

# Mechanochemical processing of sialon compositions

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Received 1 March 2002; received in revised form 5 July 2002; accepted 14 July 2002

## Abstract

Milling for 48 h in a sealed planetary ball mill was found to facilitate sialon formation in mixtures of aluminium and silicon oxides and nitrides on further heating in nitrogen at 1200–1600 °C. <sup>27</sup>Al and <sup>29</sup>Si MAS NMR indicated that milling exerts more influence on the oxide components than on the nitrides. Substitution of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by Al(OH)<sub>3</sub> as the alumina source facilitated the mechanochemical formation of Si–O–Al bonds, as monitored by MAS NMR, but the subsequent thermal conversion of these precursors to stable aluminosilicates did not enhance sialon formation. Milled precursors of  $\beta$ -sialon composition formed a mixture of  $\beta$ , O and X-sialon, decomposing to polytypoid sialons at 1600 °C. Milled O-sialon precursors formed monophase O-sialon at 1600 °C, while some X-sialon compositions formed X-sialon at 1400 °C which decomposed to mullite and corundum at 1600 °C. A ground mixture of Ca  $\alpha$ -sialon composition formed  $\beta$ , O and X-sialons at 1600 °C, but no Ca sialon because of the depletion of Ca by the preferential formation of a Ca feldspar. Without milling, all these mixtures were unreactive, and generally did not form sialons on heating in nitrogen up to 1600 °C.

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**Keywords:** Mechanochemical processing; Milling; Phase development; Sialons; Sintering

## 1. Introduction

Sialons are silicon aluminium oxynitride ceramic materials with a range of technically important applications, from cutting tools to specialised refractories. Since they can have a wide range of compositions and occur in several different families of crystal structures, the properties of sialons can be tailored for specific purposes. The more commonly encountered forms of sialon are:

*$\beta$ -sialon*, Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub>, where  $z$  can have values from 0 (pure Si<sub>3</sub>N<sub>4</sub>) to about 4. These sialons are isostructural with  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.

*O-sialon*, Si<sub>2-x</sub>Al<sub>x</sub>O<sub>1+x</sub>N<sub>2-x</sub>, where  $x$  can have values from 0 (pure Si<sub>2</sub>N<sub>2</sub>O) to about 0.4. These sialons are isostructural with Si<sub>2</sub>N<sub>2</sub>O.

*X-sialon*, nominally Si<sub>12</sub>Al<sub>18</sub>O<sub>39</sub>N<sub>8</sub>. These sialons are isostructural with mullite, and can be regarded as solid solutions of mullite with Si<sub>3</sub>N<sub>4</sub>.

*$\alpha$ -sialons*, a series of phases isostructural with  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, which can be formed in the presence of stabilising metal ions such as Mg, Y or Ca.

Sialons can be synthesised by a number of routes, including carbothermal and silicothermal reactions of oxides and clay minerals,<sup>1–4</sup> and direct solid-state reaction of the oxide and nitride components under nitrogen. All these processes are energy-intensive, typically requiring temperatures of > 1400 °C for carbothermal and silicothermal reaction, and even higher temperatures for direct solid-state reaction.

The temperatures of solid-state reactions in a number of oxide systems can be lowered, in some cases by as much as 400 °C, by mechanochemical activation, i.e. milling or grinding of the reactant mixture in a high-energy ball mill. This procedure, which is also called mechanochemical alloying when applied to metallic powders, has been found to promote the reaction

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between  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ,<sup>5</sup>  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ ,<sup>6</sup>  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ ,<sup>7</sup>  $\text{SiO}_2$  and  $\text{MgO}$ ,<sup>8</sup> and in a number of other reactions including metal alloying.<sup>9</sup> In this paper the terms “high-energy milling” and “high-energy grinding” are used interchangeably to denote mechanochemical processing in a planetary ball mill. A theoretical consideration of the physical processes operating under mechanochemical conditions (friction, particle deformation, crack formation, comminution) has been given by Boldyrev,<sup>10</sup> while the chemical interactions of oxide and hydroxide surfaces during high-energy grinding have also been treated.<sup>11</sup> In addition to lowering the temperature of solid state reactions in oxide systems, mechanochemical processing offers the advantage of producing extremely homogeneous precursors which on thermal treatment can form fine-grained (down to nanosized) monophasic crystalline products without the need for multiple re-firings. The fine grain size of the crystalline product, which is marked contrast to the grain growth often found in solid-state reaction products, facilitates further processing such as sintering.

It would be of considerable interest to know whether the benefits of mechanochemical processing could be extended to the synthesis of oxynitrides such as sialons. Therefore the present survey study was undertaken of the effect of grinding on mixtures of  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$  formulated with the general composition of  $\beta$ -sialon ( $z=2$ ), O-sialon ( $x=0.2$ ), X-sialon and a calcium  $\alpha$ -sialon of nominal composition  $\text{Ca}_{0.75}\text{Al}_{2.25}\text{O}_{0.75}\text{N}_{15.25}$ . Since previous observations of oxide systems suggest that the presence of hydroxylated aluminium compounds such as gibbsite ( $\text{Al}(\text{OH})_3$ ) enhances the efficiency of mechanochemical reactions,<sup>12</sup> a parallel series of mixtures containing gibbsite as the aluminium oxide source was also investigated. The progress of the mechanochemical activation was monitored by XRD, but since high-energy grinding destroys the long-range order of many crystalline materials, solid state  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR was also used to determine structural changes<sup>13</sup> in the ground sialon precursors. The phases formed by heating these precursors in nitrogen at 1000–1600 °C were also determined, and compared with the products from the unground mixtures.

## 2. Experimental

The starting materials were  $\text{Si}_3\text{N}_4$  (UBE E-10),  $\text{SiO}_2$  (Snowsil superfine quartz, Commercial Minerals Ltd),  $\text{AlN}$  (A100, Advanced Refractories Technologies Inc., Buffalo, NY),  $\text{Al}(\text{OH})_3$  and  $\text{Ca}(\text{OH})_2$  (BDH reagent grade) and  $\gamma\text{-Al}_2\text{O}_3$  prepared by firing BDH  $\text{Al}(\text{OH})_3$  at 800 °C for 3.5 h. The mixtures for milling were batched according to the following stoichiometry:

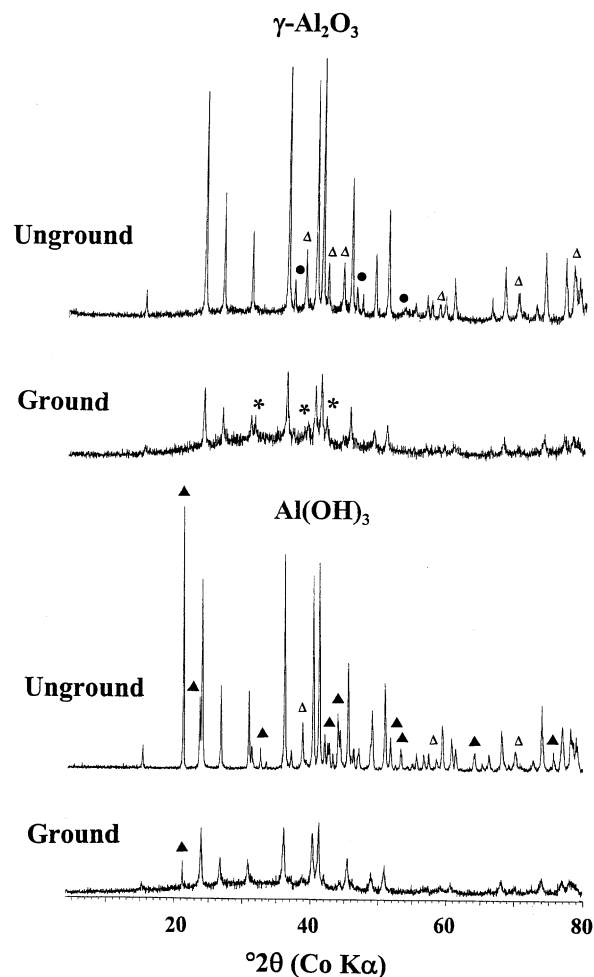
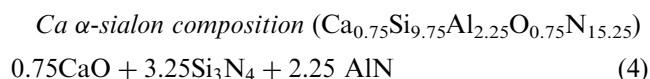
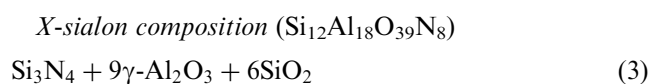
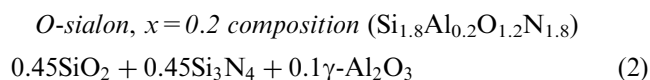
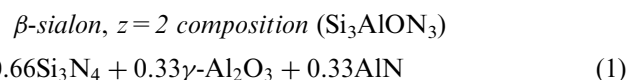


Fig. 1. X-ray diffractograms of ground and unground mixtures of  $\beta$ -sialon composition containing  $\gamma\text{-Al}_2\text{O}_3$  (upper) and  $\text{Al}(\text{OH})_3$  (lower) as the alumina source. Grinding time 48 h. All traces are plotted on the same intensity scale for comparison. Key: open triangles =  $\text{AlN}$ , filled circles =  $\gamma\text{-Al}_2\text{O}_3$ , asterisks =  $\beta\text{-Si}_3\text{N}_4$ , filled triangles =  $\text{Al}(\text{OH})_3$ . The unmarked peaks correspond to  $\alpha\text{-Si}_3\text{N}_4$ .

