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Hardness, indentation fracture toughness and compositional formula of X-phase sialon

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The hardness and indentation fracture toughness, K_{IC} of sintered X-phase sialon, produced by simultaneous carbothermal reduction and nitriding of kaolinitic clays, are determined. By comparing the values obtained for the sialon with those for a commercially pure mullite, it is suggested that X-phase sialon is a material with potential for similar applications to those in which mullite is currently used. On the basis of the oxygen/nitrogen ratios of the sialon determined by the inert gas fusion method, the analysis of the energy of the dispersed X-rays (EDAX) from thinned samples in the transmission electron microscope (TEM) and the aluminium/silicon ratios, also determined by the TEM EDAX method, a modified compositional formula is proposed for X-phase.

1. Introduction

Since the discovery of X-phase sialon by Oyama and Kamigaito [1] and Jack [2] in the early 1970s, very little has been reported about its mechanical properties. The work by Wills *et al.* [3] concluded that X-phase sialon has a detrimental effect on the fracture toughness, K_{IC}, of β′-sialon of $z = 2$ ($Si_4Al_2O_2N_6$). This conclusion was based on the mechanical properties of a composite of the two sialons. Yamagishi *et al.* [4] observed that a 15 wt% addition of X-phase sialon, formed *in situ* by the reaction sintering of mullite/β′-sialon, $z = 2$ (in which the entire amount of β′ decomposed), improved the strength and the room-temperature fracture toughness, of the mullite/X-phase sialon composite relative to mullite by about 10% and 5%, respectively. More recently, the present authors also observed [5] in a composite (with pre-produced X-phase sialon) similar to that investigated by Yamagishi *et al.* [4], an improvement in the strength and indentation fracture toughness of the composite, relative to mullite, of 5% and 10%, respectively. By a systematic microstructural investigation, it was concluded [5] that the improvement is as a result of the diminution of grain growth of the composite in the presence of X-phase sialon.

The above investigations, from which the mechanical behaviour of X-phase sialon could be inferred, are on composites; that is, there is no specific study on the mechanical properties of a material in which the only crystalline phase present is X-phase sialon. The reason for this is most probably to do with difficulty encountered in trying to produce such a material. As was initially suggested by Jack [6], and more recently confirmed in other reports [7, 8], stable X-phase sialon exists within a domain from about 52.9–59 eq (equivalent) % aluminium and a very narrow range of ≤ 1.5 eq % oxygen. So it is difficult to produce X-phase sialon devoid of other crystalline phases, such as other sialon phases, mullite and α-Al_2O_3.

The problem of producing X-phase sialon was also compounded by the fact that many stoichiometric formulae for it were advanced. However, a consensus seems to have emerged in relation to its Al/Si ratio. Hence Naik *et al.* [9], using an X-ray powder diffraction (XRD) method found this ratio to be 1.5:1 and suggested a formula of $Si_{12}Al_{18}O_{39}N_8$. Bergman *et al.* [7] found a similar Al/Si ratio using the EDAX method in scanning electron microscopy (SEM), and a formula of $Si_{12}Al_{18}O_{36}N_{10}$ was suggested. In previous work [8] by the present authors, where the three formulae, $Si_3Al_6O_{12}N_2$ [10], $Si_3Al_3O_7N$ [11] and $Si_{12}Al_{18}O_{39}N_8$ [9] were considered for the carbothermal production of a powder in which the only crystalline phase was X-phase sialon, $Si_{12}Al_{18}O_{39}N_8$ was found to be the closest representative. TEM EDAX analysis of the studies [8] also revealed a ratio of 1.5:1 for Al/Si, but the oxygen/nitrogen (O/N) ratio was not determined.

Looking at the formulae proposed by Bergman *et al.* [7] and Naik *et al.* [9], the difference only lies in the O/N ratios; while the former shows a weight ratio of 4.1:1, the latter indicates a value of 5.6:1. In all cases [7–10] where X-phase sialon was produced, it was always associated with a silica-rich phase (glass). Hence analyses based on methods that use bulk sampling (such as XRD and EDAX from SEM) in a material with a very narrow range of equivalent per cent of oxygen (and closely associated with a silica-rich phase) may not accurately reveal the true O/N ratio of the material. For example, the average cross-sectional grain size of the X-phase sialon in the work by Bergman *et al.* [7] was 2 μm, but it has been shown [12] that using an electron probe size of 7–10 nm in the SEM this sampled region increases to about 2 μm.

Thus, irrespective of the position of the beam on a 2 µm size grain, other regions with a silica-rich phase will equally be detected. In the TEM the detected X-rays come from a region of only about 100 nm.

