling balls was 0·12 wt%. The specific surface area of the powder was 4·6 m^2 g^{-1}. The spherical particle size of approximately 0·4 μm calculated from the BET data is in agreement with the SEM photograph.

Fig. 5(b) shows the behaviour of the zeta potential of β-SiAlON suspensions. For suspensions without deflocculant the pH_{iep} was found at 4·6

Table 1. The measured yield values of 60 wt% Ca-α-SiAlON suspension with deflocculant (0·3wt%)

pH	*Yield stress [Pa]*
10·5	0·02
9·1	0·25
9·0	0·46
8·1	1·15
8·0	1·11
6·95	0·8
6·0	1·0
5·1	1·7
3·9	0·38
3·8	0·38
3·1	0·38

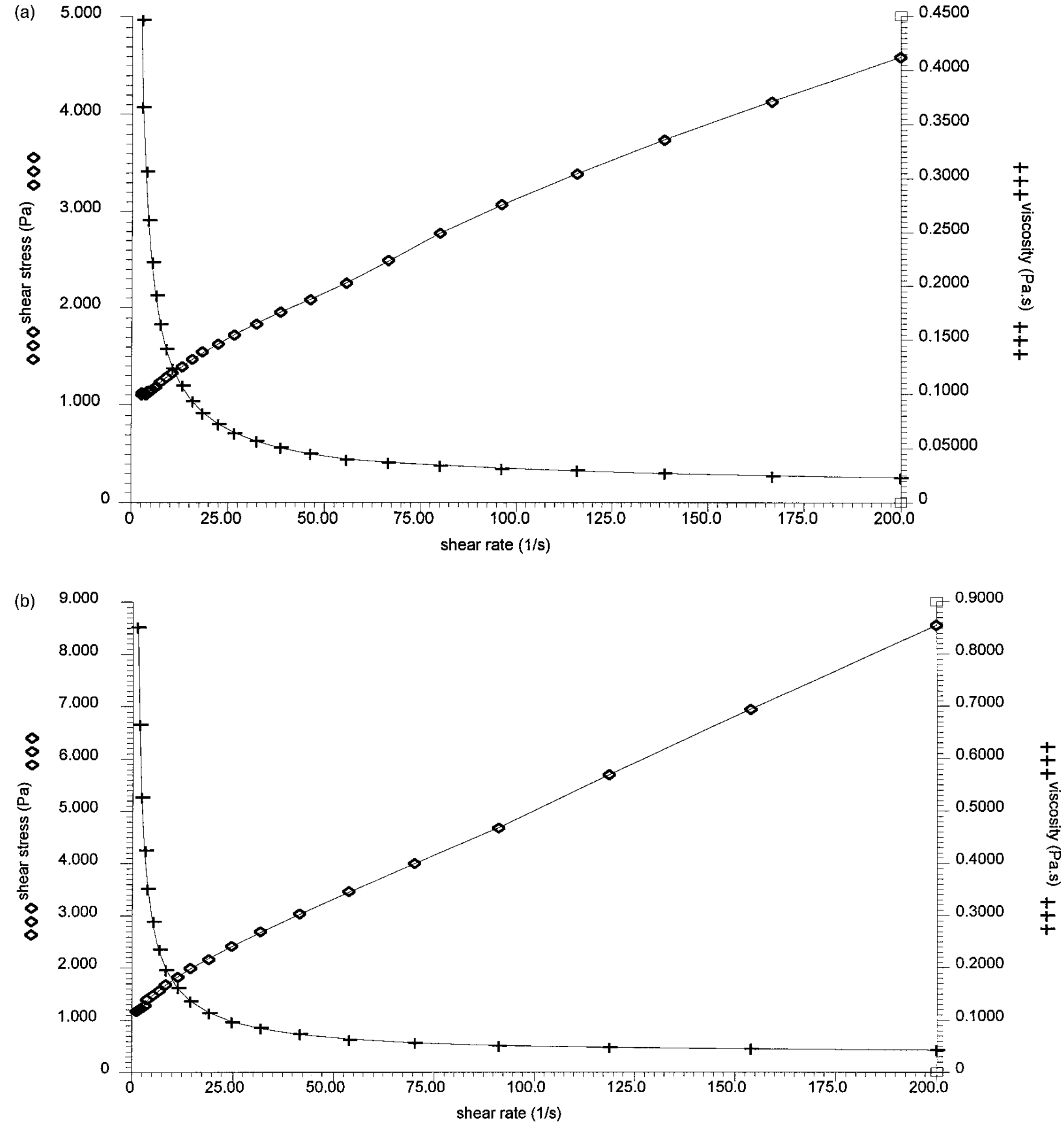


Fig. 7. (a) Shear stress and viscosity versus shear rate of 60 wt% Ca-α-SiAlON suspension with 0·3 wt% deflocculant at pH≈8·1; shear stress and viscosity versus shear rate of 60 wt% β-SiAlON suspension with 0·3 wt% deflocculant at pH≈8·

and the highest absolute values were at pH above 10. After addition of the deflocculant the pH_{iep} was shifted to 5·3 and the highest absolute zeta potential increased from about 35 to 55 mV. The viscosity was decreased after addition of deflocculant, however, without such a significant difference as in the Ca-α-SiAlON case. At high pH the deflocculant provides higher zeta potentials, lower viscosity and prevents ageing. For the suspensions containing Dolapix further properties were checked.

