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Carbothermal synthesis of β-sialon from mechanochemically activated precursors

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Abstract

Reaction mixtures of halloysite clay and fine carbon for carbothermal reduction and nitridation (CRN) synthesis of β-sialon were ground in a planetary ball mill under flowing nitrogen for varying periods before being converted to sialon by heating in nitrogen at 1200–1400 °C. After 4 h grinding the XRD reflections of the halloysite were destroyed and some of the octahedrally-coordinated Al was converted to four- and five-fold coordination. ^{27}Al and ^{29}Si MAS NMR gave no evidence of the formation of Al─N or Si─N bonds upon grinding. Upon subsequent heating in nitrogen, the ground samples show significant differences from the unground control, the intermediate compound mullite being replaced by β-sialon ($z \approx 2$) a temperature at least 100 °C lower, but the formation of corundum (α-Al_2O_3) also occurs at a lower temperature and is more persistent than in the unground control. MAS NMR spectroscopy shows that the products from the ground mixtures contain relatively less Al─O─N units and that the formation of SiC (a transient reaction intermediate) is also facilitated by grinding. The optimum grinding time for this system was found to be 12 h.

Keywords: Sialons; Grinding; Carbothermal synthesis; XRD; MAS NMR

1. Introduction

β-Sialon is a silicon aluminium oxynitride compound isostructural with β-silicon nitride. This structure is stable over a range of compositions which can be written as $Si_{6-z}Al_zO_zN_{8-z}$ for values of z from 0 (representing pure Si_3N_4) to about 4.3. β-Sialon has engineering properties and applications similar to those of β-Si_3N_4, but has the advantage that it can be tailored to particular applications by manipulation of its aluminium content.

One of the most versatile of the synthesis methods for β-sialon is the carbothermal reduction and nitridation (CRN) of a clay mineral such as kaolinite or halloysite[1] in which the clay is mixed with finely powdered carbon and heated at >1400 °C in flowing purified nitrogen. The β-sialon produced thus from kaolinite has an expected z-value of 3, but compounds with other z-values can readily be obtained by adjusting the composition of the reaction mixture with additional alumina or silica. Carbothermal synthesis of β-sialon ($z = 3$) from kaolinite clay can be represented by the overall equation:

$$3Al_2Si_2O_5(OH)_4 + 15C + 5N_2 \rightarrow 2Si_3Al_3O_3N_5 + 6H_2O\uparrow + 15CO\uparrow \ldots \quad (1)$$

In common with the production of all high-performance advanced ceramic materials, the synthesis of the sialons is energy-intensive and methods for lowering the processing temperature have been sought. One possible method is mechanochemical processing (high-energy grinding) of the reactants. A previous study[2] has shown that a number of sialon compounds including β-sialon can be prepared from appropriate mixtures of the component compounds (Si_3N_4, SiO_2, AlN, Al_2O_3) at temperatures at least 200 °C lower if the mixtures are mechanochemically activated before being heated in nitrogen. Since the temperatures involved are high (>1600 °C) and the products contain a mixture of different

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sialon types, this is not a particularly favourable route for sialon synthesis, even when facilitated by mechanochemical activation.

The aim of the present study was to determine whether mechanochemical activation of precursor mixtures for carbothermal sialon synthesis can lower the temperature of this more favourable synthesis route. Since mechanochemical processing is known to facilitate the formation of mullite from mixtures containing kaolinite by the formation of new Si–O–Al bonds,[3] and since mullite formation is an initial stage in the carbothermal reaction sequence,[4] it was anticipated that the combination of mechanochemical activation with CRN may have a beneficial effect. To avoid possible complications arising from atmospheric oxidation of particle surfaces freshly exposed by grinding, the mechanochemical activation was carried out under a continuously replenished atmosphere of purified nitrogen. Since prolonged grinding destroys the long-range order of crystalline materials, the effect of the grinding was monitored by solid state MAS NMR, a technique which does not depend on atomic periodicity.[5] A combination of MAS NMR and X-ray diffraction was used to determine the progress and extent of the subsequent CRN reactions carried out by heating at various temperatures in flowing nitrogen gas.