Having successfully produced [8] and sintered to 100% densification [13] a material of which the only crystalline constituent is X-phase sialon, it was considered relevant to study and document the mechanical properties of the sintered material. These properties are presented here, and their comparison with similar properties of sintered [5] commercially pure (99.92%) mullite is made. Using a thinned sample in the TEM, from which Al/Si and O/N ratios are simultaneously determined, and assessing bulk O/N ratio by inert gas fusion, further considerations for a modified formula for X-phase sialon are proposed.

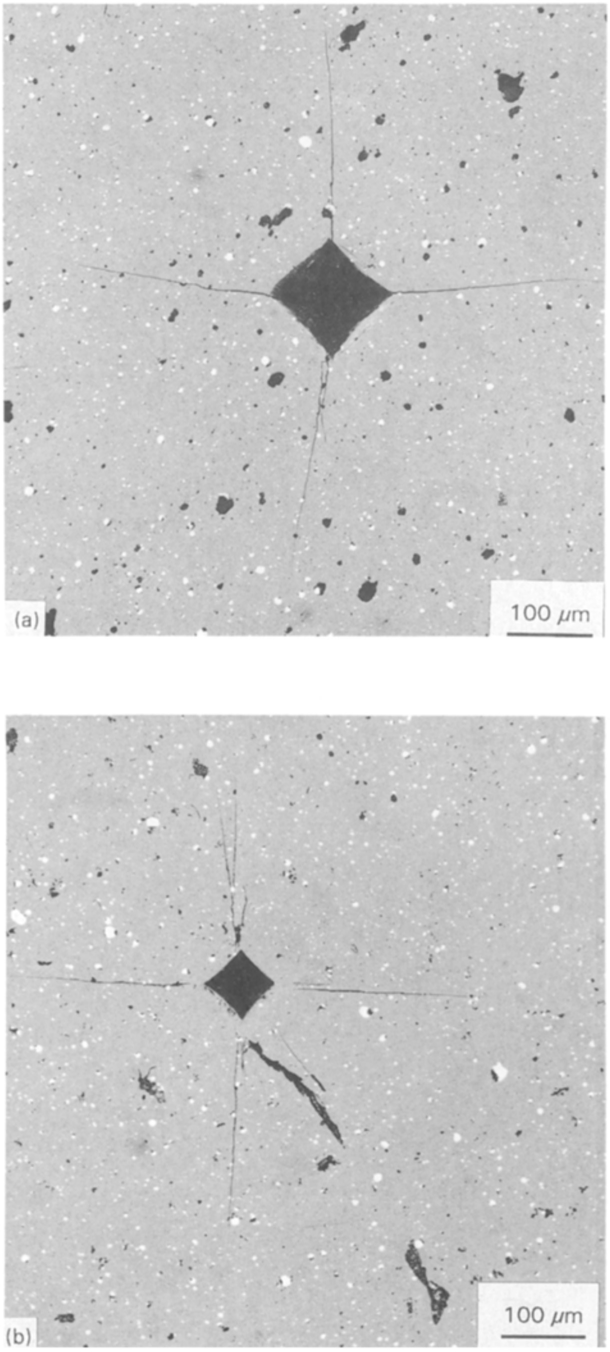


Figure 1 Appearance of an indented sample of milled X-phase sialon showing a Palmqvist type of crack; (a) unpolished, (b) polished.

2. Experimental and procedure

The sialon, sintered according to the details in a previous work by the present authors [13], was classified as-milled and unmilled. The former was from the carbothermally produced [8] powder that was rotary-milled with alumina balls for 70 h in propan 2-ol, while the unmilled material was the same as-produced powder, but was vibratory-milled for only 5 min. The hardness values of both milled and unmilled samples that sintered to 100% of theoretical density were determined using Vickers indentation, with a load of 10 kg. For each sample, five indentations were made and these indents were used to calculate the fracture toughness, K_{IC}, of the samples.

The appearance of the indented samples in (a) the original indented state and (b) after subsequent polishing, of which an example for the milled sialon is shown in Fig. 1 reveals that the conditions [14] for Palmqvist-type cracks were met. The linear relationship, Fig. 2, of crack lengths l and c with the applied load further confirms this; l (m) is the crack length from the corner where the crack joins the indent to its entire extension, and c is the sum of l and a. The latter is the average half-diagonal length (in m) of the indent. Hence, to calculate K_{IC} the equation proposed for Palmqvist-type cracks by Shetty *et al.* [15] was used. The equation is

$$K_{IC} = 0.0889(HP/4l)^{1/2} \qquad (1)$$

where H is the hardness (Pa), given as

$$H = 0.4636\, P/a^2 \qquad (2)$$

P is the applied load (N) on the indenter, while l and a are as defined above.