A parallel series of mixtures was also prepared in which the  $\gamma\text{-Al}_2\text{O}_3$  was replaced by  $\text{Al}(\text{OH})_3$ . 1-gram aliquots of the mixtures were weighed into a silicon nitride pot with 50 g of 2 mm silicon nitride milling balls and ground in an ITOH LA-Po.1 planetary mill at 400 rpm. The pot was sealed, allowing the self-generated grinding atmosphere to be retained, and the mill was stopped and allowed to cool for 10–15 min after each 3–4 h of grinding. In a preliminary experiment, grinding times of 2–48 h were used, and the results monitored by observing the progressive loss of the characteristic X-ray reflections of the crystalline starting materials. Based on these experiments, a grinding time of 48 h was chosen.

Simultaneous TG and DTA experiments were carried out in flowing nitrogen (50 ml/min) on 20 mg samples of the ground sialon precursors and the unground control samples at a heating rate of 10 °C/min using a Rigaku Thermoplus TG8120 thermal analyser. Small samples were also fired for 4 h in alumina boats in an electric

tube furnace in flowing oxygen-free nitrogen (50 ml/min) at 1000–1600 °C for examination by X-ray powder diffraction (Philips PW 1700 computer-controlled goniometer using Co K $\alpha$  radiation and a graphite monochromator).

The  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra of all the samples were acquired as follows:

$^{27}\text{Al}$  spectra were acquired at 11.7 T using a Varian Unity 500 MHz spectrometer and 5 mm. Doty MAS probe in which the sample was spun at 10–12 kHz. A 15° pulse of 1  $\mu\text{s}$  and a recycle time of 1 s were used. The  $^{27}\text{Al}$  spectra of some of the samples were also acquired at 14.1 T using a Chemagnetics Infinity 600 MHz spectrometer and a 3.2 mm probe in which the samples were spun at 18 kHz. A 15° pulse of 0.5  $\mu\text{s}$  and a recycle time of 1 s was used in this case, and the spectra were referenced using the secondary standard of the  $\text{AlO}_6$  resonance of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  at 0.7 ppm w.r.t.  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ .

The  $^{29}\text{Si}$  spectra were acquired at 11.7 T at an MAS spinning speed of 10 kHz using a 90° pulse of 6  $\mu\text{s}$  and a

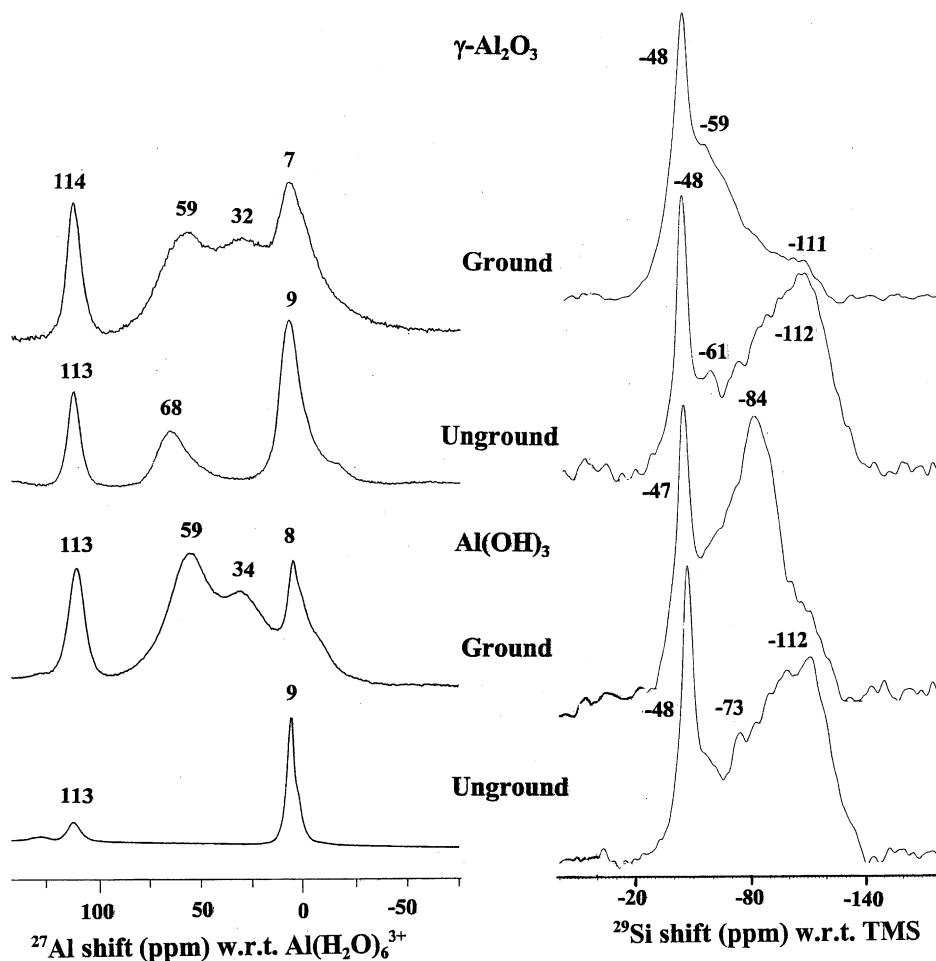


Fig. 2. 14.1 T  $^{27}\text{Al}$  and 11.7 T  $^{29}\text{Si}$  MAS NMR spectra of ground and unground mixtures of  $\beta$ -sialon composition containing  $\gamma\text{-Al}_2\text{O}_3$  (upper) and  $\text{Al}(\text{OH})_3$  (lower) as the alumina source. Grinding time 48 h.

recycle time of 100 s, and were referenced to tetramethylsilane (TMS).

### 3. Results and discussion

#### 3.1. Mixtures of $\beta$ -sialon composition

Fig. 1 shows a series of typical X-ray diffractograms of ground and unground  $\beta$ -sialon composition mixtures. These indicate that grinding for 48 h produces a significant loss of intensity from all the crystalline phases, especially AlN and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and an increase in the amorphous component, evidenced by pronounced curvature of the background. The ground mixture containing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed evidence of conversion of some of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> starting material to the  $\beta$ -form (indicated by asterisks), but this did not occur in the mixture containing gibbsite as the alumina source, suggesting that the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> does not arise from contamination by the milling media. The relatively long grinding times required in these experiments arise from the low density of the silicon nitride grinding media, chosen for its chemical similarity with the sample to avoid excessive contamination from the milling debris.

The 14.1 T <sup>27</sup>Al MAS NMR spectra of the ground and unground samples are shown in Fig. 2. The spectra of the unground samples are as expected, showing the peak of AlN at 113 ppm and the octahedral Al–O peak of Al(OH)<sub>3</sub> at 9 ppm (lower spectrum). The sample containing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> shows the expected tetrahedral and octahedral Al–O peaks at 68 and 9 ppm respectively.<sup>13,14</sup> Grinding has no effect on the AlN resonance, but produces new Al–O sites in the alumina component. The new resonances at 59 and 34 ppm are as expected when Al(OH)<sub>3</sub> is ground,<sup>15</sup> and the 32 ppm resonance (often attributed to five-coordinated Al–O) has also been observed to a lesser extent in ground  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>12</sup> The 11.7 T <sup>29</sup>Si MAS NMR spectra (Fig. 2) of the unground mixtures show that the Si–N resonance at –46 ppm is unchanged by grinding, but the Si–O resonance at –112 to –115 ppm is more affected, being reduced in intensity by conversion into other Si–O phases [Si–O–N at –59 ppm in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-containing mixture and Si–O–Al at about –90 ppm in the mixture containing Al(OH)<sub>3</sub>]. The latter result is consistent with the known reactivity of gibbsite with silica under mechanochemical conditions.<sup>12</sup> Thus, the NMR spectra indicate that the nitrogen-containing components of these mixtures are relatively unaffected by grinding, but the oxygen-containing components enter into aluminosilicate or oxynitride environments, depending on the relative hydroxyl concentrations of the starting materials.

