

# Microstructure and Mechanical Properties of $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ Ceramics

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## Abstract

The properties of 21 different ceramics of  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$  were measured. The sialons were prepared by three methods: reaction sintering in a gas pressure sintering furnace, reaction hot-pressing and sintering of sialon powder produced by carbothermal reaction from kaolin. Furthermore, the series differed in kind ( $\text{CeO}_2$  or  $\text{CaO}$ ) and concentration of additive and process conditions. The quantities measured were composition (X-ray diffraction), density, microstructure, Vickers hardness (2 N), Young's modulus, Poisson's ratio, fracture toughness (SENB) and bi-axial strength. Generally the room temperature properties were hardly influenced by the production route, composition or process conditions. Fracture toughness and bi-axial strength were most sensitive to the process conditions. The mechanical properties of kaolin-derived sialon appeared to be as good as those of the other sialons.

Die Eigenschaften von 21 keramischen  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$  Werkstoffen wurden untersucht. Die Sialone wurden mittels dreier Verfahren hergestellt: Reaktionssintern in einem Gasdrucksinterofen, Reaktionsheißpressen und normales Sintern von Sialon-Pulver, das durch karbothermische Reaktion aus Kaolin hergestellt wurde. Ferner wurden in der Versuchsserie die Art ( $\text{CeO}_2$  oder  $\text{CaO}$ ) und die Menge der Additive sowie die Verfahrensparameter variiert. Folgende Daten wurden gemessen: Zusammensetzung (XRD), Dichte, Gefüge, Vickers Härte (2 N), E-Modul, Poissonzahl,  $K_{Ic}$  (SENB) und die bi-achsial gemessene Festigkeit. Im allgemeinen

zeigte sich bei Raumtemperatur keine Abhängigkeit der Werkstoffeigenschaften vom Herstellungsverfahren, der Zusammensetzung oder den Verfahrensparametern. Die bi-achsial gemessene Festigkeit und der  $K_{Ic}$ -Wert wiesen die größte Abhängigkeit gegenüber den Verfahrensparametern auf. Die mechanischen Eigenschaften der aus Kaolin gewonnenen Sialon-Werkstoffe zeigten gegenüber dem konventionell erhaltenen Material ebensogute Eigenschaften.

On a mesuré les propriétés de 21 différentes céramiques  $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ - $\beta'$ . Les sialons étaient préparés selon trois méthodes: frittage réaction dans un four de frittage sous pression de gaz, frittage réaction sous charge et frittage de poudre sialon produite par réaction carbothermique à partir du kaolin. De plus, les séries différaient de part la nature ( $\text{CeO}_2$  ou  $\text{CaO}$ ) et la concentration de leurs ajouts de frittage et de part les conditions d'élaboration. On a mesuré les propriétés suivantes: composition (diffraction X), densité, microstructure, dureté Vickers (2 N), module de Young, coefficient de poisson, ténacité (SENB) et résistance mécanique en contrainte bi-axiale. Les propriétés à température ambiante étaient généralement peu influencées par la voie de production, la composition ou les conditions d'élaboration. La ténacité et la résistance mécanique en contrainte bi-axiale étaient davantage sensibles aux conditions d'élaboration. Les propriétés mécaniques des sialons dérivés du kaolin étaient équivalentes à celles des autres sialons.

## 1 Introduction

Sialon can be considered as silicon nitride, in which part of the silicon is replaced by aluminium and part

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of the nitrogen by oxygen.<sup>1</sup> According to the two structural modifications of silicon nitride ( $\alpha$  and  $\beta$ ), two types of sialon can be formed:  $\alpha'$ -sialon and  $\beta'$ -sialon. In this report a  $\beta'$ -compound,  $\beta'$ -Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub> with  $z = 3$ , is studied.

$\beta'$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> can be produced by reaction sintering of a mixture of Si<sub>3</sub>N<sub>4</sub>, AlN and Al<sub>2</sub>O<sub>3</sub> but also by carbothermal reaction of kaolinite (2SiO<sub>2</sub> · Al<sub>2</sub>O<sub>3</sub> · 2H<sub>2</sub>O). The reaction sintering process starts with a green product of a mixture of Si<sub>3</sub>N<sub>4</sub>, AlN and Al<sub>2</sub>O<sub>3</sub>. During the sintering process the product is densified and converted to sialon. During carbothermal production of sialon a mixture of kaolin and carbon is converted under a nitrogen flow into  $\beta'$ -Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub>, CO and H<sub>2</sub>O. After the carbothermal production of sialon the powder has to be milled and shaped prior to the sintering process. An advantage of this method is the relatively low cost of the raw materials kaolin and carbon. Thus an engineering ceramic may be obtained at relatively low costs. Impurities in the kaolin, however, can deteriorate the properties of the sintered product.

In this report the properties of 21 different sialons are compared. The sialons were prepared by reaction sintering in a gas pressure sintering furnace, reaction hot-pressing and sintering of sialon powder produced by carbothermal reaction of kaolin. For all sialons described here the densification process is a liquid-phase sintering process. For detailed information refer to references 1 and 2. The differences between the sialons prepared in this report are between the kind (CeO<sub>2</sub> or CaO) and the concentration of additive and the process conditions.