Al/Si and O/N ratios of the milled sample were determined using an EDAX facility, attached to a Philips EM 400T transmission electron microscope. The ion-beam thinned sample in the TEM was tilted

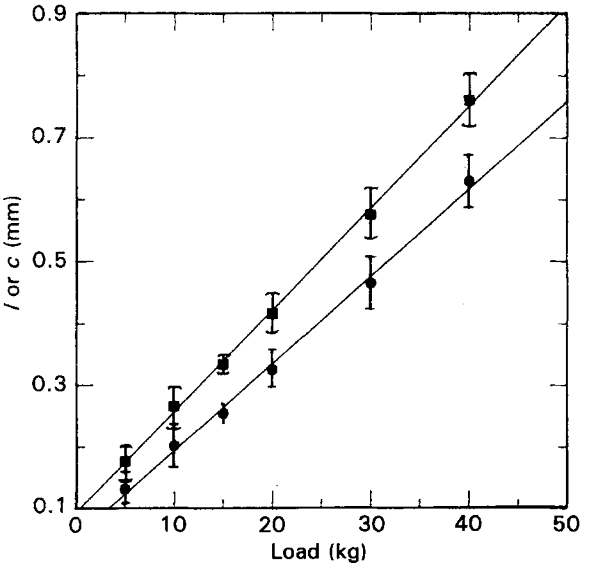


Figure 2 Linear relationship of (●) l and (■) c of milled X-phase sialon with indentation load.

30° to the detector, and the beryllium window was removed so that oxygen and nitrogen elements could be detected simultaneously with aluminium and silicon. Probe sizes of 100 nm and occasionally of 200 nm were used.

A scanning electron microscope (SEM) was used to obtain micrographs of hydrofluoric acid-etched samples of unmilled and milled sialon in order to quantify by how much the milling operation had reduced the grain size. With the aid of the macrostage of an image analyser, Olympus Q2M, the scanning microelectron graphs were used to determine the grain sizes of the samples. These micrographs were also used to determine manually the volume fraction of the glassy (silica-rich phase) constituent of the sialon material. The lineal intercept method, as proposed by Hilliard and Cahn [16] for randomly dispersed features was employed for this purpose. A total of 200 intercepts were made in thirteen different fields.

A Leco machine (Leco Corporation, St Joseph USA), based on the principle of inert gas fusion was utilized for the determination of the O/N ratio of the milled sialon samples.

3. Results and discussion

3.1. Hardness and indentation fracture toughness, K_{IC}, of X-phase sialon

Table I summarizes the hardness, indentation fracture toughness, K_{IC}, and grain size of both milled and unmilled X-phase sialon. There is much in common between X-phase sialon and mullite; for example, the growth morphology [7] and structure [10] of the sialon have both been described as being similar to those of mullite, and the present authors have shown [13] X-phase nucleating from mullite, under conditions where transformation is favourable. Indeed Jack [2] referred to X-phase as "nitrogen mullite". Hence Table I also includes the results of a commercially pure mullite (CPM) that was sintered [5] under conditions similar to those of the milled sample of X-phase.

The volume fraction of the glassy constituent of the milled sialon, which sintered to 100% of its theoretical density was found to be 13.6% ± 3.7%. Despite this concentration of glass in the sialon material, it can be seen from Table I that with about the same grain size as that of CPM (99.92% pure) of density 98.4% of its theoretical value, the mullite shows values of hardness and K_{IC} of only about 5% and 6% higher respectively, over those of the milled sialon. It has also been shown [17] that in the presence of glass, due to a decrease in viscosity, ceramic materials having larger amounts of glassy constituents tend to show higher values of K_{IC} at temperatures above 1000 °C. Hence X-phase sialon with this amount of glass may develop better K_{IC} values than those of mullite when tested at high temperature (above 1000 °C).

The marginal improvement of 6% in both hardness and K_{IC} adduced by milling the sialon for 70 h is noteworthy. Milling also led to the sialon sintering to its theoretical density of 3.01 g cm^{-3} at 1620 °C for 1 h, compared to full densification at a higher temperature of 1665 °C for 1 h achieved for the unmilled sialon. Microstructurally, the former (Fig. 3a) is of lower grain size (1.6 ± 1 μm) than that obtained from the unmilled powder (2.7 ± 1 μm). Thus, as in all engineering materials, obtaining reduced grain sizes in sintered X-phase sialon improves its mechanical properties.