##### 3.1.1. Effect of heating these precursors in nitrogen

Typical thermal analysis curves for the ground and unground  $\beta$ -sialon compositions heated in flowing

nitrogen are shown in Fig. 3. In compositions containing both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al(OH)<sub>3</sub>, grinding produces a new DTA endotherm at about 1000 °C typically associated with the formation of an aluminosilicate phase. Grinding also significantly reduces the intensity of the endothermic dehydroxylation event in the Al(OH)<sub>3</sub>-containing sample, rendering the associated weight loss smaller and much less abrupt. In this respect, grinding affects the thermal behaviour of the alumina-containing component of the mixture as expected from previous mechanochemical experiments on gibbsite.<sup>15</sup> Weight gains due to the uptake of nitrogen are observed > 1000 °C in the TG curves of all the samples, but in the ground mixtures, especially that containing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the onset of nitridation is about 130 °C lower than in the corresponding unground sample, probably due to the increased gas-solid reactivity of the smaller particles. The nitridation weight gain continues beyond the temperature limit of the present apparatus and, as was found in the subsequent static heating experiments, many of the reactions in these samples occur > 1400 °C.

The phases detectable by XRD in the samples of  $\beta$ -sialon composition heated for 4 h in flowing nitrogen are shown semi-schematically in Fig. 4. It is seen that

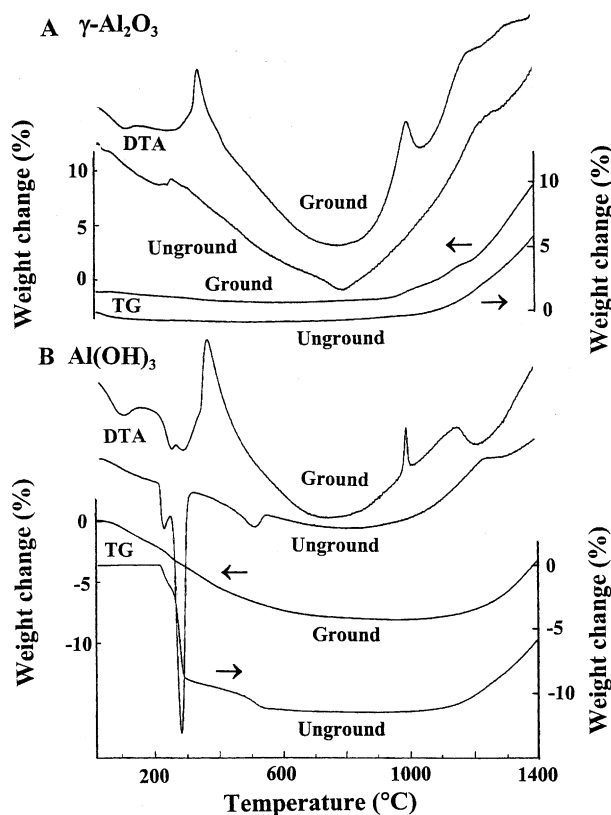


Fig. 3. Thermal analysis curves of unground and ground mixtures of  $\beta$ -sialon composition in flowing nitrogen (50 ml min<sup>-1</sup>). Sample mass 15–20 mg, heating rate 10 °C min<sup>-1</sup>.

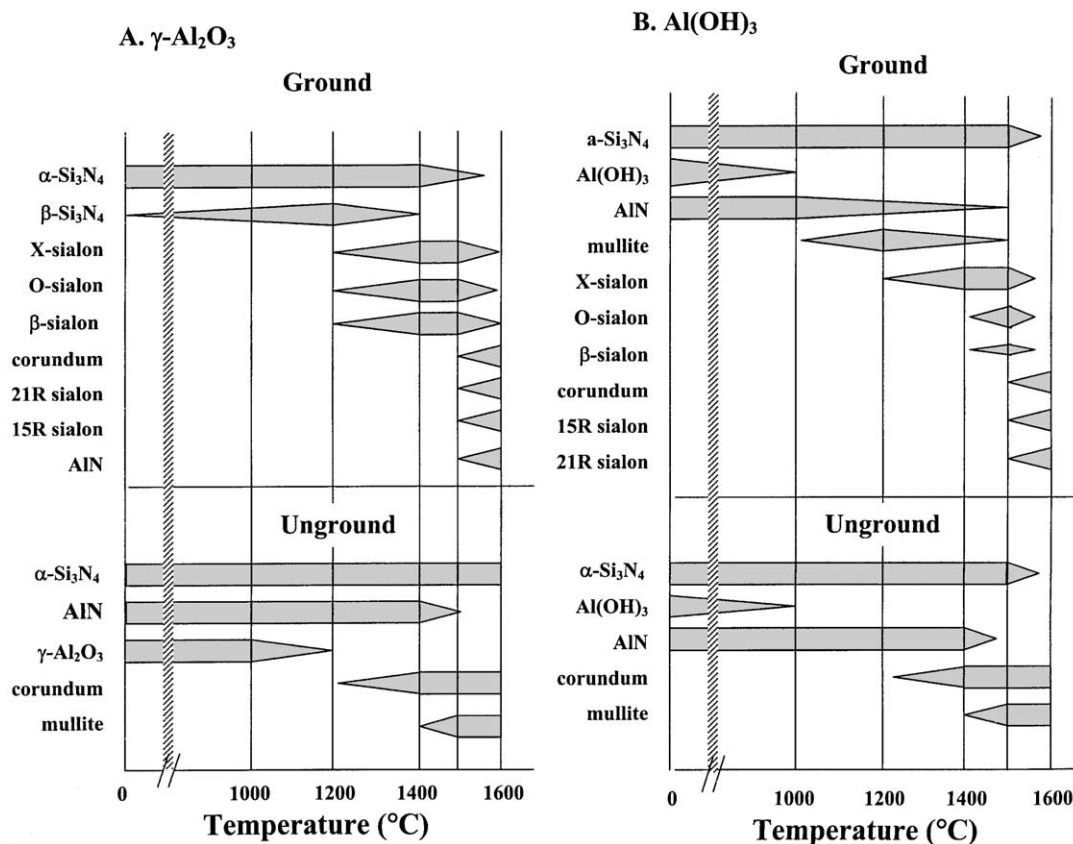


Fig. 4. Semi-schematic representation of the crystalline phases formed as a function of temperature in ground and unground mixtures of  $\beta$ -sialon composition heated in flowing nitrogen ( $50 \text{ ml min}^{-1}$ ) for 4 h.

very little reaction occurs under these conditions in the unground mixtures until  $1500\text{--}1600 \text{ }^\circ\text{C}$ , when  $\alpha\text{-Al}_2\text{O}_3$  (corundum) and mullite appear, the silica source for the latter arising from surface oxidation of  $\text{Si}_3\text{N}_4$ . By contrast, the ground samples form mixtures of sialons, including  $\beta$ -sialon, which, together with X-sialon and O-sialon, is converted to polytypoid sialons (15R, 21R) at  $1600 \text{ }^\circ\text{C}$ . The sample containing  $\text{Al}(\text{OH})_3$  as the alumina source forms mullite at  $1200 \text{ }^\circ\text{C}$ , reflecting the enhanced formation of Al–O–Si bonds during grinding. This result is consistent with previous observations<sup>5</sup> that mullite formation from mechanochemically-processed alumina–silica mixtures is enhanced when the alumina source contains hydroxyl groups, as in  $\text{Al}(\text{OH})_3$ . The mullite formed in the present mixtures is transitory, however, probably reacting with the  $\text{Si}_3\text{N}_4$  present to form X-sialon. Thus, in these mixtures, grinding facilitates sialon formation at least  $200 \text{ }^\circ\text{C}$  lower than in the corresponding unground samples, but the products are a mixture of sialon phases rather than monophase  $\beta$ -sialon.

These XRD results are confirmed by the  $^{27}\text{Al}$  MAS NMR spectra (not shown), which enable the Al environments of the various phases to be distinguished by

their characteristic spectral signatures. Thus, in the unground mixture containing  $\gamma\text{-Al}_2\text{O}_3$ , the continued presence of Al–N bonds throughout the heating process is confirmed by the Al–N resonance at 113 ppm, while the tetrahedral/octahedral Al signature of  $\gamma\text{-Al}_2\text{O}_3$  is replaced at  $1400 \text{ }^\circ\text{C}$  by the sharp octahedral peak of corundum at 13 ppm. At  $1500 \text{ }^\circ\text{C}$  the characteristic  $^{27}\text{Al}$  NMR spectrum of mullite appears, consisting of an octahedral resonance and a square-topped tetrahedral peak containing unresolved contributions from normal tetrahedral sites (ca. 66 ppm) and from tricluster sites (ca. 43 ppm).<sup>16</sup> By contrast, the  $^{27}\text{Al}$  NMR spectra of the heated ground mixtures containing  $\gamma\text{-Al}_2\text{O}_3$  show additional features not apparent from the X-ray results, particularly with respect to the Al–N resonance. This peak progressively decreases, disappearing at  $1500 \text{ }^\circ\text{C}$  only to reappear at  $1600 \text{ }^\circ\text{C}$ , possibly as part of the polytypoid sialon signature which also contains a weak, broad octahedral peak,<sup>17,18</sup> but more likely as pure AlN, shown by XRD to form at  $1600 \text{ }^\circ\text{C}$  (Fig. 4). The presence of the Al–N resonance below  $1400 \text{ }^\circ\text{C}$  is not readily explicable; it is probably not associated with precursors to the O- or X-sialon crystallising at  $1500 \text{ }^\circ\text{C}$ , since these phases contain only tetrahedral and octahe-