## 2 Experimental

The starting material for reaction sintering and reaction hot-pressing was a mixture of Si<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and AlN. As sintering additives CaO and CeO<sub>2</sub> were used. The CeO<sub>2</sub> additive was chosen because of the resemblance between the Ce-Si-O-N and Y-Si-O-N phase systems,<sup>1</sup> suggesting that sintering behaviour and properties of the CeO<sub>2</sub>-doped sialons will be similar to those doped with Y<sub>2</sub>O<sub>3</sub>. Y<sub>2</sub>O<sub>3</sub> is known as a good but expensive sintering additive. CeO<sub>2</sub> is cheaper and therefore more suitable for application in kaolin-derived sialons. Studies of the carbothermal production of sialon from kaolin showed that CaO has a 'catalytic' effect on the reaction and seems to stabilize the sialon structure.<sup>3</sup> Therefore CaO was chosen as sintering additive, although it is known that CaO-doped materials do not yield optimum high-temperature strength. The

influence of impurities that can be present in kaolin (Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>) was studied on reaction-sintered sialon doped with CaO.

Detailed information on the raw materials, the powder processing and reaction sintering and reaction hot-pressing procedures has been given in previous reports.<sup>4-6</sup> The green samples for reaction-sintered sialons (batches 1-11, see Table 1) consisted of tablets of 7 g with a diameter of 18.5 mm and density of 2.1 g cm<sup>-3</sup>. The samples were sintered in a two-step sintering procedure: specimens were sintered during a time  $t_1$  at a temperature  $T_1$  and nitrogen pressure of 0.5 MPa, followed by a sintering step of  $t_2$  at a temperature  $T_2$  and nitrogen pressure of 10 MPa. The sintering times  $t_1$  and  $t_2$  and temperatures  $T_1$  and  $T_2$  of each batch are given in Table 1. The green samples for hot-pressed sialons (batches 14-21) consisted of tablets of 20 g with a diameter of 29 mm and density of 2.1 g cm<sup>-3</sup>. The samples were hot-pressed at 21.8 MPa, which was applied at about 1450°C. The hot-pressing times and temperatures are given in Table 1.

Batches 12 and 13 are sialons sintered from sialon powder prepared by carbothermal reaction from kaolin. These batches were sintered in the gas pressure sintering furnace in a one-step sintering procedure at 0.5 MPa nitrogen pressure. The sintering times and temperatures are given in Table 1. The green samples for these batches had a diameter of 17.5 mm and density of 1.7 g cm<sup>-3</sup>. The carbothermal production of sialon from kaolin and a description of the raw materials has been presented previously.<sup>6,7</sup> The sialon powder for batches 12 and 13 was prepared in one procedure. The only difference between the two batches was an extra milling procedure for batch 13, resulting in a decrease of the median agglomerate size from 3.8  $\mu$ m (batch 12) to 1.3  $\mu$ m (batch 13). This reduced agglomerate size made it possible to use a considerably shorter time and lower temperature.

The density of the sintered and hot-pressed samples was determined by the Archimedes technique in water. The composition (of the crystalline phase) was analysed by X-ray diffraction. The (semi)quantitative analysis used was based on the adiabatic principle of auto-flushing.<sup>6,8-10</sup>

Young's modulus ( $E$ ) and Poisson's ratio ( $\nu$ ) were obtained with the pulse-echo method. The longitudinal wave velocity and the transverse wave velocity were measured at 10 and 5 MHz respectively. The measurements were performed on ground samples with a surface roughness of 2  $\mu$ m. The attenuation being small, no corrections were made for internal damping.

Out of one sample of each batch, four specimens

**Table 1.** Process conditions, resulting density ( $\rho$ ) and Vickers hardness (HV2) for the sialon batches with the indicated additive. Given are the sintering temperature and time during both sintering steps ( $T_1$ ,  $T_2$  and  $t_1$ ,  $t_2$ ) for the (reaction) sintered batches 1–13. The  $\text{N}_2$  pressure is 0.5 MPa at the first step and 10 MPa at the second step. The hot-pressing temperature and time are given for the hot-pressed batches 14–21.

Number	Additive (wt%)	$T_1$ ( $^{\circ}\text{C}$ )	$t_1$ (h)	$T_2$ ( $^{\circ}\text{C}$ )	$t_2$ (h)	$\rho$ ( $\text{g cm}^{-3}$ )	HV2 (GPa)
1	1.0 CeO <sub>2</sub>	1600	0.5	1650	0.5	3.091	15.1
2	3.0 CeO <sub>2</sub>	1600	0.5	1650	0.5	3.137	15.3
3	5.0 CeO <sub>2</sub>	1600	0.5	1650	0.5	3.168	15.3
4	1.0 CeO <sub>2</sub>	1650	0.5	1700	0.3	3.096	14.9
5	3.0 CeO <sub>2</sub>	1650	0.5	1700	0.3	3.132	14.5
6	1.0 CaO	1550	0.5	1600	0.5	3.085	15.2
7	3.0 CaO	1550	0.5	1600	0.5	3.098	14.2
8	1.0 CaO	1600	0.5	1650	0.5	3.083	14.7
9	1 CaO, 0.5 SiO <sub>2</sub>	1600	0.5	1650	0.5	3.077	14.7
10	1 CaO, 0.5 TiO <sub>2</sub>	1600	0.5	1650	0.5	3.085	15.5
11	1 CaO, 0.5 Fe <sub>2</sub> O <sub>3</sub>	1600	0.5	1650	0.5	3.081	15.5
12	Kaolin (coarse) <sup>a</sup>	1800	4.0			3.113	14.0
13	Kaolin (fine) <sup>a</sup>	1690	1.0			3.100	14.9
14		1800	0.75			3.077	15.7
15	0.5 CeO <sub>2</sub>	1700	0.75			3.092	15.3
16	1.0 CeO <sub>2</sub>	1650	0.75			3.101	15.7
17	3.0 CeO <sub>2</sub>	1600	0.75			3.130	15.3
18	3.0 CeO <sub>2</sub>	1600	0.08			3.208	17.3
19	0.5 CaO	1675	0.75			3.080	15.3
20	1.0 CaO	1650	0.75			3.081	15.3
21	3.0 CaO	1625	0.75			3.082	14.5