Reduced grain sizes of sintered bodies are most effectively guaranteed if the starting powder is of fine particles. It has been argued [18] that if the same powder with two different average particle sizes, R_1 and R_2 ($R_1 > R_2$), each sintered separately within a given time to the same value of initial relative shrinkage, $\Delta L/L_0$, then

$$\Delta L/L_0 = (D_1/R_1^3T_1)^m = (D_2/R_2^3T_2)^m \qquad (3)$$

where m is approximately 0.5, D is the rate-controlling diffusion coefficient, and T is the sintering temperature (a function of the activation energy necessary for the sintering process) corresponding to R_1 and R_2, respectively. Thus, R_2 being less than R_1, would require less activation energy, and hence lower sintering temperatures. Because the initial shrinkage usually can account for up to 90% of the total shrinkage, particularly when a liquid phase is present, and because the stages of a sintering cycle most often are described with respect to a given temperature, it is rational to conclude that Equation 3 applies for the entire sintering cycle.

The benefit of lowering the sintering temperature is the realization of sintered bodies with relatively re-

TABLE I Hardness, indentation fracture toughness, K_{IC}, and grain sizes of sintered samples

Material	Condition sintered		Density		Grain size (μm)	Hardness[a] (MPa)	l (10^{-3}m)	K_{IC} (MPa m$^{1/2}$)
	(°C)	(h)	(g cm^{-3})	(% Th.)				
Milled X-phase	1620,	1	3.01	100	1.6 ± 1	11 103 ± 339	0.202 ± 0.030	3.3 ± 0.2
Unmilled X-phase	1665,	1	3.01	100	2.7 ± 1	10441 ± 310	0.208 ± 0.031	3.1 ± 0.1
Milled CPM[b]	1720,	2	3.11	98.4	2 ± 1	11 643 ± 184	0.183 ± 0.027	3.5 ± 0.2

[a] To convert MPa to kg mm^{-2} (VHN); divide by 9.80665.

[b] Commercially pure mullite.

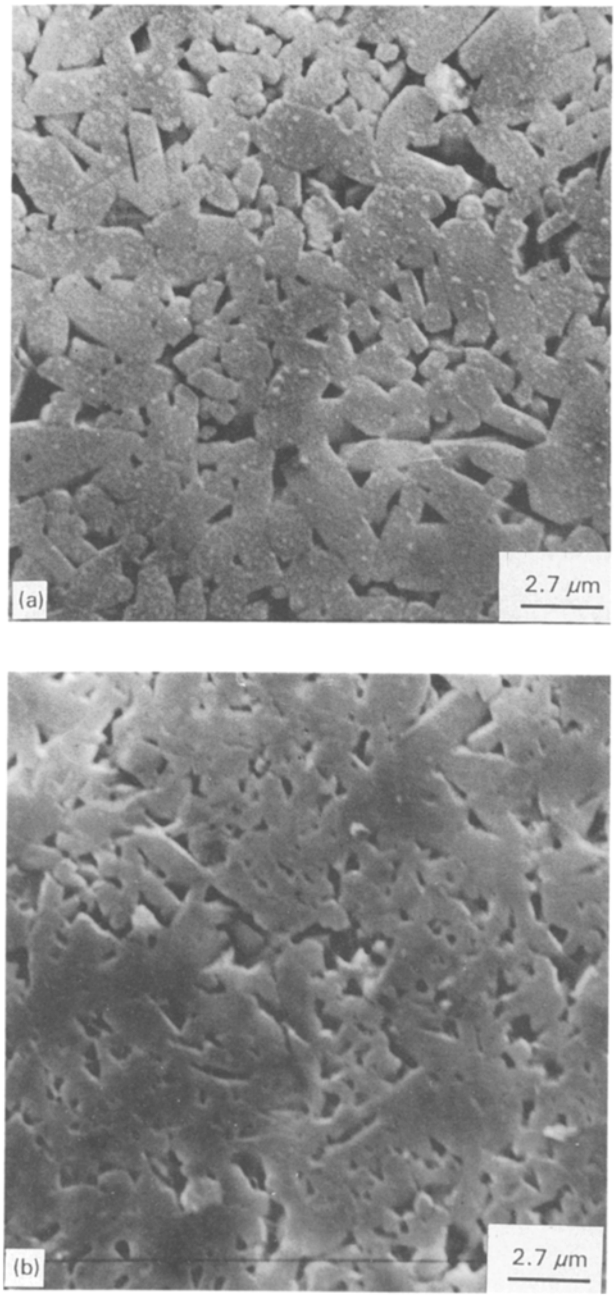


Figure 3 Scanning electron micrographs of (a) sintered milled X-phase sialon, (b) sintered unmilled X-phase sialon.

