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Total Aqueous Processing of Carbothermally Produced β-Sialon

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Abstract

β-Sialon with chemical formula $Si_3Al_3O_3N_5$ is synthesised from meta-kaolin/coal mixtures which are pelletised and heat treated at 1500°C in flowing nitrogen. Typically batches produced contain 300 g powder with 90 wt% β-sialon and 10 wt% 15-R phase. The powders are attrition milled to submicron size, suspended in water and mixed with yttrium oxide as a sintering aid. Suspensions are pH and polyelectrolyte stabilised. The suspensions are used to slip cast discs which are sintered in a nitrogen atmosphere of 100 kPa at 1450°C for 150 minutes.

Typical properties are ball-on-ring strength at room temperature 450 MPa, density 3.31 g/ml, HV2 Vickers hardness 12·5 GPa and K_{IC} 5·4 MPa $\sqrt{m}$. © 1996 Elsevier Science Limited.

1 Introduction

β-Sialon is a well known ceramic material with mechanical properties which are comparable to those of silicon nitride. The material is generally produced by reaction sintering of aluminium oxide silicon nitride and aluminium nitride, but also carbothermal reduction and nitridation of aluminium oxide/silicon oxide mixtures, or of aluminosilicates are used for the synthesis of sialon ceramics.[1–7]

CTK has been working on the synthesis and processing of sialon ceramics for more than ten years and several theses and a number of publications have been produced on this subject.[1–5,8,9] The synthesis of β-sialon by carbothermal reduction and nitridation of meta-kaolin, discussed here, has been scaled up to the kg scale and further processing of the sialon powder is taking place by ultrafine grinding and colloidal (pressure) filtration to fabricate complex shapes.

The sialon is produced by carbothermal reduction and nitridation of meta-kaolin according to the following overall reaction:[1]

$$3\,(2SiO_2.Al_2O_3.2H_2O) + 15C + 5N_2 \rightarrow 2\,Si_3Al_3O_3N_5 + 15CO + 6H_2O \quad (1)$$

In this paper we report on the processing by slip casting of β-sialon, starting from carbothermal production up to sintering of the final products and the determination of relevant properties.

2 Experimental

Pellets were produced by tumbling kaolin (Monarch, Cyprus Industrial Minerals Company) and Carbon (Elftex 125, Cabot) with water in an Eirich mixer (Labormischer RO2). The pellets were approximately 1–10 mm in diameter. The specifications of these materials are listed in Table 1. Synthesis of the β-sialon was performed in a horizontal tube furnace with a hot zone of approximately 400 mm (High Temperature Horizontal Tube Furnace, Carbolite, Sheffield, UK). The pellets were placed in an alumina tube with an inner diameter of 50 mm, using a packed bed of approximately 200 mm in length. The packed bed was formed using alumina fibre material as a plug. During the whole experiment 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 (measured at normal temperature and pressure). The reaction process was followed by monitoring the concentration of the carbon monoxide in the exhaust gas (IFC/GFC gas analyser, Defor, Maihak).

The composition of the reaction products was examined using XRD techniques (Rigaku, 35 kV, 20 mA, scanning speed 4° 2θ/min, Cu K_α radiation). The calculations used are based on the adiabatic principle of auto-flushing. The method

Table 1. Specification of precursor powders used for the sialon synthesis

Material	*Purity (%)*	d_{50} *(μm)*	*BET* (m^2/g)	*LOI(wt%)*
Monarch kaolin	>97·5	2	6·7	13·9
Elftex 125	>98	-	27	<0·1
Yttrium oxide, HC Starck	>99·95	<0·8	10–16	--

assumes that the intensity–concentration relationship between each and every pair of components in a multi-component mixture is not perturbed by the presence or absence or other components. It is also assumed that the mixture analysed contains only crystalline phases.[2]

The resulting β-sialon pellets from the carbothermal reduction were dry milled in a hammer crusher (Retsch Mühle, Retsch). The powder was then heated up to 750°C in air to remove any residual coal. The resulting powder was wet milled in an attrition mill (HD 01, Union Process, 1·4-l tefzel coated tank, 7 mm silicon nitride balls) using ultra-pure water (AlphaQ, Millipore). During attrition milling, yttrium oxide (grade fine, HC Starck) as a sintering additive and ammonium polyacrylate (Dolapix CE64, Zschimmer & Schwartz) as a deflocculant were added. After milling, the particle size was analysed by a sedimentation method (Sedigraph 5100, Micromeritics) and the specific surface area was measured using the BET method (Flowsorb II 2300, Micromeritics).