<sup>a</sup> Starting material is kaolin-derived sialon powder.

were prepared for fracture toughness measurements. These specimens are  $1 \times 3 \times 15$  mm with a notch of approximately 0.45 mm in their centre (SENB specimens). This type of specimen makes efficient use of the material available, while retaining accuracy and reliability.<sup>11</sup> Knoop indentations (20 N) were made on both sides of the specimen at the root of the notch for crack initiation. The experiments were done in a nitrogen atmosphere at a relative humidity of 1% (dew point  $-35^{\circ}\text{C}$ ). The notch depth ( $a$ ) was measured after the Knoop indentations were made. The relative notch depth ( $a/W$ , where  $W$  is the height of the sample;  $W = 3$  mm) varied from 0.16 to 0.26. The average value was 0.20.

The strength of the sialons was determined by a ball-on-ring test. According to the literature,<sup>12,13</sup> for ceramics bi-axial strength measurements have advantages over the beam tests commonly used. In three- and four-point bending tests there is always a chance of measuring edge effects. Reviews of several bi-axial strength testing methods are given by Shetty *et al.*<sup>14</sup> and de With & Wagemans.<sup>13</sup>

In the ball-on-ring test a disk specimen is supported on a ring and centrally loaded with a ball. To minimize frictional stress a circular ball-bearing (radius  $a_s$ ) with freely moving balls is used instead of a continuous ring support. Generally the stress distribution for the ball-on-ring test in the loaded central area is approximated by a region of uniform

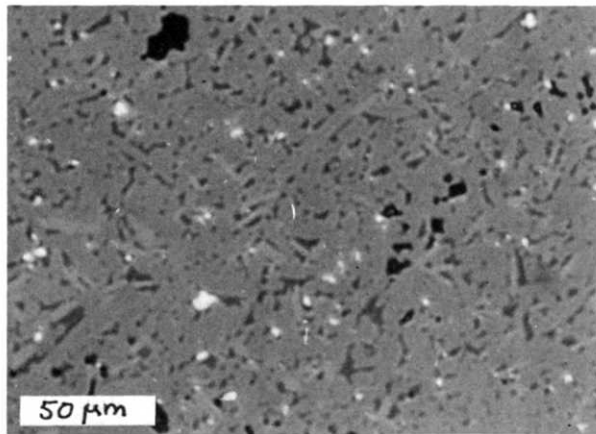
surface pressure with radius  $b$ . Analysis of the stress at the central area of the disk<sup>13</sup> showed that  $b$  can be safely approximated by one-third of the thickness. Further, the influence of the size of the loading ball appeared to be negligible.

The strength was measured on nine samples for each batch of Table 1. The samples of the (reaction) sintered batches each had a radius of about 9 mm, thickness of 1 mm and were tested with a radius  $a_s$  of 6 mm. All specimens were ground to a surface roughness of  $0.2 \mu\text{m}$ . The samples of the hot-pressed batches had a radius of approximately 16 mm, thickness of 1 mm and were tested with a radius  $a_s$  of 10 mm. The crosshead speed for the hot-pressed samples was  $108 \text{ mm h}^{-1}$  and for the (reaction) sintered samples  $84 \text{ mm h}^{-1}$ , resulting in a strain rate of  $4.7 \times 10^{-4} \text{ s}^{-1}$  and  $5.8 \times 10^{-4} \text{ s}^{-1}$  respectively. The measurements were performed at ambient temperature in nitrogen at a dew point of  $-35^{\circ}\text{C}$  (relative humidity 1%).

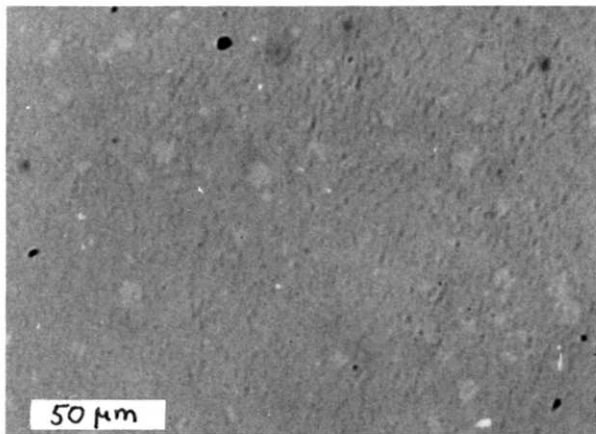
### 3 Results and Discussion

#### 3.1 Density, composition, microstructure and hardness

The density of the sintered and hot-pressed samples is given in Table 1. The calculated relative density is more than 99.5% for all batches. However, optical



(a)



(b)

Fig. 1. Residual porosity of sialon derived from (a) kaolinite and (b) reaction-sintered sialon.

microscopy showed a larger porosity (up to 2%). This difference is due to inaccuracy of the calculated theoretical density; the theoretical density was calculated assuming a completely crystalline material of sialon with additive. The highest porosity ( $\pm 5\%$ ) was observed for the 'kaolin' sialons (see Fig. 1).