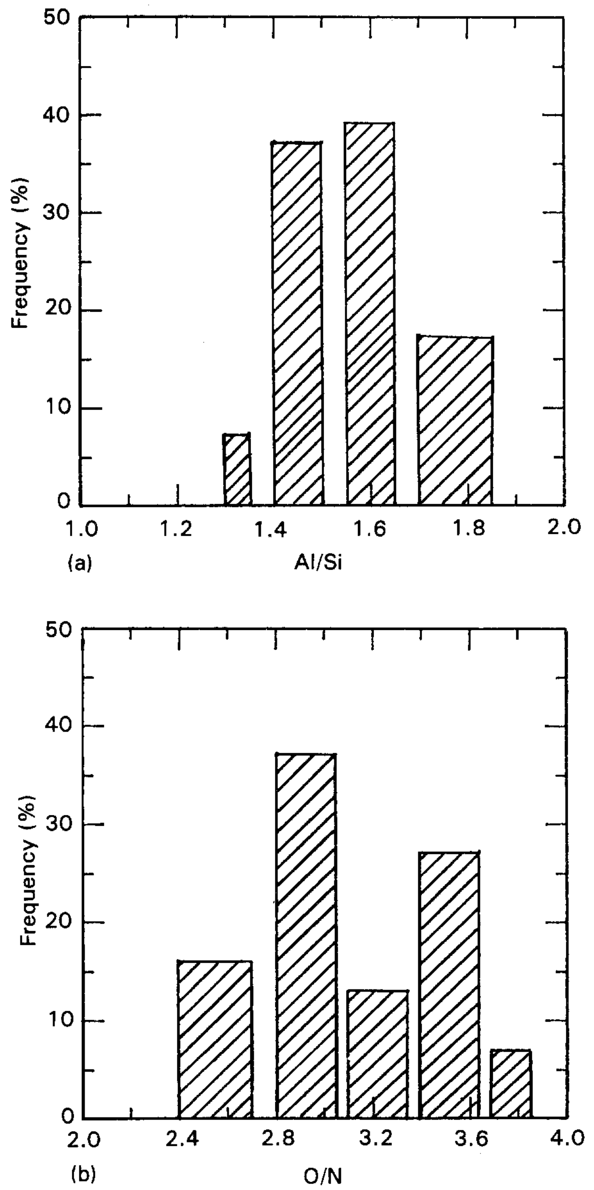


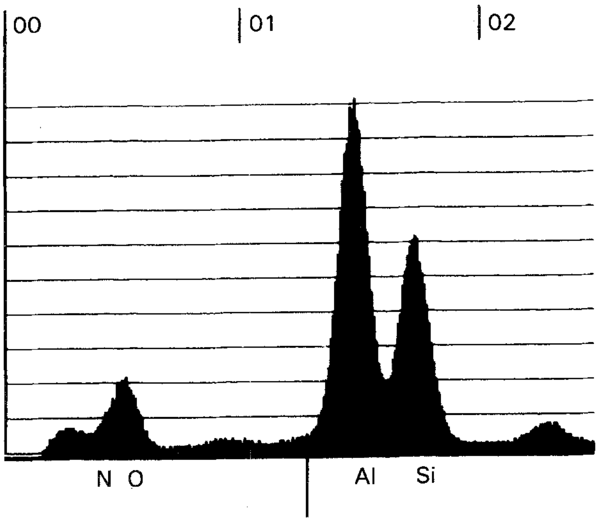
Figure 4 Histograms of ratios of (a) Al/Si, (b) O/N in sintered X-phase sialon.

duced grain sizes which, in turn, would guarantee superior mechanical properties. Therefore, it could be expected that further comminution of the starting powders of such relatively inexpensively produced sialon, and a tailoring of the sintering temperatures to suit the particle sizes, would lead to higher values of the mechanical properties of the sialon than those obtained in this study.

3.2. Compositional formula of X-phase sialon

Sintering of X-phase sialon is very sensitive to process parameters [13]. For example, an excessive porosity and 95% of the theoretical density of the sialon were obtained when the material was sintered either 15 °C above or below the optimal temperature for full densification. It was also shown that under given processing conditions the presence of 5 wt % transformable mullite in X-phase sialon leads to a 25 °C reduction in the sintering temperature, without even attaining a full densification of the sintered body. Consequently, it is highly desirable to minimize (or totally eliminate) the presence of other transformable crystalline materials, if a fully densified X-phase sialon material is to be obtained. Also, given the suggested narrowness of the domain of existence in the phase diagram, precise knowledge of the phase composition is essential if the sialon is to be produced with no additional crystalline phases.