dral Al–O resonances.<sup>3,19</sup> Although the  $^{27}\text{Al}$  NMR spectrum of  $\beta$ -sialon can contain an Al–N resonance, this is shifted to ca. 110 ppm by the presence of adjacent oxygen atoms;<sup>15</sup> furthermore, the disappearance of the Al–N peak at 1500 °C, the temperature  $\beta$ -sialon appears in these samples, suggests that the 114 ppm Al–N peak is not associated with a  $\beta$ -sialon precursor. Thus, the most likely explanation is that this resonance arises from pure Al–N, which, although amorphised by grinding, retains its atomic environment which is thermally stable. Another feature of the thermal reactions of this ground mixture is the appearance at 1200 °C of the characteristic corundum resonance at 13 ppm, progressively increasing in intensity with heating temperature. This result indicates the establishment of a corundum-like  $\text{AlO}_6$  environment long before the appearance of crystalline corundum at 1600 °C. A similar result was observed in the  $^{27}\text{Al}$  NMR spectra of the heated  $\beta$ -sialon mixture containing  $\text{Al}(\text{OH})_3$  as the alumina source, in which a resonance at 13 ppm was detected at 1200 °C, with an abrupt intensity increase upon the appearance of crystalline corundum at 1600 °C. In all other respects, the spectra of this mixture, both ground and unground, were consistent with the XRD result.

The  $^{29}\text{Si}$  NMR spectra of the heated unground samples of  $\beta$ -sialon composition confirm the X-ray results, remaining largely unchanged at all temperatures. The predominant resonances in all these spectra are those characteristic of Si–N and Si–O (–48 and –112 ppm respectively). Additional spectral intensity between these extremes indicates the presence of Si–O–N units of varying composition,<sup>20</sup> while at higher temperatures, the growth of a Si–O–Al resonance at ca. –86 ppm as found in mullite<sup>16</sup> indicates the formation of aluminosilicate units. The  $^{29}\text{Si}$  NMR spectra of the ground samples confirm the persistence of Si–N and various Si–O–N bonds throughout the temperature range, and the abrupt appearance of O-sialon at 1400–1500 °C is evidenced by the resonance at 62 ppm. A broad major resonance in the  $\gamma$ - $\text{Al}_2\text{O}_3$ -containing mixture between –87 and –115 ppm which becomes prominent at 1500–1600 °C indicates the presence of aluminosilicate and silica species, which, not being detected by XRD, must be X-ray amorphous. A similar resonance at –88 ppm in the mixture containing  $\text{Al}(\text{OH})_3$  heated at 1200–1400 °C arises from mullite which in this case is sufficiently crystalline to be detected by XRD, due to the more efficient mechanochemical processing of this mixture.

### 3.2. Mixtures of O-sialon composition

The X-ray diffractograms of ground and unground mixtures of O-sialon composition are shown in Fig. 5. As with the  $\beta$ -sialon compositions, grinding significantly

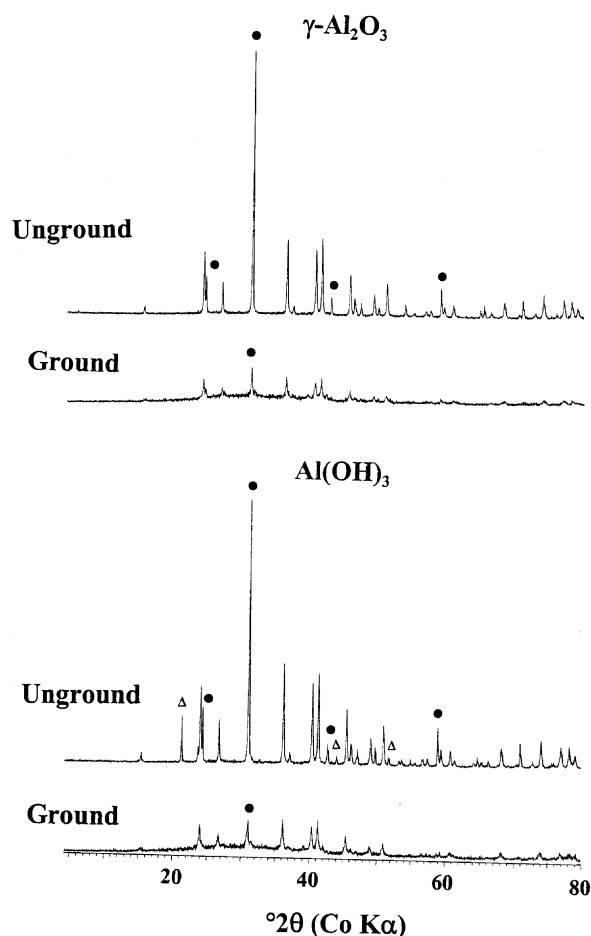


Fig. 5. X-ray diffractograms of ground and unground mixtures of O-sialon composition containing  $\gamma$ - $\text{Al}_2\text{O}_3$  (upper) and  $\text{Al}(\text{OH})_3$  (lower). Grinding time 48 h. All traces are plotted on the same intensity scale. Key: filled circles = quartz, open triangles =  $\text{Al}(\text{OH})_3$ . The unmarked peaks correspond to  $\alpha$ - $\text{Si}_3\text{N}_4$ .

reduces the intensity of all the X-ray peaks, especially those of  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{Al}(\text{OH})_3$ , the latter being destroyed completely by grinding. The mechanochemical treatment produces no new phases in these mixtures, but the curvature of the X-ray background indicates the formation of amorphous material by grinding.

The  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra of these samples are shown in Fig. 6. The  $^{27}\text{Al}$  spectra of the unground mixtures are as expected for the two different Al sources, containing the typical octahedral and tetrahedral resonances of  $\gamma$ - $\text{Al}_2\text{O}_3$  at 8 and 67 ppm respectively, or the octahedral resonance of  $\text{Al}(\text{OH})_3$  of gibbsite at 8–9 ppm. Grinding brings about the appearance of a new tetrahedral Al resonance at 56 ppm in both mixtures, with additional broad, unresolved intensity appearing in the vicinity of 30 ppm. The  $^{29}\text{Si}$  spectra all show the Si–N resonance at about –48 ppm which is unchanged by grinding, but the position of the Si–O resonance at

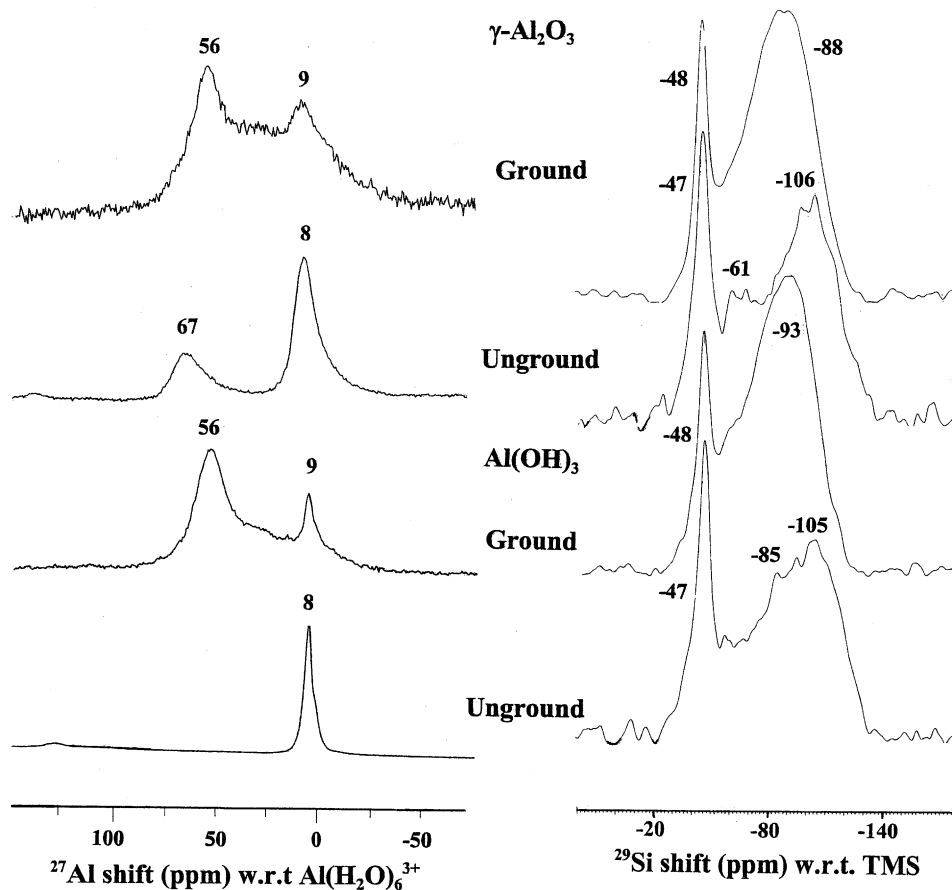


Fig. 6. 14.1 T  $^{27}\text{Al}$  and 11.7 T  $^{29}\text{Si}$  MAS NMR spectra of ground and unground mixtures of O-sialon composition containing  $\gamma\text{-Al}_2\text{O}_3$  (upper) and  $\text{Al}(\text{OH})_3$  (lower) as the alumina source. Grinding time 48 h.

about  $-106$  ppm is shifted in both mixtures to  $-88$  to  $-93$  ppm by grinding, reflecting the formation of a proportion of Si–O–Al bonds. The changes in the NMR spectra of these mixtures on grinding are thus similar to those found in the  $\beta$ -sialon mixtures, but less marked, being masked by the greater concentration of silica in the O-sialon mixtures.