The isoelectric point determined with ESA signal zero at pH 5·5 closely corresponded to the one found with zeta potential measurements at 5·3. An increased flocculation was observed at pH 4·6 as shown by the median grain size determined by Sedigraph measurements. For the β-SiAlON suspension the highest sediment volume with the clearest supernatant was found between pH 5 and 6 while the lowest sediment volume with a misty supernatant was observed at about pH 10–11 [Fig. 6(b).

Results of the rheological measurements of 60 wt% β-SiAlON suspensions versus pH are presented in Fig. 8(b). As an example a complete flow curve of the 60 wt% suspension pH is shown in Fig. 7(b). Here the Bingham plastic behaviour is also applicable and the yield values are presented in Table 2. The highest viscosity (168 mPa s) with the highest yield value (16 Pa) were observed at pH≈5, while the lowest viscosity (below 10 mPa s) and lowest yield value (0·04 Pa) were obtained at pH≈10.

4 Discussion

4.1 Powder properties

Particle sizes and particle size distributions obtained by different techniques (Sedigraph, SEM,

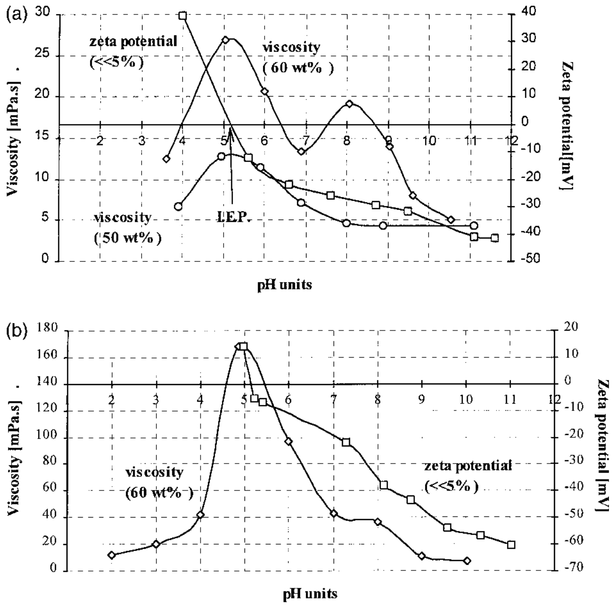


Fig. 8. (a) Zeta potential and viscosity of Ca-α-SiAlON suspension with 0·3 wt% deflocculant as a function of the pH. The solid content is indicated in the figure; (b) zeta potential and viscosity of β-SiAlON suspension with 0·3 wt% deflocculant as a function of the pH.

Table 2. The measured yield values of 60 wt% β-SiAlON suspension with deflocculant (0·3 wt%)

pH	*Yield stress [Pa]*
10·1	0·04
8·95	0·19
8·02	1·33
7·05	5·4
6·0	14·1
4·85	16·3
4·00	6·6
3·00	1·6
2.00	1·48

BET) of attrition milled Ca-α-SiAlON and β-SiAlON powders gave varying results, but also revealed some dependencies among the different techniques (see Table 3). According to the SEM investigation the differences between the two powders are quite significant: Ca-α-SiAlON showed non-uniform grain shapes [Fig. 4(a)] compared to the quite uniform grain shape of β-SiAlON [Fig. 4(b)].

The grain size of both powders at d_{10} (Sedigraph) and calculated from the specific surface area (BET) correlated very well (Table 1). This is probably due to the fact that Sedigraph and BET calculations assume spherical particles and that BET gives more weight to small particles while Sedigraph to larger ones. This explains also why the difference between the powders is greater at d_{90} than at d_{50} (1·4 and 1 μm, respectively). Therefore, Sedigraph measurement show a quite complete picture of the grain size distribution of both powders demonstrating the larger grains in Ca-α-SiAlON powder, which remained after milling.