Fig. 4 gives histograms of the weight ratios of aluminium to silicon, (Fig. 4a) and oxygen to nitrogen (Fig. 4b) obtained by sampling 30 grains of the milled sialon. Three of the 30 spectra and the energy values of the elements under study are shown in Fig. 5. The average value of the Al/Si ratio was found to be 1.5 ± 0.1, while the O/N was 3.1 ± 0.1. The EDAX spectra of the natural minerals used for standardization indicated that at the voltage used (100 KV) the

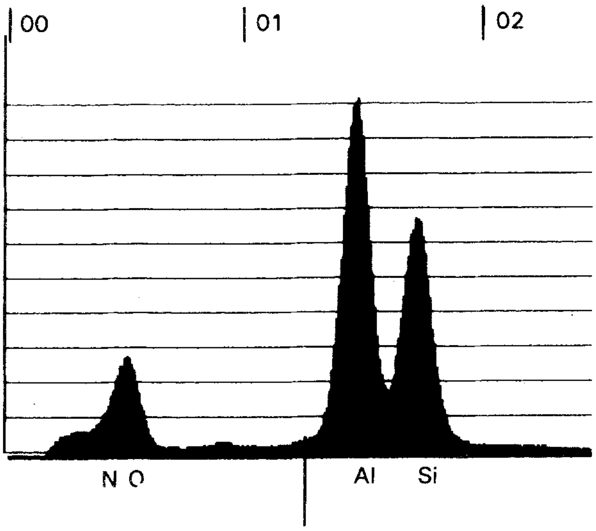


CURSOR (keV) = 01.280 EDAX

LIST :

ELEM	c.p.s.	BKGD	P/B
N K	29.575	12.950	2.284
O K	92.269	11.040	8.358
Al K	489.062	15.040	32.518
Si K	314.075	14.710	21.351

(a)

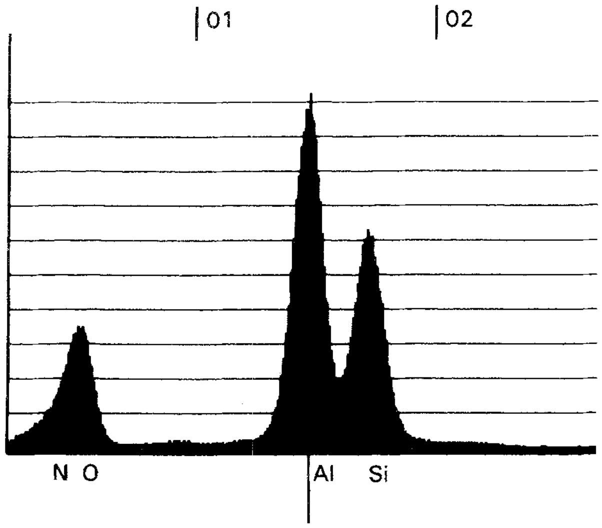


CURSOR (keV) = 01.260 EDAX

LIST :

ELEM	c.p.s.	BKGD	P/B
N K	74.472	39.809	1.871
O K	263.123	28.559	9.213
Al K	1073.350	45.079	23.811
Si K	750.949	46.059	16.304

(b)



CURSOR (keV) = 01.480 EDAX

LIST :

ELEM	c.p.s.	BKGD	P/B
N K	133.257	14.120	9.438
O K	338.391	17.590	19.238
Al K	1031.532	16.390	62.938
Si K	681.922	16.050	42.488

(c)

Figure 5(a–c) Typical EDAX spectra of sintered X-phase sialon from a lot of 30.

observed ratios of the elements of the minerals (aluminium, silicon and oxygen) were consistent with their composition, and therefore the Cliff–Lorimer factor, $K_{Al/Si}$, in the Equation below [12] is 1

$$C_{Al}/C_{Si} = K_{Al/Si}(I_{Al}/I_{Si}) \qquad (4)$$

C and I are respectively, the fractional weight composition and characteristic intensity of elements. Because the observed ratios of the standard samples were consistent with their formulae without any correction factor, and because the energy value of nitrogen is very close to that of oxygen it was assumed that the observed O/N ratio of the sample under study is consistent with the formula of the sialon.