The results of XRD analysis are given in Table 2. The sialons prepared from kaolin-derived sialon powder contained traces of  $\text{Fe}_3\text{Si}$  and  $\text{TiN}$ . The larger amount of 15R ( $\text{SiAl}_4\text{O}_2\text{N}_4$ ) in batch 12 in comparison to batch 13 is probably due to the long sintering time at high temperature, resulting in decomposition of  $\beta\text{-Si}_3\text{Al}_3\text{O}_3\text{N}_5$ . For the CaO-doped sialons the amount of 15R increases with increasing CaO content. The hot-pressed samples with  $\text{CeO}_2$  and CaO additive contained some  $\alpha\text{-Si}_3\text{N}_4$ . The concentration of  $\alpha\text{-Si}_3\text{N}_4$  increases with the additive content. At low concentrations the distinction between the X-ray patterns of  $\alpha$ -sialons and  $\alpha\text{-Si}_3\text{N}_4$  is not very clear. Thus the formation of Ca- $\alpha'$ -sialon instead of  $\alpha\text{-Si}_3\text{N}_4$  cannot be excluded. On the other hand, Ce- $\alpha'$ -sialon has not been identified unequivocally and the matter will have to be solved in future work.

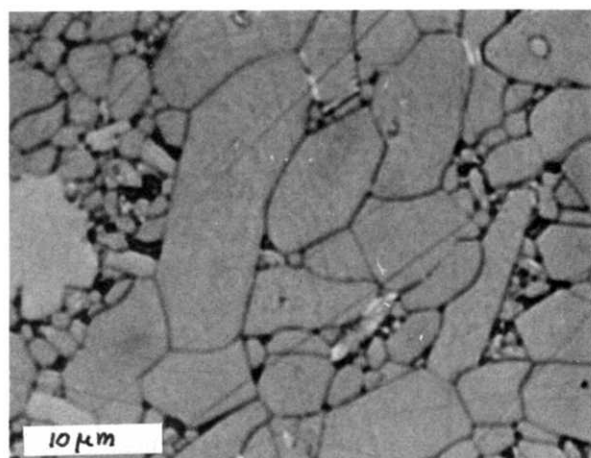
The microstructure of the different sialons is illustrated in Figs 2 and 3. All reaction-sintered and reaction hot-pressed samples contain large clusters of 15R phase, visible as lightly coloured regions. The

Table 2. Young's modulus ( $E$ ), Poisson's ratio ( $\nu$ ), fracture toughness ( $K_{Ic}$ ), bi-axial strength ( $\sigma_{bi}$ ) with its sample standard deviation ( $\Delta\sigma_{bi}$ ) and composition of the sialon materials prepared under the conditions given in Table 1

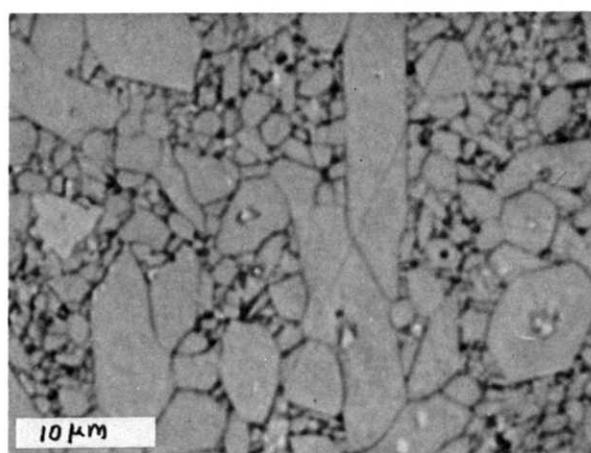
Number	$E$ (GPa)	$\nu$	$K_{Ic}$ ( $\text{MPa m}^{1/2}$ )	$\sigma_{bi}$ (MPa)	$\Delta\sigma_{bi}$ (MPa)	Composition (wt%) <sup>a</sup>						
						1	2	3	4	5	6	
1	229.0	0.300	4.06	455	35	98	2					
2	229.8	0.298	3.63	467	58	95	5					
3	228.5	0.296	3.20	438	37	93	7					
4	230.0	0.300	3.70	485	38	97	3					
5	230.4	0.298	2.80	480	26	96	4					
6	229.7	0.297	2.81	385	39	96	4					
7	227.5	0.300	2.60	356	41	86	14					
8	229.2	0.297	2.79	490	28	97	3					
9	228.1	0.297	2.68	428	35	97	3					
10	228.4	0.297	2.79	442	47	97	3					
11	227.2	0.296	2.89	441	45	94	6					
12	220.7	0.292	3.07	378	16	90	9 <sup>b</sup>					
13	218.3	0.299	2.51	452	50	96	3 <sup>b</sup>					
14	226.3	0.302	3.51	347	45	98	1			1		
15	228.3	0.302	3.53	469	52	96			2	2		
16	228.3	0.300	3.52	460	51	95			3	2		
17	225.8	0.298	3.94	443	62	89			8	3		
18	248.5	0.285	3.26	389	68	62			23		10	5
19	227.2	0.300	2.60	346	40	96			3	1		
20	225.2	0.297	2.46	374	37	92			2	4	2	
21	219.6	0.285	2.72	383	36	80			7	11	2	

<sup>a</sup> 1 =  $\beta\text{-Si}_3\text{Al}_3\text{O}_3\text{N}_5$ , 2 = 15R, 3 =  $\alpha\text{-Si}_3\text{N}_4$ , 4 =  $\beta\text{-Si}_3\text{N}_4$ , 5 =  $\text{Al}_2\text{O}_3$ , 6 =  $\text{AlN}$ .

<sup>b</sup> Both 'kaolin' sialons contained traces of  $\text{TiN}$  and  $\text{Fe}_3\text{Si}$ .