Table 3. Ca-α-SiAlON and β-SiAlON powder characteristics

	Grain size				*Specific surface area*	
Technique	*SEM (μm)*	*d_{90} (μm)*	*Sedigraph d_{50} (μm)*	*d_{10} (μm)*	*BET (μm)*	*BET ($m^2 g^{-1}$)*
Ca-α-SiAlON	1·7	5·1	2.3	0·6	0·5	3·7
β-SiAlON	< 1	3·7	1·3	0·4	0·4	4·6

A five minute ultrasonic treatment lowered the d_{50} value of the attrition milled Ca-α-SiAlON from 2·3 to about 2·15 μm implying further breaking up of weakly bonded agglomerates in the suspension. After ultrasonic treatment the median particle size of the β-SiAlON powder was below 1·0 μm. The ultrasonic treatment hardly influenced the values of the grain size distribution. Since the weak agglomerates were found to form back even after a short time storage (24 h) this treatment was not applied for further measurements.

A somewhat broader grain size distribution (Ca-α-SiAlON) can be profitable for obtaining low viscosity values but disadvantageous during sintering.

The necessary milling time was 8 hours to obtain a median grain size (d_{50}) of 2·3 μm while reaching a grain size of about 1 μm for β-SiAlON took only 4 h. The requirement for an extended attrition milling time was probably caused by the larger primary particle size, sintered agglomerates (lack of hammer crushing), higher hardness and the higher amount of liquid phase (as shown by milling balls wear) of Ca-α-SiAlON powder as compared β-SiAlON.

4.2 Comparison of properties of Ca-α-SiAlON and β-SiAlON suspension

The Ca-α-SiAlON and β-SiAlON water suspensions have different isoelectric points, pH 3·4 and 4·6, respectively. The difference is due to different ratio of surface species on the surfaces of the SiAlON powders. Due to the same carbothermal synthesis, the heat treatment[12] and similar bulk composition, the powders have relatively alike surface composition. The surface is similar to aluminium silicates except for the incorporated nitrogen. Thus the hydrolysed species like Si–OH, Si–NH_2 and Al–OH will govern the suspension. Ca-α-SiAlON has with Si/Al = 3·3 will have a pH_{iep} closer to pH_{iep} of silica ($\approx$2·0). The β-SiAlON with Si/Al = 1 is expected to have a pH_{iep} closer to pH_{iep} alumina ($\approx$8). The low pH_{iep} confirms that Ca-α-SiAlON contains more silica like species. At high pH these species can be partially dissolved uncovering more Al–O surface like. This can explain the similar behaviour of Ca-α-SiAlON and β-SiAlON at high pH.

The addition of deflocculant shifted the pH_{iep} to basic pH in both suspensions (5·5 for Ca-α-SiAlON and 5·3 for β-SiAlON). At pH ≈ 5 the suspensions showed differences in the absolute maximum value of the viscosities. The β-SiAlON was significantly higher ($\eta = 168$ mPa s), than for Ca-α-SiAlON ($\eta = 28$ mPa s). This may be due to easy formation of strong aggregates of the β-SiAlON powder particles, which are small and uniform, but with a high aspect ratio.[20] So the viscosity differences can partly be attributed to the morphology[34] of the Ca-α-SiAlON and β-SiAlON powders after attrition milling.

The zeta potentials of both powders as a function of pH are quite alike. At the basic pH (10–11) both suspensions reach the highest zeta potentials. A stable suspension is expected at the pH, where the highest absolute zeta potential values are reached and the lowest sediment volume with a misty supernatant sedimenting at low rates is observed. Such indications of the highest packing density for both Ca-α-SiAlON and β-SiAlON suspensions were observed at about pH 10–11 which was also confirmed by the performed rheological studies [Fig. 8(a) and (b)]. The unexpected second maximum of viscosity, which were only seen in the 60 wt% Ca-α-SiAlON suspension (at pH 8) appeared due to the deflocculant bridging and a more complex particle–particle interaction as it is suggested.

At basic pH the absolute values of zeta potentials of Ca-α-SiAlON and β-SiAlON suggested different adsorption of deflocculant. The zeta potentials were somewhat increased in β-SiAlON and not increased in Ca-α-SiAlON. This can be due to the particle size and the different ratio of the mixed species on the SiAlON surfaces, the pH and the dependence of the deflocculant adsorption on the species.[21,22] The adsorption of Dolapix is complex. However, at the high pH the deflocculant contribution to the stabilisation of the suspension will be mainly steric. In β-SiAlON the influence of the deflocculant is greater probably due to the higher content of alumina like species. From the above it is clear that because of Dolapix Ca-α-SiAlON and β-SiAlON behave (more or less) in the same way [see Table 1 and Figs 6(a) and (b), and 8(a) and (b)]. The surface composition changes with heating time and the influence of the deflocculant adsorbed on the surfaces of SiAlON powders have been investigated by us in more detail.[23]