Sedimentation experiments of diluted suspensions were used to determine the conditions for a colloidal stable suspension.[10] Also flow curves (Rotovisco RV3, Haake) were measured for concentrated suspensions at different pH values. The influence of an ultrasonic treatment (Sonifier 250, Branson Ultrasonics) on the stability of the suspensions was also studied.

Experiments were carried out to study the influence of any residual iron from the kaolin. For this study the slip was repeatedly led over a burette that contained magnets to remove any iron compounds.

Slip casting was performed on plaster of Paris moulds to form discs. The green products were carefully dried at room temperature and at elevated temperatures. Dilatometry was performed using a gas pressure sintering furnace (KCE, Germany) with a nitrogen pressure of 100 kPa. With the resulting sintering recipe, sintering was carried out in a nitriding furnace (KCE, Germany) with a nitrogen pressure of 100 kPa. For sintering, samples are embedded in a powder bed, consisting of carbothermally produced β-sialon and boron nitride (Grade HCP, Union Carbide) powders

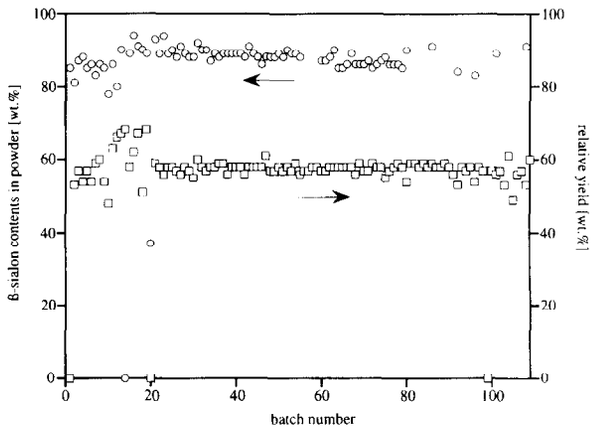

Fig. 1. β-Sialon contents in the reacted powder and relative yield versus a number of produced batches.

using a weight ratio of 3:1, inside a double BN-crucible. The boron nitride powder was added to prevent sintering of the powder bed.

After sintering, the discs were analysed for material strength with the Ball-on-Ring (BOR) test at room temperature, using the sintered discs. For a quick feedback for the optimisation of the processing, strength values obtained from testing as-sintered discs were used. All used discs had the same dimensions and all tests on unmachined samples were carried out under similar conditions (temperature, test facilities, operator). All final material strengths reported further in this paper were acquired using machined samples. Fractographical analysis were performed on several broken samples resulting from strength tests.

Also Ring-on-Ring (ROR) tests at room temperature and at 1000°C were carried out in order to calculate four-point and three-point bending strength using both the BOR and ROR results.[11] Hardness was measured by Vickers indentation. E modulus and Poisson's ratio were determined using pulse-echo method, density was measured using Archimedes' method and fracture toughness was determined by indentation. Also the coefficient of thermal expansion, the oxidation behaviour at 1000°C and at 1200°C and thermal conductivity using photo-flash method were measured. Finally, chemical resistance towards liquid aluminium was studied using wetting angle measurements and a study of reaction couples at various temperatures and times.