### 3.2.1. Effect of heating these precursors in nitrogen

The thermal analysis curves of these samples heated in flowing nitrogen (not shown) display similar features to Fig. 3, particularly with respect to the uptake of nitrogen, which begins at lower temperatures and occurs less abruptly in the ground samples. The crystalline phases formed on heating the O-sialon mixtures for 4 h in flowing nitrogen are shown semi-schematically in Fig. 7.

Again, both unground mixtures are rather unreactive, but reflect their higher silica content in the retention of quartz and  $\alpha\text{-Si}_3\text{N}_4$  and the formation of cristobalite and  $\beta\text{-Si}_3\text{N}_4$  at  $1500\text{--}1600$  °C. A small amount of

X-sialon was formed at  $1600$  °C in the mixture containing  $\gamma\text{-Al}_2\text{O}_3$ , but the Al-rich phases in the gibbsite-containing mixture were corundum and AlN. The thermal behaviour of the ground mixtures is very different; both form X-sialon as a transitory phase at  $1400$  °C, but O-sialon is the sole phase present at  $1600$  °C. The formation of O-sialon is preceded in the ground gibbsite-containing mixture by the transitory appearance of the low-temperature O''-form.<sup>21</sup> The X-ray diffractogram of the gibbsite-containing mixture is also characterised by the persistence over a wide temperature range ( $1000\text{--}1400$  °C) of a curved baseline corresponding to X-ray amorphous phases. These results indicate that grinding is effective in causing mixtures of O-sialon composition to form monophase O-sialon at  $1600$  °C, whereas without grinding, these mixtures are relatively unreactive.

These XRD results are in general consistent with the  $^{27}\text{Al}$  NMR spectra of the heated samples, apart from the behaviour of a resonance at 13 ppm associated with an octahedral Al–O similar to that found in  $\alpha\text{-Al}_2\text{O}_3$

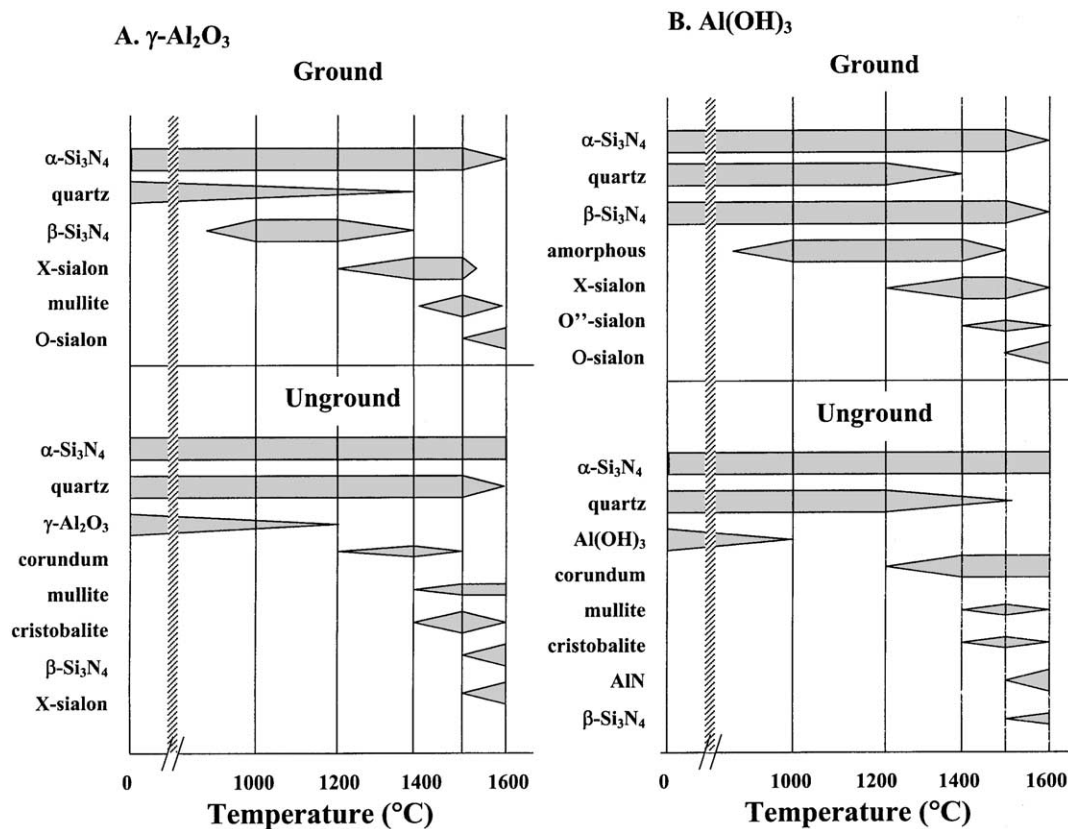


Fig. 7. Semi-schematic representation of the crystalline phases formed as a function of temperature in ground and unground mixtures of O-sialon composition heated in flowing nitrogen ( $50 \text{ ml min}^{-1}$ ) for 4 h.

(corundum). As in the ground mixtures of  $\beta$ -sialon composition, this peak appears and increases in intensity in the ground O-sialon compositions in samples showing no corundum XRD pattern [the  $\gamma$ - $\text{Al}_2\text{O}_3$ -containing samples heated at  $1500$ – $1600$  °C and the  $\text{Al}(\text{OH})_3$ -containing samples heated at  $1200$ – $1600$  °C]. This corundum-like Al environment appears to result from the thermal decomposition of the  $\gamma$ - $\text{Al}_2\text{O}_3$  present either as a reactant or as the intermediate decomposition product of  $\text{Al}(\text{OH})_3$ . Its formation in the present systems seems to be facilitated by grinding, especially in the presence of hydroxyl groups, in which samples it may be associated with a significantly increased X-ray amorphous phase observed over the same temperature range (Fig. 7B).

The  $^{29}\text{Si}$  NMR spectra of the heated unground mixtures (not shown) indicate the predominant presence of both Si–N and Si–O species over the whole temperature range. The Si–O resonances are more intense at the lower temperatures, whereas the Si–N resonance becomes more significant as nitridation proceeds at higher temperatures, at which spectral intensity characteristic of Si–O–Al units also develops. These findings are consistent with the XRD results. By contrast, the

ground samples initially show evidence of Si–O–Al formation. As was also observed in the ground  $\beta$ -sialon mixtures, the aluminosilicate species formed by grinding essentially disappear on heating at  $1000$  °C, but gradually reappear as X-sialon forms at higher temperatures. The Si–N units in the unheated mixture remain significant up to ca.  $1500$  °C, but are replaced at  $1600$  °C by the Si–O–N resonance characteristic of O-sialon.

### 3.3. Mixtures of X-sialon composition

The X-ray diffractograms of unground and ground mixtures of X-sialon composition are shown in Fig. 8. Grinding significantly reduces the X-ray intensity of all the crystalline components, especially in the mixture containing  $\gamma$ - $\text{Al}_2\text{O}_3$ , in which much of the  $\alpha$ - $\text{Si}_3\text{N}_4$  has also been converted to the  $\beta$ -form by grinding. Destruction of the crystalline lattices appears to have been slightly less efficient in the mixture containing  $\text{Al}(\text{OH})_3$ , and no  $\beta$ - $\text{Si}_3\text{N}_4$  was formed in this mixture. The MAS NMR spectra of the unground and ground mixtures (Fig. 9) show that grinding is efficient in forming new  $^{27}\text{Al}$  resonances at  $53$ – $63$  and  $32$ – $34$  ppm, corresponding to 4- and possibly 5-coordinated Al–O