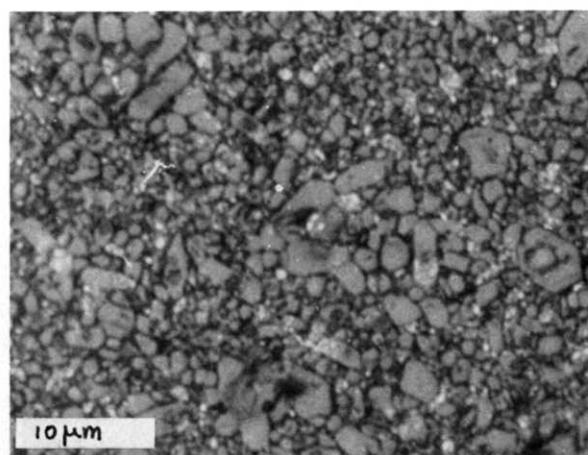
(a)



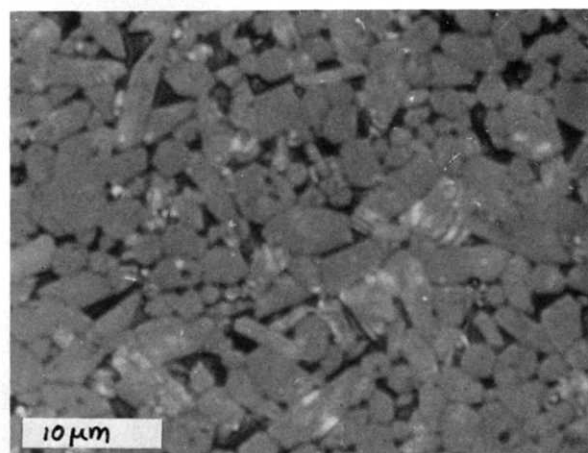
(b)

**Fig. 2.** Microstructure of reaction-sintered sialon, sintered under different conditions: (a) 0.5 h, 1600°C, 0.5 MPa followed by 1 h, 1700°C, 10 MPa; (b) 0.5 h, 1600°C, 0.5 MPa followed by 0.5 h, 1650°C, 10 MPa.

fact that the regions of 15R are of similar size for all specimens indicates that the presence of these clusters is caused by insufficient powder processing. The grain size in reaction-sintered sialons is larger than that in hot-pressed sialons and depends on the exact processing conditions. Longer sintering times and/or higher sintering temperatures result in coarsening of the structure (Fig. 2(a) and (b)). The grains of reaction-sintered specimens are needle shaped with an average aspect ratio of 4. The maximum needle length for CaO-doped sialons was 5–10  $\mu\text{m}$  and for  $\text{CeO}_2$ -doped sialons 10–30  $\mu\text{m}$ .  $\text{CeO}_2$ -doped reaction-sintered specimens have a very broad grain size distribution. Space between large needles is filled with small needles, resulting in a bi-modal grain size distribution. The maximum grain size of the hot-pressed specimens is 2  $\mu\text{m}$  and these grains are nearly equiaxed. The fracture surfaces in Fig. 4 also show the large difference in



(a)



(b)

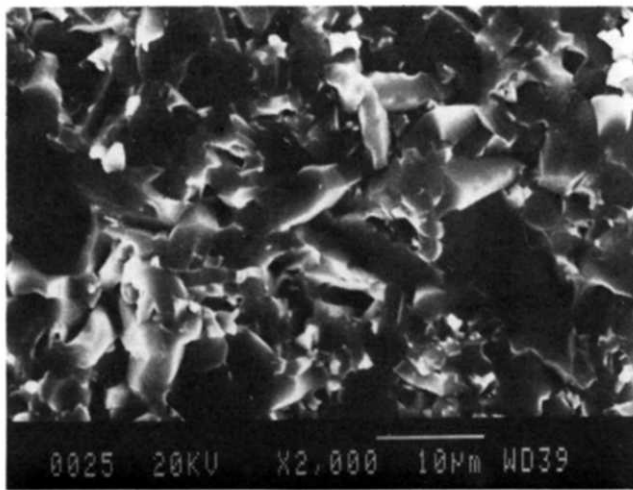
**Fig. 3.** Microstructure of (a) hot-pressed sialon (batch 14) and (b) sialon prepared from kaolinite (batch 13).

grain size between the reaction-sintered and the hot-pressed sialons.

The hardness of the different sialons is given in Table 1. The concentration and process conditions did not influence the hardness significantly. The average hardness of all batches is  $15.2 \pm 0.7$  GPa. The only batch with a significantly higher hardness is batch 18. This batch was hot-pressed with 3 wt%  $\text{CeO}_2$  for only 0.08 h, resulting in incomplete conversion of  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ .

The indentation diagonal is about 15  $\mu\text{m}$  (2 N) with a read-off error of 0.3  $\mu\text{m}$ . This error results in a deviation in the hardness of 0.7 GPa. Thus it can be concluded that within the accuracy of the measurement the hardness is not influenced by the kind and concentration or additive nor by the process conditions.

Some hardness data given in the literature are 15 GPa for hot-isostatic-pressed  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ <sup>15</sup> and 16.7 and 17.3 GPa for a reaction-sintered  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$  with and without heat treatment.<sup>2</sup> Lee



(a)



(b)

Fig. 4. Fracture surfaces of two  $K_{Ic}$  specimens: (a) batch 1, reaction-sintered with 1 wt%  $CeO_2$ ; (b) batch 17, hot-pressed with 3 wt%  $CeO_2$ .