3 Results and Discussion

3.1 Synthesis

The pellets were used for carbothermal reduction without sieving or any additional handling.[12] No influence was found on the β-sialon yield when different size fractions of pellets were used

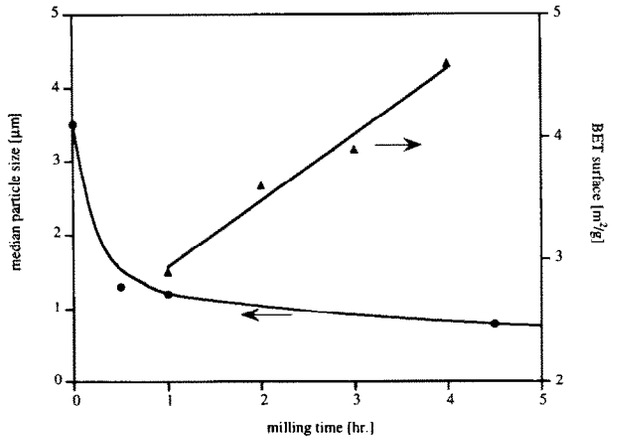

Fig. 2. Median particle size and BET specific surface area versus attrition milling time (at 400 rpm).

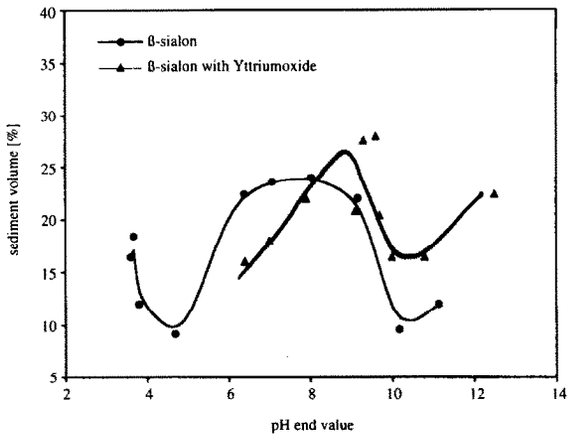

Fig. 3. Stability of β-sialon and β-sialon with addition of yttrium oxide as a function of pH of the suspension.

separately. This is in agreement with the findings of Kokmeijer *et al.*[9]

The packed bed was produced using 500 g of pellets. Nitrogen gas flowed through the tube at a rate of 35 l/h when temperature in the furnace was higher than 155°C. The reaction time at 1500°C was 29 h for the batch size and conditions used here. Heating and cooling rates used were 120°C/h.

The average mass after carbothermal reduction was 300 g. Batches contained typically 90 wt% β-sialon and 10 wt% 15-R phase, analysed using XRD techniques (see Fig. 1).

3.2 Powder and suspension processing

The synthesised powder was first dry milled batch-wise in a hammer crusher, heated at 750°C for 10 h in air to remove any residual coal and then wet milled in an attrition mill to sub-micron size. The attrition milling was optimised to achieve sub-micron powder at an acceptably low wear of the milling media. The optimisation, which was carried out using Taguchi type approach and some additional common sense, led to the milling recipe reported below.

The typical loading of an attrition milling batch was: 550 g of β-sialon, 55 g yttrium oxide powder, 3·7 g deflocculant, 263 g ultra-pure water and 1770 g silicon nitride milling balls. The resulting suspension has a solids content of about 70 wt% (40 vol%). The median particle size after 4 h attrition milling at 400 rpm is less than 1·0 μm. The specific surface area of the powder increases from 1·3 to 4·6 m^2/g after 4 h milling (Fig. 2). The wear of the silicon nitride media is less than 0·12 wt% when milled for 8 h at 400 rpm.

Sedimentation experiments on diluted suspensions are used to determine the conditions for a colloidal stable suspension.[10] The suspensions used in these experiments should be diluted to distinguish a difference in sediment behaviour. The sediment

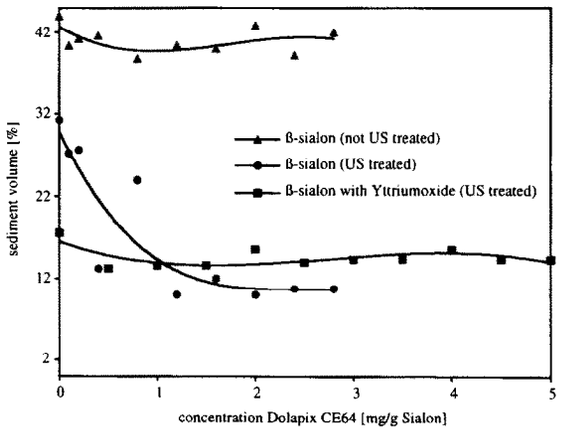

Fig. 4. Sediment volume of β-sialon with and without addition of yttrium oxide as a function of the added amount of deflocculant, Dolapix CE64 (pH is set to 10·0, US means Ultrasonic).