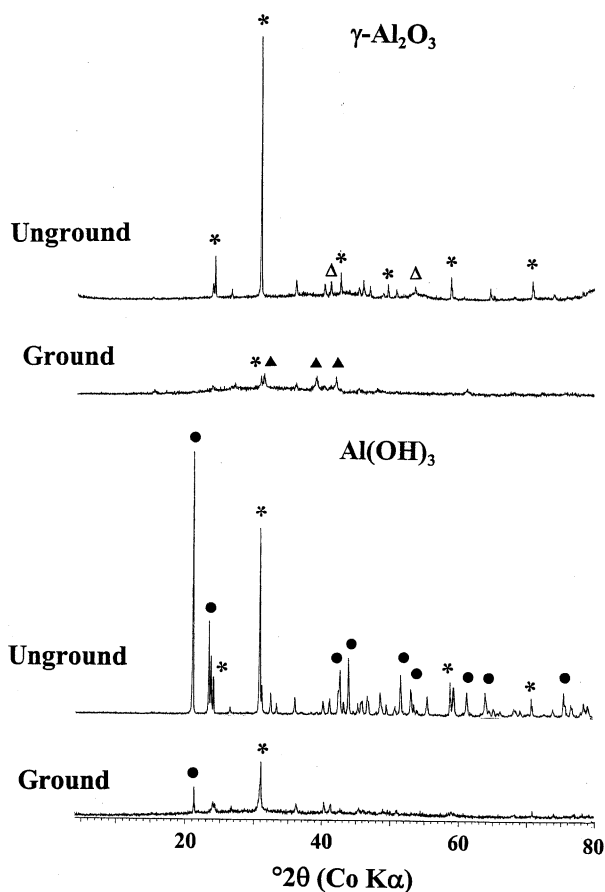


Fig. 8. X-ray diffractograms of ground and unground mixtures of X-sialon composition containing  $\gamma\text{-Al}_2\text{O}_3$  (upper) and  $\text{Al}(\text{OH})_3$  (lower). Grinding time 48 h. All traces are plotted on the same intensity scale. Key: asterisks = quartz, open triangles =  $\text{AlN}$ , filled triangles =  $\beta\text{-Si}_3\text{N}_4$ , filled circles =  $\text{Al}(\text{OH})_3$ . The unmarked peaks correspond to  $\alpha\text{-Si}_3\text{N}_4$ .

species respectively. The formation of the latter is particularly marked in the mixture containing  $\gamma\text{-Al}_2\text{O}_3$ . The formation of Al–O–Si bonds in both mixtures on grinding is confirmed by the loss of the  $^{29}\text{Si}$  Si–O resonance at about  $-106$  to  $-109$  ppm and the appearance of a major new resonance at  $-83$  to  $-87$  ppm. The NMR results confirm the XRD observation that the grinding was apparently more efficient in the mixture containing  $\gamma\text{-Al}_2\text{O}_3$  as the alumina source, contrary to findings for mechanochemically treated Al and Si pure oxide systems<sup>5</sup> in which the presence of structural hydroxide groups as in gibbsite produces more homogeneous ceramic precursors.

### 3.3.1. Effect of heating these precursors in nitrogen

The thermal analysis curves of the mixtures of X-sialon composition heated in nitrogen (not shown) show

similar features to those of the  $\beta$ - and O-sialon mixtures, indicating the exothermic formation of mullite at about  $1000$  °C in the ground samples. This feature was not seen in the unground samples, which however contained a smaller broader exotherm at about  $1280$  °C probably related to mullite formation. A lowered onset temperature for nitrogen uptake was again observed in the ground mixture originally containing  $\gamma\text{-Al}_2\text{O}_3$ , but this effect was less evident in the sample originally containing gibbsite.

The crystalline phases detected by XRD in the ground and unground mixtures of X-sialon composition heated in flowing nitrogen for 4 h are shown semi-schematically in Fig. 10. Mullite was formed at higher temperatures in both the unground mixtures, but there was no evidence of its reaction with  $\text{Si}_3\text{N}_4$  to form X-sialon even at  $1600$  °C, although other sialons ( $\beta$  and 15R polytypoid forms) were detected at  $1600$  °C in the unground gibbsite-containing mixture. By contrast, mullite was present in both ground mixtures at  $1000$ – $1200$  °C, reacting at  $1400$  °C with the  $\text{Si}_3\text{N}_4$  present to form X-sialon in the mixture originally containing  $\gamma\text{-Al}_2\text{O}_3$ . Although both mullite and  $\alpha\text{-Si}_3\text{N}_4$  were present in the ground mixture originally containing gibbsite, X-sialon did not form in this case, possibly due to the lower homogeneity of this precursor (as judged from the  $^{27}\text{Al}$  NMR spectra). Alternatively, the presence of  $\beta\text{-Si}_3\text{N}_4$ , produced in the mixture originally containing  $\gamma\text{-Al}_2\text{O}_3$  by grinding, may be necessary for the formation of X-sialon. The X-sialon formed in the ground mixture containing  $\gamma\text{-Al}_2\text{O}_3$  decomposed above  $1500$  °C.

As was found for the mixtures of  $\beta$ - and O-sialon composition, the  $^{27}\text{Al}$  NMR spectra of the heated ground and unground samples of X-sialon composition were consistent with the XRD results in all respects apart from the appearance of a corundum-like  $^{27}\text{Al}$  peak at 13 ppm at  $1200$ – $1600$  °C in the ground  $\gamma\text{-Al}_2\text{O}_3$ -containing samples, and at  $1200$ – $1400$  °C in the ground  $\text{Al}(\text{OH})_3$ -containing samples, although no crystalline corundum was detected by XRD. Since this behaviour is displayed consistently by the ground samples, it may arise from lattice distortions introduced by grinding which facilitate thermal decomposition of the alumina component at temperatures too low for crystallisation of corundum.

The  $^{29}\text{Si}$  NMR spectra of the unground mixtures (not shown) indicate a predominance of Si–O species, with smaller amounts of Si–N and Si–O–N also present. Si–O remains dominant over the whole range of heating temperatures up to  $1600$  °C, at which temperature the characteristic Si–O–Al resonance becomes more important. The lack of intensity corresponding to the various Si–O–N units characteristic of X-sialon<sup>3,20</sup> confirms the absence of significant sialon formation in these mixtures even at the highest temperatures. By contrast, the  $^{29}\text{Si}$  spectra of the ground samples are dominated by spectral

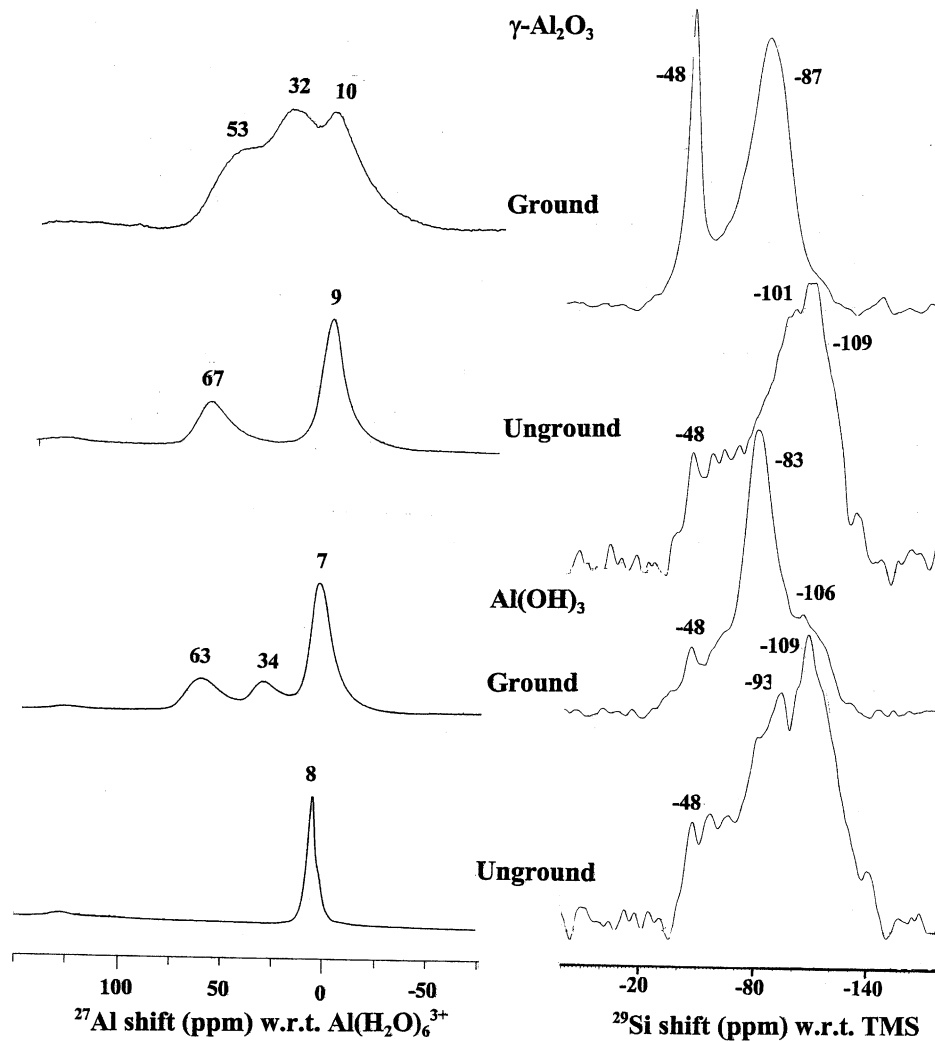


Fig. 9. 14.1 T  $^{27}\text{Al}$  and 11.7 T  $^{29}\text{Si}$  MAS NMR spectra of ground and unground mixtures of X-sialon composition containing  $\gamma\text{-Al}_2\text{O}_3$  (upper) and  $\text{Al}(\text{OH})_3$  (lower) as the alumina source. Grinding time 48 h.

intensity in the Si–O–Al region, with a smaller amount of Si–N. At an early stage in the heating, the Si–O resonance becomes more intense, but the intensity in the Si–O–Al region is regained on heating to higher temperatures, with the concomitant appearance of the various other Si–O–N groups characteristic of X-sialon.<sup>3,20</sup> These results are generally consistent with the XRD conclusions that mullite formation at an early stage of heating and its subsequent reaction with  $\text{Si}_3\text{N}_4$  is facilitated by grinding.