4.3 Comparison with Si_3N_3 based materials

Comparing the results of both investigated SiAlON powders with results published by others[17] a good agreement can be concluded. At pH 10, both with and without yttrium oxide as a sintering additive, green compacts as well as sintered bodies of carbothermally prepared β-SiAlON with a satisfactory quality were previously prepared by the aqueous processing of 60 wt% suspension.[17] Studies of a 70 wt% solid content suspension of β-SiAlON powder (21R polytypoid phase prepared by reaction sintering)[24] also showed that the best deflocculation can be obtained at pH 11. A very low viscosity (10 mPa s) and near Newtonian flow behaviour of the suspension were observed for this pH despite the fact that the isoelectric point was found at about pH 7·5 (higher pH_{iep} value than obtained in this study). The shifted isoelectric point was explained by the fact the 21R SiAlON phase has a surface more like Al_2O_3 ($pH_{iep} \approx 8$). We expect a certain analogy in suspension behaviour between Si_3N_4 and especially Ca-α-SiAlON (high Si and N content) powder due to a structural and bulk composition resemblance as well as easy oxidation of Si_3N_4 surface. Si_3N_4 has been studied in much more detail than SiAlON's[2,3,9,25–32] and more is known about its surface composition. For Si_3N_3, it has been shown that the powder preparation method has a strong influence on the isoelectric point. For instance, for powders prepared by direct nitridation of silicon values of $pH_{iep} \approx$ 4·5, 6·1, 7 and 8[9] have been reported, for carbothermally prepared powder $pH_{iep} \approx 4{\cdot}5$, and 5 made from dimide decompositon. Suspension and surface characterisation studies, of the mentioned Si_3N_4, showed that the ratio between silanol groups and amine groups is the suspension influencing parameter. Although in SiAlON also species containing Al exist the isoelectric point of carbothermally prepared Si_3N_4 ($pH \approx 4{\cdot}5$) and our SiAlON's powders ($pH \approx 3{\cdot}4$ of Ca-α-SiAlON and 4·6 of β-SiAlON) are relatively close to each other. This shows that oxidised surface species play an important role also on SiAlON surface. In both cases the degree of oxidation is considered as the dominating factor for the surface and suspension characteristics.

Table 4. Ca-α-SiAlON and β-SiAlON suspension properties with deflocculant (0·3 wt%)

	Start[a] *(pH)*	pH_{IEP}				
		Zeta potential	*ESA*	*The severest floc formation*	*The highest viscosity*	*The highest yield value*
Ca-α-SiAlON	9·2	5·3	5·3	4·9	5–6	5·1
β-SiAlON	9·1	5·3	5·5	4·6	5–6	4·9

[a] pH just after attrition milling.

4.4 Comparison of suspension characterisation techniques

Our last, but not least, goal apart from the powder characterisation itself was to evaluate different suspension characterisation techniques with respect to the convenience, reproducibility, time and amount of material needed to gain the necessary information. In order to show the good correlation among the three techniques used (rheometry, sedimentation and electrophoresis) combined plots are presented. Fig. 8(a) and (b) showed that the maximum in viscosity is at zero zeta potential. It has to be noted that the zeta potential was measured in a very diluted suspension ($\approx 5\%$) while with the ESA 25 wt% suspensions were used. The good correlation between the results of the two techniques indicates that the particle interaction did not significantly influence the outcome of the measurements. Fig. 6(a) and (b) presented the coherent results between zeta potential and sedimentometry for Ca-α-SiAlON and β-SiAlON suspensions. All the used different techniques gave results which are in good agreement and are complementary to one another. The data have already been explained and discussed in Section 4.2. Our results indicate that the rheological and zeta potential measurements are the most reliable and suitable ones for characterisation of suspensions meant for a slip casting process, in agreement with results from the literature.[33–35]

5 Conclusions

The Ca-α-SiAlON and β-SiAlON suspensions in water have different isoelectric points (pH 3·4 and 4·6, respectively). The difference in IEP is caused by divergent bulk composition and oxidation treatment. Mainly the latter forms on the SiAlON surface aluminium silicate like species. They are either silica (Ca-α-SiAlON) or alumina (β-SiAlON) rich. However, the dependence of both zeta potentials as a function of pH are quite alike. After the addition of deflocculant the differences are completely disguised and the suspensions behave nearly identically. This can be very profitable in determining optimum parameters for processing α and β-SiAlON powder mixtures.

Both powders have the best characteristics for the slip casting process at pH 10–11, showing the lowest viscosities (below 10 mPa s), the lowest sediment volumes and the largest zeta potentials. Under such conditions both suspensions are almost fully deflocculated.

Rheometry and zeta potential measurements were found to be useful techniques for obtaining the parameters that are critical for good slip casting behaviour. These parameters can be obtained quickly and reliably.

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