volume for diluted sialon aqueous suspensions, obtained after several weeks, is lowest at pH 4–6 and pH 10–11, indicating a high packing density and stable suspension in these pH ranges (Fig. 3). For β-sialon/yttrium oxide, the sediment volume increases from pH 7 and has a minimum again at pH 10–11. The curve for β-sialon indicates the position of the isoelectric point at pH 7–8, which is in the same range as reported by Kicevic *et al.*[13] for this type of oxynitride. The deflocculant used is known to be most effective at pH ≥ 10.[14] Sedimentation experiments were also used to estimate an optimal concentration for the used deflocculant. The curves in Fig. 4 show a minimum amount of 2 mg/g β-sialon is needed to obtain a stabilised slip. The powder for these experiments was not attrition milled. Also it was found that an ultrasonic treatment further decreased the sediment volume. During attrition milling an amount of 6 mg/g β-sialon deflocculant was needed to produce an optimal slip for slip casting, which is more than three times as much as is needed for the unmilled powder and can be explained by the increase of surface area by a factor of more than three.

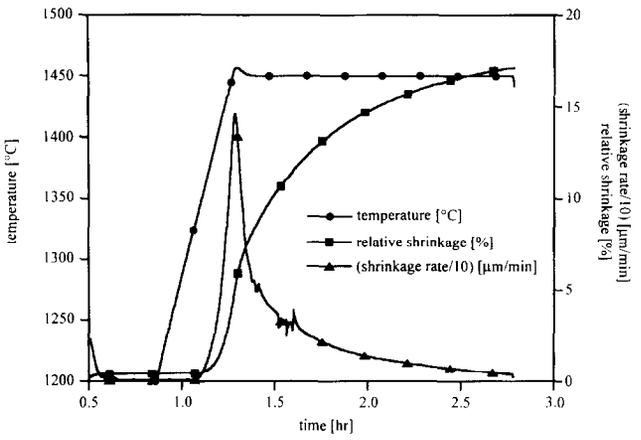

Fig. 5. Dilatometer curve for β-sialon, obtained in gas pressure furnace at 100 kPa N_2.

The influence of a magnetic treatment of the slip was also studied. The kaolin used contains approximately 0·33 wt% iron oxide. It was attempted to remove this iron oxide magnetically by leading the slip repeatedly over a burette containing small magnets to remove iron oxide from the suspension. A residual part of slip was clearly visible on the magnets after the treatment. Slip treated this way was used to slip cast discs and to perform dilatometer experiments. The results, however, showed no significant difference in sintering behaviour between magnetically treated and untreated suspensions.

The slip produced was sieved over a screen with openings of 33 μm. No residual powder could be observed on the screen. The slip was evacuated at a pressure of 1·3 kPa for approximately two minutes, to remove all air from the slip. Finally the pH of the suspension was checked and adjusted if necessary before slip casting, using ammonia (Merck p.a. quality). Discs (ø 35 × 3 mm) were slip cast on plaster of Paris moulds and then carefully dried. The filtration constant was typically 1·0 mm/√min.

The cast discs were dried at room temperature for at least 8 h. During this drying step a small wetted paper was used to cover the discs. In this way a gradation in the drying process was avoided. After removal of the paper, the discs were dried at 40°C (still placed on the moulds) for at least 8 h. Finally the discs were taken from the moulds and put in a furnace at a temperature of 100°C for at least 24 h. The resulting green density was typically 60% of theoretical density.

3.3 Sintering

Sintering curves were obtained using a graphite dilatometer installed in a gas pressure sintering furnace, using small bars (5 × 5 × 15 mm^3), produced from slip cast discs by machining on fine grinding paper. Different samples were analysed: samples from β-sialon powder that was attrition milled for 1, 4 or 8 h and containing 3, 5 and 9 wt% yttrium oxide respectively as a sintering aid were used. Also some magnetically treated suspensions were thus analysed on their sintering properties. The curves were taken from 1100°C up to 1700°C, varying the holding time and heating rates at temperatures above 1100°C. No (more) shrinkage was observed for any sample at temperatures above 1500°C for all samples.