### 3.4. Mixture of Ca $\alpha$ -sialon composition

The effect on the X-ray diffractogram of grinding this mixture is shown in Fig. 11A. The intensity of all the XRD peaks is decreased by grinding, but only those of

the  $\text{Ca}(\text{OH})_2$  (portlandite) used here as the calcium source were completely destroyed. The formation of a significant amount of X-ray amorphous material is indicated by the curvature of the X-ray diffraction background. The NMR spectra (Fig. 11B) suggest that grinding this mixture has little or no effect on either the Al–N or Si–N bonds present, judged from the  $^{27}\text{Al}$  Al–N resonance at 114 ppm and the  $^{29}\text{Si}$  Si–N resonance at about  $-48$  ppm. Grinding does however produce a new tetrahedral Al resonance at 60 ppm and the replacement in the  $^{29}\text{Si}$  spectrum of the Si–O resonance at  $-112$  ppm by a broad Al–O–Si feature at  $-83$  ppm and a Si–O–N feature at  $-60$  ppm. These results indicate that, as with the other sialon compositions, grinding has a greater influence of the oxide components than the nitride components.

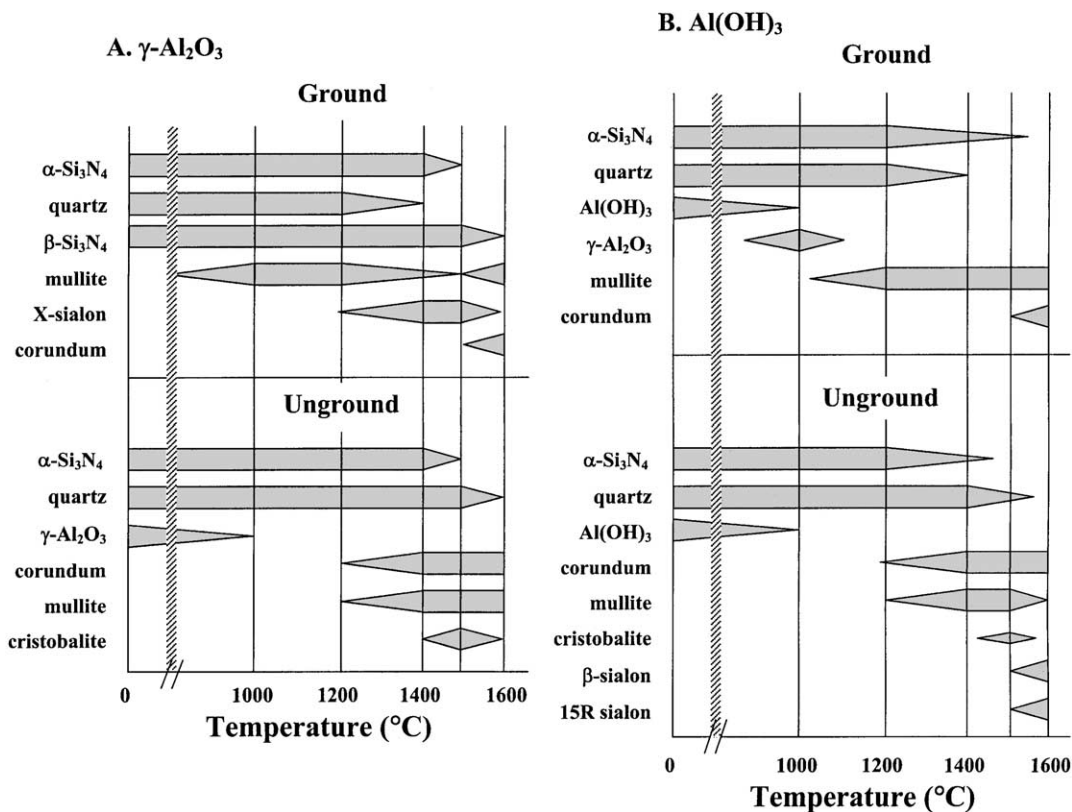


Fig. 10. Semi-schematic representation of the crystalline phases formed as a function of temperature in ground and unground mixtures of X-sialon composition heated in flowing nitrogen ( $50 \text{ ml min}^{-1}$ ) for 4 h.

### 3.4.1. Effect of heating these precursors in nitrogen

The thermal analysis curves of this mixture heated in nitrogen (not shown) indicate that grinding exerts a significant influence on the thermal behaviour of the  $\text{Ca}(\text{OH})_2$  component, replacing its sharp dehydroxylation endotherm at about  $400^\circ\text{C}$  with a broader feature at about  $650^\circ\text{C}$ . The associated mass loss in the ground sample is also more gel-like, extending from about  $570$  to  $690^\circ\text{C}$ . The similarity between this result and that for ground gibbsite suggest that this behaviour might be common to inorganic hydroxides. The onset temperature of nitrogen uptake by these samples was only slightly lowered by grinding, but the amount of uptake up to  $1400^\circ\text{C}$  was significantly less in the ground sample. The DTA curves of both the ground and unground samples showed evidence of melting at about  $1400^\circ\text{C}$ .

The crystalline phases detectable by XRD in the ground and unground mixtures heated in nitrogen for 4 h are shown semi-schematically as a function of temperature in Fig. 12. The unground mixture showed little sign of reaction up to  $1400^\circ\text{C}$ , apart from the formation of small amounts of mullite and an unidentifiable phase, possibly a calcian feldspar. By contrast, the ground sample formed a mixture of sialon phases (but not Ca

$\alpha$ -sialon) at  $1400^\circ\text{C}$ . The lack of a Ca sialon phase appears to be due to the preferential formation of calcian albite (PDF no. 20–548), effectively removing the calcium source from the system. Thus, although in this and the other sialon compositions, grinding is effective in promoting sialon formation by producing precursors which are homogeneous at least in their oxide regions, if the grinding is too effective in facilitating the formation of a stable oxide compound, further reaction to form a desired oxynitride may be hindered. This appears to be the case with the Ca  $\alpha$ -sialon mixture.

The  $^{27}\text{Al}$  NMR spectra of the heated unground samples are consistent with the XRD results in retaining the AlN resonance at 114 ppm throughout, but the appearance at  $1400^\circ\text{C}$  of a strong, broad tetrahedral peak together with a trace of a broad octahedral feature and a sharper peak at ca 12 ppm cannot be explained in terms of the mullite which is the sole crystalline oxygen-containing phase at  $1400^\circ\text{C}$  (Fig. 12). This spectrum suggests the presence of an incipient feldspar phase containing predominantly tetrahedral Al. Crystallisation of this compound could not however be verified because the unground sample melted  $>1400^\circ\text{C}$ , but a similar tetrahedral resonance was found to accompany