*et al.*<sup>16</sup> reported a hardness of 13.3 GPa for a 'kaolin' sialon. In view of the variation in hardness data due to the influence of the indentation load, temperature and relative humidity (as discussed by Czernuszka & Page<sup>17</sup>), these data are in agreement with the data obtained in this study.

### 3.2 Young's modulus and Poisson's ratio

The values for  $E$  and  $\nu$ , given in Table 2, are averages of all nine samples within one batch. The average Young's modulus and Poisson's ratio are  $226.9 \pm 3.5$  GPa and  $0.298 \pm 0.04$  respectively. Batch 18 is not included in these averages because of its different composition (see Table 2). Young's modulus and Poisson's ratio of hot-pressed  $Al_2O_3$  are 400 GPa and 0.24<sup>18</sup> respectively, and for  $Si_3N_4$  are 304 GPa and 0.24.<sup>19</sup> Thus the higher Young's modulus and lower Poisson's ratio of batch 18 are caused by the

presence of  $Al_2O_3$  and  $Si_3N_4$ . The values for  $E$  and  $\nu$  obtained are in good agreement with those of Wills *et al.*<sup>20</sup> They reported, for a sialon with a  $z$ -value of two and density of  $3.00 \text{ g cm}^{-3}$ , 234 GPa for  $E$  and 0.29 for  $\nu$ .

Both properties are hardly influenced by the production method or the concentration and kind of additive. They seem to decrease slightly with increasing amount of additive, though this effect is not significant. The Young's modulus of the sialons derived from kaolin is lower than that of the reaction-sintered or reaction hot-pressed sialons. This may be caused by the higher concentration of impurities or the somewhat higher porosity of the 'kaolin' sialons. A generally applied relation between Young's modulus and porosity is given by<sup>21</sup>

$$E = E_0(1 - 1.9P + 0.9P^2)$$

where  $P$  is the porosity and  $E_0$  is the Young's modulus of the completely dense material. Assuming an  $E_0$  of 235 GPa, the Young's modulus of a material with 1% and 4% porosity is 230 and 219 GPa respectively, in agreement with the experimental data.

### 3.3 Fracture toughness

The results of the  $K_{Ic}$  measurements are given in Table 2. The sample standard deviation in the measurements of one batch of four specimens is about 10%. The average  $K_{Ic}$  for  $CeO_2$ -doped sialons is  $3.5 \text{ MPa m}^{1/2}$  and for  $CaO$ -doped sialons it is  $2.7 \text{ MPa m}^{1/2}$ . The fracture toughness of reaction-sintered sialons is similar to that of hot-pressed sialons with comparable composition. The fracture toughness of hot-pressed sialon without additive is equal to that of the  $CeO_2$ -doped specimens. A comparison of batch 1 with 2, 4 with 5 and 6 with 7 indicates that an increase of the additive content results in a decrease of  $K_{Ic}$ . For the hot-pressed batches this effect cannot be observed because every batch was hot-pressed under different conditions. For the reaction-sintered batches with  $CeO_2$  a higher sintering temperature seems to result in a lower  $K_{Ic}$  (compare batches 1 and 2 with 4 and 5). This is not observed for  $CaO$ -doped sialons (batch 6 and 8). For the 'kaolin' sialons  $K_{Ic}$  is highest for the batch with the higher sintering temperature and longer sintering time. The addition of small amounts of  $TiO_2$ ,  $SiO_2$  and  $Fe_2O_3$  does not influence the fracture toughness. The fracture mode is mainly transgranular (Fig. 4).

Generally the influence of temperature and additive concentration on the fracture toughness is

stronger for the  $\text{CeO}_2$ -doped sialons as for the CaO-doped sialons. This may be explained by the fact that  $\text{CeO}_2$  transforms to  $\text{Ce}_2\text{O}_3$ , resulting in excess oxygen. The excess oxygen can react with the nitrides to give more  $\text{SiO}_2$ -based liquid phase during the sintering process, thereby degrading the fracture toughness.

Fracture toughness data for sialons, given in the literature,<sup>2,15,16,20</sup> were obtained by the indentation technique. Wills *et al.*<sup>20</sup> reported, for a reaction-sintered sialon with  $z = 2$ , a  $K_{Ic}$  of  $2.2 \text{ MPa m}^{1/2}$ . The fracture toughness of a sialon with  $z = 3$  was  $1.9 \text{ MPa m}^{1/2}$ .<sup>2</sup> This increased to  $2.2 \text{ MPa m}^{1/2}$  after a heat treatment. Ekström & Olsson<sup>15</sup> studied  $K_{Ic}$  as a function of the  $z$ -value for sialons prepared by hot-isostatic-pressing. They found that  $K_{Ic}$  decreased with increasing  $z$  and measured a fracture toughness of  $3 \text{ MPa m}^{1/2}$  for  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ . Thus the measured  $K_{Ic}$  values of  $3.5$  and  $2.7 \text{ MPa m}^{1/2}$  for  $\text{CeO}_2$ - and CaO-doped sialons respectively compare favourably with these data. The average  $K_{Ic}$  for kaolin-derived sialon,  $2.8 \text{ MPa m}^{1/2}$ , is also reported by Lee *et al.*<sup>16</sup>

### 3.4 Strength

The results of the strength measurements are summarized in Table 2. The strength for (reaction) sintered specimens is comparable to the strength of hot-pressed specimens with similar composition. The average strength of all samples with CaO (405 MPa) is lower than that of samples with  $\text{CeO}_2$  (462 MPa).