Samples prepared from suspensions attrition milled for 4 h at 400 rpm, containing 9 wt% of yttrium oxide as a sintering additive, showed the best sintering properties resulting in the highest final density and mechanical strength. The analysis in Fig. 5 was carried out with a sample prepared using this procedure. For this analysis a constant heating rate of 600°C/h was used and temperature was held at 1450°C. It can be seen that the liquid phase sintering is maximal at 1450°C and densification is completed after 150 min at that temperature. The resulting density for the sample resulting from this analysis was near 100% of theoretical density.

Discs are embedded in a powder bed inside a BN crucible and then sintered in a nitriding furnace using a nitrogen atmosphere at 100 kPa. The samples are sintered at 1450°C (pyrometer controlled) for 150 min with a heating and cooling rate of 600°C/h.

3.4 Optimisation of the total processing

In general, machining ceramics samples is very laborious and time-consuming. To speed up the process optimisation, β-sialon discs were tested using a shorter route. The progress of the optimisation of the processing is inferred from the mechanical strength of the as-sintered samples. Fractographical investigation showed that defects in the volume of the discs caused failure (and not at the surface), so using unmachined samples is permitted if conditions, like testing parameters and volume of the discs, are kept constant.

Best results so far have been obtained using the following processing recipe: Hammer-crushed β-sialon powder and 9 wt% yttrium oxide powder are milled in an attrition mill for 4 h with a rotation speed of 400 rpm. An amount of 6 mg/g deflocculant is added and the suspension is stabilised at pH 10 using ammonia if necessary. The suspension is sieved over a screen with openings of 33 μm. Then the suspension is evacuated at a pressure of 1·3 kPa until all air bubbles have been removed. After this, green samples are slip cast on dried plaster of Paris moulds using brass rings. The green samples are carefully dried at room temperature for at least 8 h, subsequently dried at

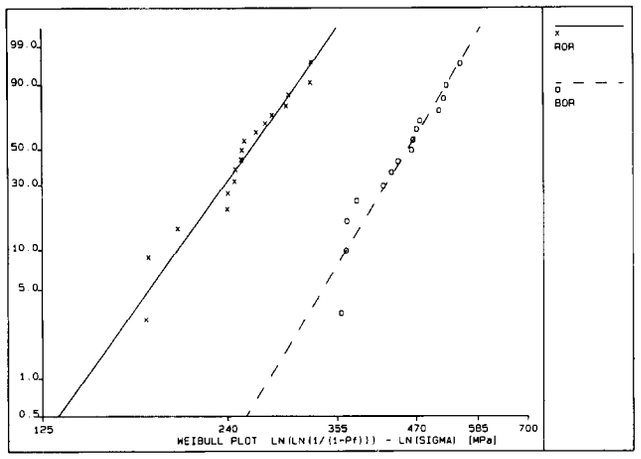

Fig. 6. Weibull plot for Ball-on-Ring and Ring-on-Ring results at room temperature.

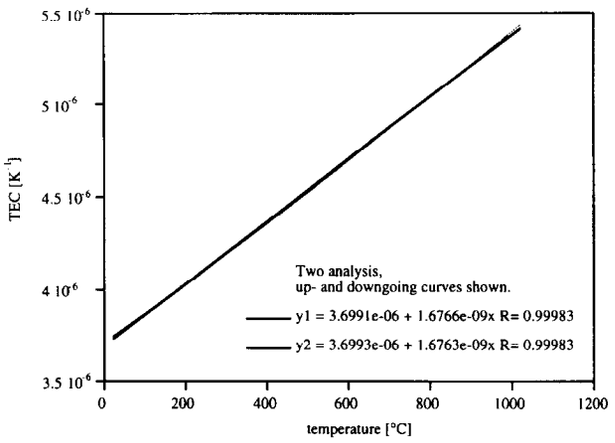

Fig. 7. Duplo analysis of the thermal expansion coefficient of β-sialon ceramics in temperature region 20–1000°C.