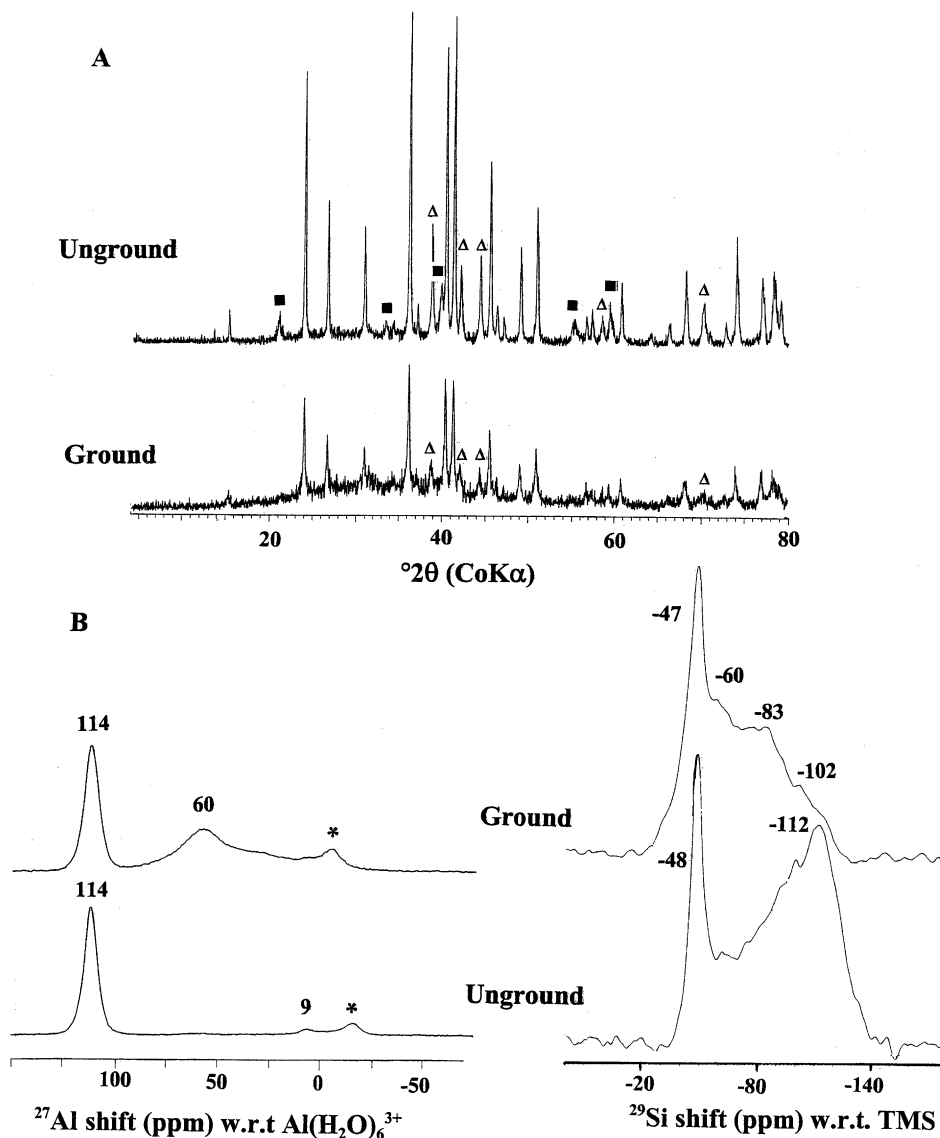


Fig. 11. A. X-ray diffractograms of ground and unground mixtures of Ca  $\alpha$ -sialon composition. Grinding time 48 h. All traces are plotted on the same intensity scale. Key: open triangles = AlN, filled squares = Ca(OH) $_2$ . The unmarked peaks correspond to  $\alpha$ -Si $_3$ N $_4$ . B. 14.1 T  $^{27}\text{Al}$  and 11.7 T  $^{29}\text{Si}$  MAS NMR spectra of ground and unground mixtures of Ca  $\alpha$ -sialon composition. The asterisks denote spinning sidebands.

the formation of crystalline calcian albite at 1200 °C in the corresponding ground sample. The sialon phases formed at 1400 °C in the ground sample will contain both tetrahedral and octahedral Al, but the size of the small octahedral Al peak in the 1400 °C spectrum suggests that these phases contribute only a small proportion of the tetrahedral peak intensity.

The  $^{29}\text{Si}$  NMR spectra of the heated unground mixture (not shown) indicate that of the Si–N and Si–O resonances originally present, the latter is progressively replaced in the early stage of heating by Si–O–Al species possibly associated with an unidentified feldspar. The spectra of the ground mixture also contain pre-

dominantly Si–N prior to heating, which is replaced by the Si–O–N units of O-sialon at 1200 °C. These Si–O–N species persist up to 1400 °C. Thus, the NMR spectra have provided detailed information about the appearance and disappearance of the various structural units during the grinding and heating processes in all the sialon mixtures.

#### 4. Conclusions

Mixtures of silicon and aluminium nitrides and oxides with stoichiometry corresponding to  $\beta$ , O, X and Ca

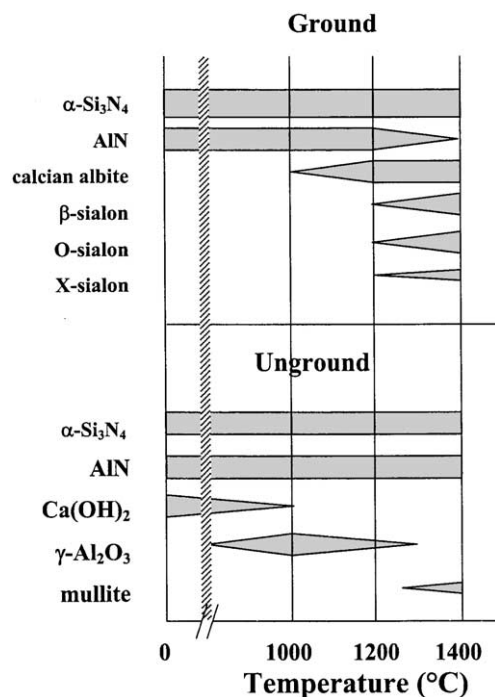


Fig. 12. Semi-schematic representation of the crystalline phases formed as a function of temperature in ground and unground mixtures of Ca  $\alpha$ -sialon composition heated in flowing nitrogen ( $50 \text{ ml min}^{-1}$ ) for 4 h.

$\alpha$ -sialons ground for 48 h in a self-generated atmosphere in a sealed pot were found to form a variety of sialon products when subsequently heated up to  $1600 \text{ }^\circ\text{C}$  in nitrogen. Without grinding, the same mixtures were comparatively unreactive over the same temperature range.

In all mixtures, grinding produced a significant amount of X-ray-amorphous material, reflected by the loss of XRD intensity of the crystalline phases, but produced no new phases, although significant conversion of the original  $\alpha$ - $\text{Si}_3\text{N}_4$  to the  $\beta$ -form occurred on grinding the  $\beta$ -sialon and X-sialon compositions containing  $\gamma$ - $\text{Al}_2\text{O}_3$ . Substitution of  $\gamma$ - $\text{Al}_2\text{O}_3$  by  $\text{Al}(\text{OH})_3$  as the alumina source facilitated the production of Al–O–Si bonds during grinding, but had little influence on the Al–N bonding.  $^{29}\text{Si}$  NMR spectroscopy showed that grinding also affects the Si–O component of the mixture more than the Si–N components.

On heating the ground mixtures of  $\beta$ -sialon composition in nitrogen, a mixture of  $\beta$ -, X- and O-sialon is formed below  $1500 \text{ }^\circ\text{C}$ , decomposing to polytypoid sialons and corundum at  $1600 \text{ }^\circ\text{C}$ . The unground mixture forms only mullite and corundum up to  $1600 \text{ }^\circ\text{C}$ .

The ground mixture of O-sialon composition forms monophase O-sialon at  $1600 \text{ }^\circ\text{C}$  in nitrogen, via X-sialon and in some cases a low-temperature form of O-sialon. The unground mixture forms only corundum, mullite and cristobalite at  $1600 \text{ }^\circ\text{C}$ , with a small amount of X-sialon also appearing at  $1600 \text{ }^\circ\text{C}$  in the mixture containing  $\gamma$ - $\text{Al}_2\text{O}_3$ .

Heating the ground X-sialon composition mixture containing  $\gamma$ - $\text{Al}_2\text{O}_3$  in nitrogen produces X-sialon at  $1500 \text{ }^\circ\text{C}$ ; this decomposes to mullite and corundum at  $1600 \text{ }^\circ\text{C}$ . The unground mixtures produce corundum, mullite and cristobalite and, with  $\text{Al}(\text{OH})_3$  as the alumina source,  $\beta$ -sialon and polytypoid sialon (but no X-sialon) at  $1600 \text{ }^\circ\text{C}$ .

Ca  $\alpha$ -sialon was not formed on heating either the ground or unground mixture of this composition, but a mixture of  $\beta$ -, O- and X-sialons was formed in the ground precursor on heating in nitrogen. The lack of a Ca-containing sialon phase in this material is explained by the preferential formation of calcium feldspar (calcian albite) facilitated by grinding and by the use of  $\text{Al}(\text{OH})_3$ , the hydroxyl groups of which facilitate the formation of homogeneous aluminosilicate precursors. These form stable aluminosilicate phases at lower temperatures, depriving the system of reactive Al–O species for sialon formation. Thus, grinding conditions favourable for aluminosilicate formation are not necessarily the most desirable for sialon formation.

All the ground mixtures show at an early stage of heating an octahedral  $^{27}\text{Al}$  NMR resonance at 13 ppm typical of corundum. Since crystalline corundum appeared in these samples only at much higher temperatures, this peak is thought to result from the thermal decomposition of  $\gamma$ - $\text{Al}_2\text{O}_3$  [or  $\text{Al}(\text{OH})_3$ ] to an amorphous form containing Al–O in a hexagonal environment. The presence of this phase may provide sufficient reactive Al–O species for sialon formation at lowered temperatures.

## Acknowledgements

One of us (K.M.) is indebted to the Royal Society of New Zealand for funding from the International Science and Technology Linkages Fund under the research contract 01-BRAP-65-MACK. JT thanks the Japan Society for the Promotion of Science for a research fellowship under which part of this work was carried out. MES thanks the EPSRC for its contribution to the NMR facilities at Warwick and the Royal Society and Leverhulme Trust for provision of a Senior Research Fellowship.

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