The strength of batch 8, with 1 wt% CaO, is relatively high at 490 MPa. Apparently the higher sintering temperature in comparison to batch 6 results in an increase in strength. Probably the samples of batch 8 contain less microporosity, though the densities of these samples are not higher than those from batch 6. The high strength of batch 8 indicates that the average lower (room-temperature) strength for the CaO-doped sialons is not due to the presence of CaO itself. Addition of impurities lowers the strength; the strength of batches 9–11 sintered under similar conditions as batch 8 have a lower strength than batch 8.

Generally the variation of the additive content from 0.5 to 5 wt% does not influence the strength significantly. Only from a comparison of batch 6 and 7, sintered at similar conditions, might it be concluded that an increasing amount of CaO decreases the strength.

The strength of batches 4 and 5 is somewhat higher than that of batches 1 and 2. This also indicates that a higher sintering temperature in-

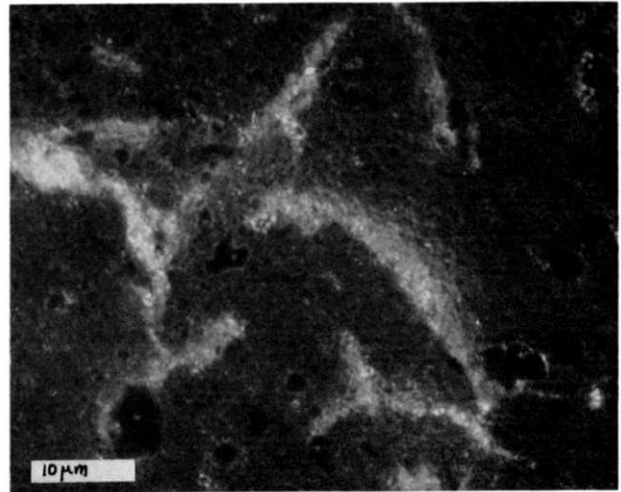


Fig. 5. Microcracks in a hot-pressed material (batch 18) visible in polarized light.

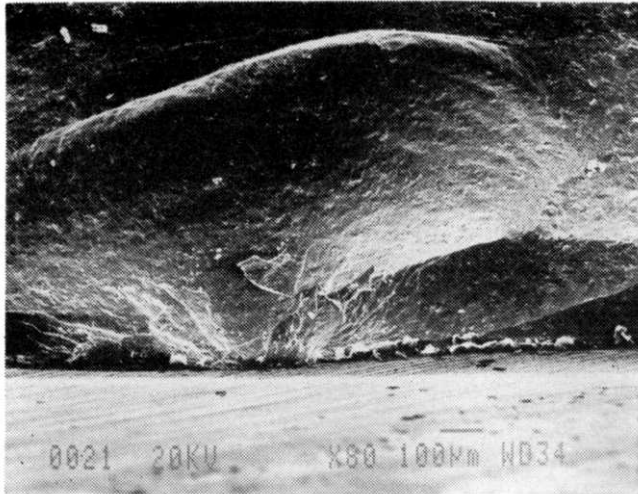
creases the strength. In view of the much coarser structure of the batches 4 and 5, this is unexpected. Possible explanations are a homogenization of the structure or a decrease in the microporosity at higher sintering temperatures. However, analysis could not confirm this.

The strength of batches 13 and 14, sintered from sialon powder derived from kaolin, is 378 and 452 MPa respectively. Thus the strength of the sialon prepared from the powder with the smaller agglomerate size and the resulting smaller grain size is much higher.

The strength of batch 18 (3 wt%  $\text{CeO}_2$  hot-pressed for 0.08 h at  $1600^\circ\text{C}$ ) is relatively low at  $389 \pm 68 \text{ MPa}$ . This is probably due to the presence of microcracks (see Fig. 5). The presence of these cracks can be explained as follows: at the application of the pressure during the hot-pressing procedure cracks are introduced in the samples. If the hot-pressing time is long enough these cracks are healed. Because of the short hot-pressing time of batch 18 some of the cracks were still present.

Microscopic analysis of the fracture surfaces showed that the cracks were not introduced by large microstructural defects. The fractures were mainly transgranular. It is likely that the strength is strongly determined by the surface finish of the specimens. McKinney & Herbert<sup>22</sup> showed that the fracture stress and surface finish are related for low porosity ceramics. Figure 6 shows the crack origin in a hot-pressed sample introduced by the grinding procedure.

Kishi *et al.*<sup>23</sup> recently suggested a heat treatment in air to reduce the influence of surface machining flaws. Therefore a few spare specimens of hot-pressed batches were heat treated in air for 2 h at  $1100^\circ\text{C}$ . The bi-axial strength of these specimens was



**Fig. 6.** Crack origin in a hot-pressed sample. The crack originates from a defect introduced by the grinding procedure.

453, 640, 456, 565 and 616 MPa for samples of batch 14, 18, 19, 20 and 21 respectively. The strength of these five samples is significantly higher than the average strength of the corresponding batches (see Table 2). To study the influence of surface oxides and other effects caused by the heat treatment, like the removal of residual stresses, more samples should be tested after different heat treatments.

The variation of the strength within one batch can be analysed by the Weibull statistics.<sup>24,25</sup> Although only nine samples of each batch were available, the Weibull moduli were estimated. The average Weibull modulus for (reaction) sintered batches is  $14 \pm 5$  and for hot-pressed batches  $9 \pm 2$ . This lower modulus for the hot-pressed batches may be caused by the possible presence of cracks introduced by the application of the pressure.