40°C for at least 8 h and finally dried at 100°C for at least 24 h.

3.5 Characterisation

All final data reported here refer to β-sialon material, attrition milled for 4 h at 400 rpm, containing 9 wt% yttrium oxide, sintered at 1450°C for 150 min, using a nitrogen atmosphere of 100 kPa. Discs used for the analysis were flattened at approximately 2·0 mm and polished until roughness (r_a) was less than 0·2 μm.

Young's modulus and Poisson's ratio were determined using the pulse-echo method (Grindosonic, n = 5). The average Young's modulus and Poisson's ratio are 240 ± 3·5 and 0·292 ± 0·007, respectively. Density was measured by Archimedes' method and was found to be 3·31 ± 0·03 g/cm^3, whereas theoretical density of β-sialon with addition of 10 wt% yttrium oxide is 3·28 g/cm^3 calculated using the rule of mixture.

All BOR and ROR tests were performed in air using slip cast and sintered discs of 29·90 ± 0·10 mm in diameter and 2·00 ± 0·01 mm in thickness, thus a test volume of 1·41 ± 0·02 cm^3. In the data shown n represents the number of discs tested and

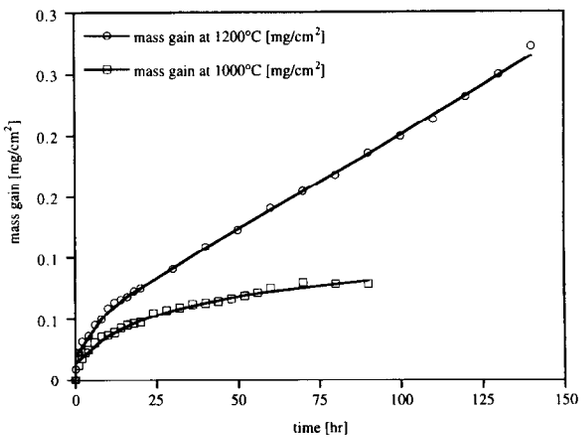

Fig. 8. Mass gain of β-sialon during oxidation experiment at 1000°C and 1200°C.

m represents the calculated Weibull modulus. There are several methods to calculate the Weibull parameters; because of the limited number of samples, the following failure probability is most appropriate:[11]

$$P_{fi}=(i\text{-}0{\cdot}5)/n \qquad (2)$$

P_{fi} is the failure probability of the ith ranked specimen and n is the total number of specimens used. The average (arithmetic mean) BOR strength is 451 ± 60 MPa (n=15, m=8·3) measured at room temperature. Kokmeijer[2] published a maximum average BOR strength of 452 ± 50 MPa for β-sialon powder derived from meta-kaolin, using a test volume of only 0·064 cm^3. If we recalculate the BOR strength according to formula(3)[11] from the test volume used to the volume used by Kokmeijer in order to make a comparison, a BOR strength of 578 MPa is found. It should be noted that the samples produced by Kokmeijer were gas pressure sintered at 1690°C for 1 h at 500 kPa nitrogen pressure.[2]

$$\sigma_2/\sigma_1 = (V_2/V_1) - (1/m) \qquad (3)$$

where σ is the bending strength, V is the volume tested and m is the Weibull modus.

The average (arithmetic mean) ROR strength determined at room temperature is 257 ± 40 MPa (n=10, m=7·2). The average (arithmetic mean) ROR strength determined at 1000°C is 241 ± 41 MPa (n=10, m=6·4). This means ROR strength is little influenced by temperature and the β-sialon does not lose strength at elevated temperatures up to 1000°C. The Weibull plot for BOR and ROR at room temperature is shown in Fig. 6.