The Al/Si ratio of the present work is consistent with those found by other workers [7, 9], but the O/N ratio is different. The formula, $Si_{12}Al_{18}O_{39}N_8$ proposed by Naik *et al.* [9] shows the O/N weight ratio to be 5.6, while that proposed by Bergman *et al.* [7] ($Si_{12}Al_{18}O_{36}N_{10}$) shows it to be 4.1. Their determinations were made on bulk samples, and Bergman *et al.* [7] did not obtain directly the analysis of nitrogen, but rather calculated what the value should be using the electroneutrality condition. Being bulk samples, some amorphous regions must also have been detected, hence leading to the high oxygen content. Owing to the high counts of aluminium and silicon, the effect of sampling would have more effect on O/N than as on Al/Si. Hence such amorphous regions should not affect the Al/Si ratio. Therefore the Al/Si ratio would still be left practically the same.

Let p, q, y and z represent the number of atoms of aluminium, silicon, oxygen and nitrogen respectively, in the formula, $Si_qAl_pO_yN_z$ of X-phase sialon. The observed Al/Si weight ratio of 1.5:1 dictates that

$$27p/28q = 1.5 \qquad (5)$$

Similarly, the O/N ratio leads to

$$16y/14z = 3.1 \qquad (6)$$

Let M represent the total number of atoms in a mole of the sialon. Hence

$$M = p + q + y + z \qquad (7)$$

The sum of the mole fractions of n elements (M_i, $i = 1, 2, \cdots, n$) should be equal to 1; that is

$$\sum_{i=1}^{n} M_i = 1 \tag{8}$$

The electroneutrality condition also demands that the cations balance the anions. Thus

$$3p + 4q = 2y + 3z \tag{9}$$

Hence the simplest formula that satisfies Equations 5–9 is $Si_4Al_6O_{11}N_4$. Considering silicon and nitrogen to be 1, the spread of Al/Si and O/N ratios between 1.35 and 1.85, and 2.5 and 3.85, respectively, can be understood as the statistical spread in analysis.

The milled sialon sample was observed to have a volume of glassy (amorphous) constituent of 13.6% ± 3.7%. Because the density of 3.01 $\mathrm{g\,cm^{-3}}$ achieved for this zero-porosity sample represents its theoretical value [10], it can be assumed that the glassy constituent has a density similar to that of X-phase owing to accommodation of impurities of the clay, from which the sialon was made (silica glass has a density of 2.65 $\mathrm{g\,cm^{-3}}$). Therefore, the volume percentage can be considered as a weight percentage of the glassy constituent in the composite of X-phase/glass. After compensating for the fraction of oxygen belonging to the glassy constituent, the inert gas fusion method showed an average O/N ratio of 2.5 ± 0.1. This value falls within the lower range of those observed by the EDAX analysis of the present work. It is therefore proposed that the formula for X-phase sialon is $Si_4Al_6O_{11}N_4$.

If the three formulae are used to design a carbothermal reduction/nitriding process for producing X-phase sialon from kaolinitic clays, the following equations are obtained for the formulae proposed in the present study, work by Bergman *et al.* [7] and the investigation by Naik *et al.* [9]

$$3(2SiO_2{\cdot}Al_2O_3) + 6C + 2N_2 \rightarrow Si_4Al_6O_{11}N_4 + 2SiO_2 + 6CO \tag{10}$$

$$9(2SiO_2{\cdot}Al_2O_3) + 15C + 5N_2 \rightarrow Si_{12}Al_{18}O_{36}N_{10} + 6SiO_2 + 15CO \tag{11}$$

and

$$9(2SiO_2{\cdot}Al_2O_3) + 12C + 4N_2 \rightarrow Si_{12}Al_{18}O_{39}N_8 + 6SiO_2 + 12CO \tag{12}$$

Equations 10–12 imply that 9.8 wt % C, 8.3 wt % C and 5.8 wt % C, respectively, would be required to produce X-phase sialon, each associated with 19 wt % silica for the formulae proposed here, $Si_{12}Al_{18}O_{36}N_{10}$ [7] and $Si_{12}Al_{18}O_{39}N_8$ [9]. The highest value of carbon indicated by the present formula is consistent with the observation in a previous work [8] by the present authors of the necessity for such amounts of carbon in a carbothermal reduction/nitriding process for the production of a material characterized by the appearance of X-phase as the only crystalline phase.