To compare the bi-axial strength data obtained with uni-axial strength data presented in the literature both methods should be related to each other. Dortmans & de With<sup>26</sup> compared three different models to predict bi-axial from uni-axial strength data. The predictions for the mean strength by the three models do not differ substantially. For a Weibull modulus of 10 and a failure probability of 50% the three-point bending strength (for specimens of  $50 \times 4.5 \times 3.5$  mm) appeared to be about 75% of the bi-axial strength.<sup>26</sup>

Mitomo *et al.*<sup>27</sup> reported a strength of 370 MPa for reaction-sintered  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ . This value was obtained by a three-point bending test. The average bi-axial strength of the reaction-sintered  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$  (batches 1 to 5) with  $\text{CeO}_2$  is  $465 \pm 19$  MPa, from which a three-point bending strength of 350 MPa is calculated. Thus within the accuracy of the data the strength of the  $\text{CeO}_2$ -doped sialons is equal

to the strength data of Mitomo.<sup>27</sup> The calculated three-point bending strength of batch 8, with 1 wt%  $\text{CaO}$ , is 370 MPa. The strength of the other  $\text{CaO}$ -doped sialons, 310 MPa calculated three-point bending strength, is lower than the strength obtained by Mitomo.

For two hot-pressed sialons with  $z = 2$  and slightly different compositions three-point bending strengths of 430 and 470 MPa were reported.<sup>28</sup> The calculated three-point bending strengths of hot-pressed sialon without additive, with  $\text{CaO}$  and with  $\text{CeO}_2$  are 260, 290 and 360 MPa respectively. Batch 18 is not included in the average for  $\text{CeO}_2$ -doped sialons because of the different composition. Two reasons can be given for the lower strength observed. Firstly, the strength decreases with increasing  $z$ -value; Tani *et al.*<sup>29</sup> reported a three-point bending strength decreasing from 490 to 370 MPa for  $z$  increasing from 1 to 4. Secondly, as mentioned before, it is possible that, because of the hot-pressing procedure used, cracks are introduced in the samples.

Kishi *et al.*<sup>23</sup> prepared two sialons with  $z = 0.5$ : one using the common mixture of  $\text{Si}_3\text{N}_4$  and  $\text{Al}_2\text{O}_3$ , and one using a spray-dried mixture of  $\text{Si}_3\text{N}_4$  and aluminium isopropoxide solution. The three-point bending strength of these (hot-pressed) sialons was 484 and 1480 MPa respectively. However, these values are measured after a heat treatment which, as shown earlier in this section, can increase the strength by about a factor of 1.5. Taking this into account the strength for the conventional powder-processed sialon is rather low in comparison with a sialon with  $z = 1$  of Tani *et al.*,<sup>29</sup> while the sialon prepared from the spray-dried mixture is about twice as strong. This can be explained by the homogeneous structure of this sialon and shows once more the large improvement of properties that can be obtained by optimum powder processing.

The effect of additives on the three-point bending strength of hot-pressed  $\beta'$ - $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$  (with  $z = 1$ ) has been studied by Nakamura *et al.*<sup>30</sup> The strengths for sialons without additive, with 5 wt%  $\text{CeO}_2$  and with 5 wt%  $\text{TiO}_2$  were 465, 855 and 580 MPa respectively.<sup>30</sup> Though the addition of  $\text{CeO}_2$  does increase the strength, this is not as substantial as reported by Nakamura *et al.* According to Nakamura *et al.* addition of  $\text{TiO}_2$  increases the strength. For a reaction-sintered specimen, batch 7, the opposite is observed.

The highest strengths for sialons sintered from sialon powder derived from kaolinite are observed by Lee *et al.*<sup>16</sup>—250 MPa for a sialon without additive and 310 MPa for a sialon with YAG. Both



values represent three-point bending strengths. The calculated three-point bending strength for the sialon batches of kaolin are 285 MPa for the coarse powder and 340 MPa for sialon sintered from the fine powder. Thus the strength obtained for the kaolin-derived sialons is high. The strength of batch 13 (the fine sialon powder) is comparable to that of reaction-sintered sialons.

#### 4 Conclusions

The production method and process conditions have no influence on the hardness, Young's modulus and Poisson's ratio of  $\beta'$ - $\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5$ . The microstructure of the reaction-sintered and reaction hot-pressed materials is inhomogeneous, due to insufficient powder processing.

The fracture toughness as well as the bi-axial strength are influenced by the additives and process conditions. Generally the properties of the CaO-doped sialons are not as good as those of the  $\text{CeO}_2$ -doped materials. However, under certain process conditions, for reaction-sintered sialon with 1 wt% CaO, it was possible to obtain a strength similar to that of  $\text{CeO}_2$ -doped sialon. The properties of reaction-sintered material were similar to those of hot-pressed materials with comparable composition.

The relation between  $K_{Ic}$  and  $\sigma_{bi}$  and the grain size is not unambiguous. For the kaolin-derived sialon  $K_{Ic}$  increased and  $\sigma_{bi}$  decreased with increasing grain size. For  $\text{CeO}_2$ -doped reaction-sintered sialon the opposite was observed.

The impurities in the kaolin did not deteriorate the room-temperature properties. This is confirmed by the fact that addition of small amounts of  $\text{SiO}_2$ ,  $\text{TiO}_2$  or  $\text{Fe}_2\text{O}_3$  did not influence the properties of the reaction-sintered sialon significantly. A kaolin-derived sialon with mechanical properties comparable to the properties of 'conventional' sialons was obtained, opening the way for further improvement of ceramics prepared from cheap raw materials.

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