Also four-point bending strength (50 × 4·5 × 3·5 mm^3, outer span length 40 mm, inner span length 20 mm) and three-point bending strength (50 × 4·5 × 3·5 mm^3, span length 40 mm) were calculated from ROR and BOR analysis using a model published by Scholten.[11] From these calculations

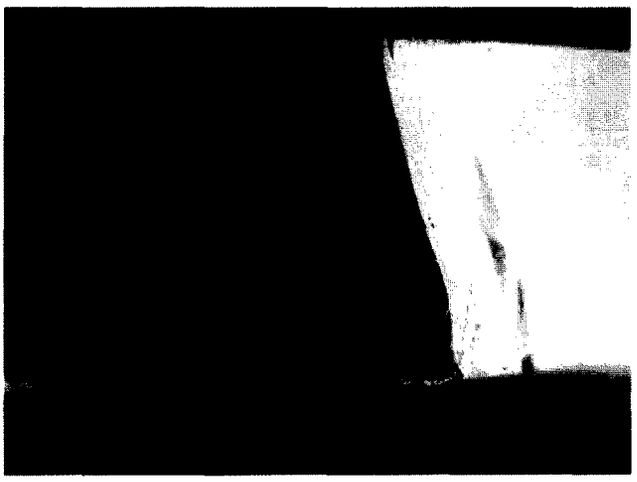

Fig. 9. SEM micrograph of fracture surface of sample 1, showing an overview of the fracture surface.

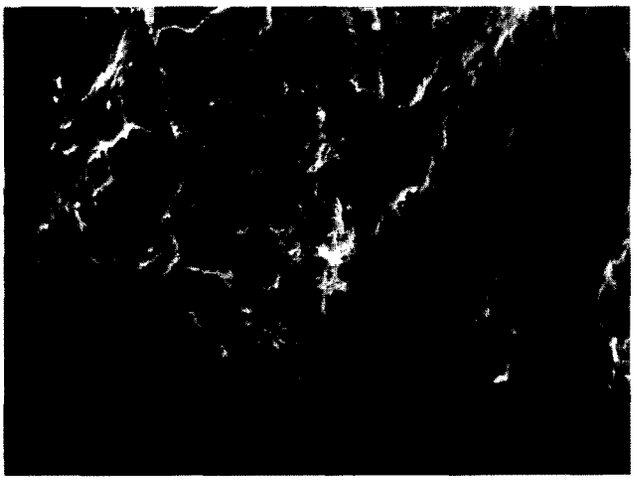

Fig. 10. SEM micrograph of fracture surface of sample 1, showing the defect, a porous zone, in detail.

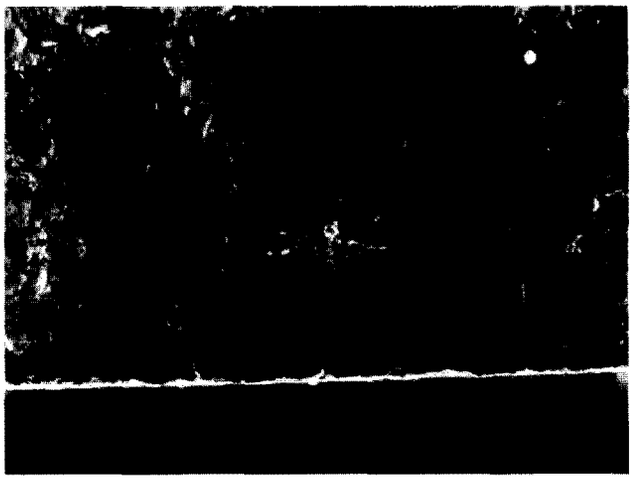

Fig. 11. SEM micrograph of fracture surface of sample 2, showing the defect in detail.

Fig. 12. SEM micrograph of fracture surface of sample 3, showing the defect.

three-point bending strength is 341 MPa and four-point bending strength is 286 MPa.

Hardness and toughness of the β-sialon material were determined by, respectively, Vickers method using a force of 2 N and indentation method using a load of 306 N. Hardness found was 12·5 ± 1·7 GPa (n=40), toughness 5·4 MPa $\sqrt{m}$ (n=10).

Thermal expansion coefficient (TEC) was measured from room temperature up to 1000°C. The result is shown in Fig. 7. TEC is $5{\cdot}50 \times 10^{-6}$ K^{-1} at 1000°C. Thermal conductivity data was measured to be 7·1 W/m K.