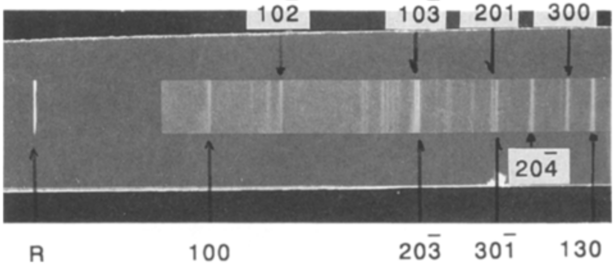


Figure 6 Low-angle section of an X-ray diffraction pattern of sintered X-phase sialon, partially indexed as triclinic with $a = 0.968$ nm, $b = 0.856$ nm, $c = 1.121$ nm, $\alpha = 91.4°$, $\beta = 124.4°$ and $\gamma = 99.2°$. R is the reference line.

As was observed in Fig. 3a, the fraction of silica-rich phase was about 13.6% ± 3.7%, which is less than the 19 wt % SiO_2 that the stoichiometric Equations 10–12 show. However, it is known that a part of the glassy phase may transform to other by-products of the process, an example being the traces of Si_3N_4 whiskers that precipitate at the relatively colder parts of the furnace atmosphere. Therefore, the amount of carbon in the stoichiometric equations represents the minimum levels required. It must also be stressed that processes designed on the basis of the other formulae are capable of giving X-phase sialon, but one or more other crystalline phases will also be present. With the formula, $Si_4Al_6O_{11}N_4$ proposed here, powders of X-phase sialon can be produced and sintered to full densification devoid of any other crystalline phase, Fig. 6.

4. Conclusions

The hardness and indentation fracture toughness of X-phase sialon, with about 13.6 wt % silica rich phase (glass) were found to be 11103 MPa and 3.3 MPa $m^{1/2}$, respectively. These values are comparable to those of a commercially pure mullite. More aggressive comminution processes, which give finer particles of the starting powder, and/or alternative routes of production with less silica-bearing raw materials may lead to higher values of these properties.

It is proposed that the formula for X-phase sialon is $Si_4Al_6O_{11}N_4$. With this formula the material can be produced devoid of any other crystalline phases, and thus its properties unambiguously assessed.

References

1. Y. OYAMA and K. KAMIGAITO, *Yogyo-Kyokai-Shi* **80** (1972) 327.
2. K. H. JACK, *Trans. J. Brit. Ceram. Soc.* **72** (1973) 376.
3. R. R. WILLS, R. W. STEWART and J. M. WIMMER, *Ceram. Bull.* **56** (2) (1977) 194.
4. C. YAMAGISHI, H. YOSHIDA, H. KAMAIKA, J. ASAUMI and N. MIYATA, *J. Jpn Soc. Powder Metall.* **37** (2) (1990) 187.
5. C. C. ANYA and A. HENDRY, *J. Eur. Ceram. Soc.*
6. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
7. B. BERGMAN, T. EKSTROM and A. MICSKI, *J. Eur. Ceram. Soc.* **8** (1991) 141.
8. C. C. ANYA and A. HENDRY, *ibid.* **10** (2) (1992) 65.
9. I. K. NAIK, L. J. GAUCKLER and T. Y. TIEN, *J. Am. Ceram. Soc.* **61** (7/8) (1978) 332.

10. D. P. THOMPSON and P. KORGUL, in "Progress in Nitrogen Ceramics", edited by F. L. Riley (Martinus Nijhoff, The Hague, The Netherlands 1983) p. 375.
11. A. W. J. M. RAE, D. P. THOMPSON and K. H. JACK, in "Ceramics for High Performance Applications", Vol II, edited by J. J. Burke, E. M. Lenoe and R. M. Katz, (Brookhill, Chestnut Hill, MA, 1978) p. 1039.
12. D. WILLIAMS, "Practical Analytical Electron Microscopy in Materials Science" (Verlag Chemie International, Philips Electronic Instruments, Deerfield Beach, FL, 1984) pp. 2, 67.
13. C. C. ANYA and A. HENDRY, *J. Eur. Ceram. Soc.* **12** (1993) 297.
14. S. PALMQVIST, *Arch. Eisenhuttenw.* **33** (1962) 629.
15. D. K. SHETTY, I. G. WRIGHT, P. N. MINCER and A. H. CLAUER, *J. Mater. Sci.* **20** (1985) 1873.
16. J. E. HILLIARD and J. W. CAHN, *Trans. TMS-AIME* **221** (1961) 344.
17. S. SOMIYA and Y. HIRATA, *Ceram. Bull.* **70** (1991) 1624.
18. T. VASILOS and W. RHODES, in "Sintering Key Papers", edited by S. Somiya and Y. Moriyoshi (Elsevier Applied Science, London, New York (1990) p. 741.

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