Oxidation measurements were carried out at 1000°C for 75 h and at 1200°C for 125 h. The result is shown in Fig. 8. At 1200°C the mass gain does not level off, no protective uniform crack-free layer seems to be formed at this temperature.

Fractographical analyses were performed on broken discs from BOR and ROR tests by optical microscopy and scanning electron microscopy (SEM). Fractographical analyses on broken discs of the ROR tests were very difficult because of the large number of fragments left after testing. Fractographical tests on fragments left from BOR tests were relatively easy to perform because of the uniform parts left after testing. In 80% of the investigated samples a defect was found in the volume of the disc. In the remaining 20% the defect could not be detected. In all detected cases the detected defects were porous zones of 24–40 μm in size. The defect sizes inferred from the porous zones are possibly due to packing defects and/or inhomogeneous distribution of sintering aid. The defect size is in reasonable agreement with the measured BOR strength according to the equation:[15]

$$\sigma_{3ps} = (0{\cdot}737\ K_{Ic}) / \sqrt{c} \qquad (4)$$

Where σ_{3ps} is the three-point bending strength, K_{Ic} is the toughness and c the critical defect size.

An overview plus close-up micrographs from fractographical analysis on typical sample 1 are shown in Figs 9 and 10. Close-up micrographs from typical samples 2 and 3 are shown in Figs 11 and 12. On these micrographs the porous zones can be clearly seen.

Table 2. Properties of carbothermally produced β-sialon ceramics, sintered with 9 wt% yttrium oxide at 1450°C for 2·5 h in 100 kPa nitrogen atmosphere.

Properties	*Measured values*
E-modulus (pulse-echo method)	240 ± 3·5 GPa
ν (pulse-echo method)	0·292 ± 0·007
BOR strength at 20°C	Mean strength 451 ± 60 MPa, m = 8·3
(v_{test} = 1·41 cm^3)	n = 15, polished samples
ROR strength at 20°C	Mean strength 257 ± 40 MPa, m = 7.2
(v_{test} = 1·41 cm^3)	n = 10, polished samples
ROR strength at 1000°C	Mean strength 241 ± 41 MPa, m = 6·4
(v_{test} = 1·41 cm^3)	n 10, polished samples
3-point strength at 20°C	341 MPa, calculated with data from BOR and ROR results
4-point strength at 20°C	286 MPa, calculated with data from BOR and ROR results
Density at 20°C	3·31 ± 0·03 g/ml (no porosity), n = 10
Vickers hardness at 20°C (HV2)	12·5 ± 1·7 GPa, n = 40 (4 samples)
K_{Ic} at 20°C with indentation using load of 306 N.	5·4 MPa$\sqrt{m}$, n = 10 (2 samples)
TEC (thermal expansion coefficient)	5·50 * 10^{-6} K^{-1} at 1000°C
	4·50 * 10^{-6} K^{-1} at 500°C
Oxidation behaviour in air at 1000°C	Δm [mg/m^2] < 0·10% after 75 h
Oxidation behaviour in air at 1200°C	Δm [mg/m^2] < 0·30% after 125 h
Chemical resistance towards liquid aluminium	Good
λ thermal conductance	7·1 W/m K

Finally the chemical resistance of the β-sialon against liquid aluminium was studied between 1000°C and 1250°C in air and in vacuum. Even at 1250°C there was hardly any attack from the liquid aluminium on the β-sialon inferred from the absence of significant reaction layers present in slices of aluminium/β-sialon investigated by SEM.

All properties mentioned in this section are summarised in Table 2.

4 Conclusions

The processing of β-sialon ($Si_3Al_3O_3N_5$) from carbothermal synthesis out of kaolin to sintering has been described, including the conditions to obtain high yield β-sialon, sub-micron powders, colloidal stable suspensions and the conditions to obtain a high sintered density. Also relevant properties of the carbothermal β-sialon sintered with 9 wt% yttrium oxide have been reported. The properties indicate that this low-cost β-sialon has very interesting possibilities, for instance to replace alumina or silicon nitride for certain applications.

Acknowledgements

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