2. Experimental

The starting materials were New Zealand halloysite (NZ China Clays Untrafine grade) and fine carbon powder (Degussa lampblack 101). Halloysite is a 1:1 layer lattice aluminosilicate of similar constitution to kaolinite but with tubular rather than platy morphology. A batch containing 25 wt.% carbon was thoroughly mixed by ball milling for 24 h in isopropanol and the solvent removed by rotary evaporator before drying at 100 °C overnight. Individual 2-g charges of this powder were milled for varying periods (2–48 h) in a planetary ball mill fitted with a 10 cm diameter zirconia pot and 3 mm diameter zirconia balls. The weight ratio of sample:balls was 1:50 and the milling speed was 400 rpm. The mill was adapted to allow the ingress and outlet of a flowing atmosphere of purified nitrogen (100 ml min^{-1}) throughout the course of the milling to prevent oxidation of the freshly exposed particle surfaces and to remove any products of early carbothermal reaction.

After milling, the mixtures were examined by X-ray powder diffraction (Philips PW 1700 computer-controlled goniometer with graphite monochromator and Co Kα radiation). ^{27}Al and ^{29}Si MAS NMR spectra were also acquired at 11.7 T using a Varian Unity 500 spectrometer and a 5 mm Doty MAS probe spun at 10–12 kHz under the following conditions:

^{27}Al: Spectrometer frequency 130.224 MHz using a 1 μs ($\pi/10$) pulse for solution with a 1 s delay, spectra referenced to $Al(H_2O)_6{}^{3+}$.
^{29}Si: Spectrometer frequency 99.926 MHz using a 6 μs ($\pi/10$) pulse with a 100 s delay, spectra referenced to tetramethylsilane (TMS).

Carbothermal conversion of the milled precursors to sialon was carried out by heating small aliquots in alumina boats in an electric tube furnace in an atmosphere of flowing oxygen-free nitrogen (100 ml min^{-1}) The carbothermal reaction temperatures varied from 1200 to 1400 °C and the firing cycle included an 8-h heat-up period followed by a 4 h holding time at the nominated temperature. After carbothermal reaction, the samples were again examined by X-ray powder diffraction and ^{27}Al and ^{29}Si MAS NMR.

3. Results and discussion

3.1. Effect of grinding on carbothermal sialon precursors

The X-ray powder diffraction patterns of the sample before and after grinding are shown in Fig. 1. The unground mixture contains the characteristic reflections of halloysite (JCPDS no. 9-453) together with the crystalline SiO_2 impurities quartz (JCPDS no. 33-1161) and cristobalite (JCPDS no. 11-695). Mechanochemical processing for 4 h removes the halloysite reflections and significantly lowers the intensity of the quartz and cristobalite peaks. The latter is completely removed by grinding for 12 h, but the intensity of the major quartz reflection remains largely unchanged by further grinding, even up to 48 h (not shown in Fig. 1). On this basis, grinding times >12 h appear to have little further effect on the crystallinity of the precursor.

The ^{27}Al and ^{29}Si MAS NMR spectra of the unground and ground precursors are shown in Fig. 2. The ^{27}Al spectrum of the unground starting mixture (Fig. 2A) shows the expected single octahedral Al resonance of halloysite at 3 ppm. On grinding, this octahedral peak progressively broadens and becomes more negative (−4 ppm after grinding for 12 h). Grinding also brings about the formation of a new tetrahedral resonance at 54 ppm and a resonance at 27 ppm, variously ascribed[5] to Al(V)–O or severely distorted Al(IV)–O. The appearance of lower Al coordination numbers as a result of grinding is a typical feature of hydrated Al compounds.[6] More prolonged grinding broadens these resonances, especially that at 27 ppm, which becomes progressively less well resolved as a result (Fig. 2D). The spectra show no evidence of the formation of Al–N bonds during grinding; these would give rise to a resonance at about 112 ppm.[5] Neither is there any evidence in the ^{27}Al spectra of the formation of various Al–O–N units, which appear at about 70–105 ppm.[5]

The ^{29}Si MAS NMR spectrum of the unground mixture (Fig. 2E) shows the typically sharp resonance at −92 ppm

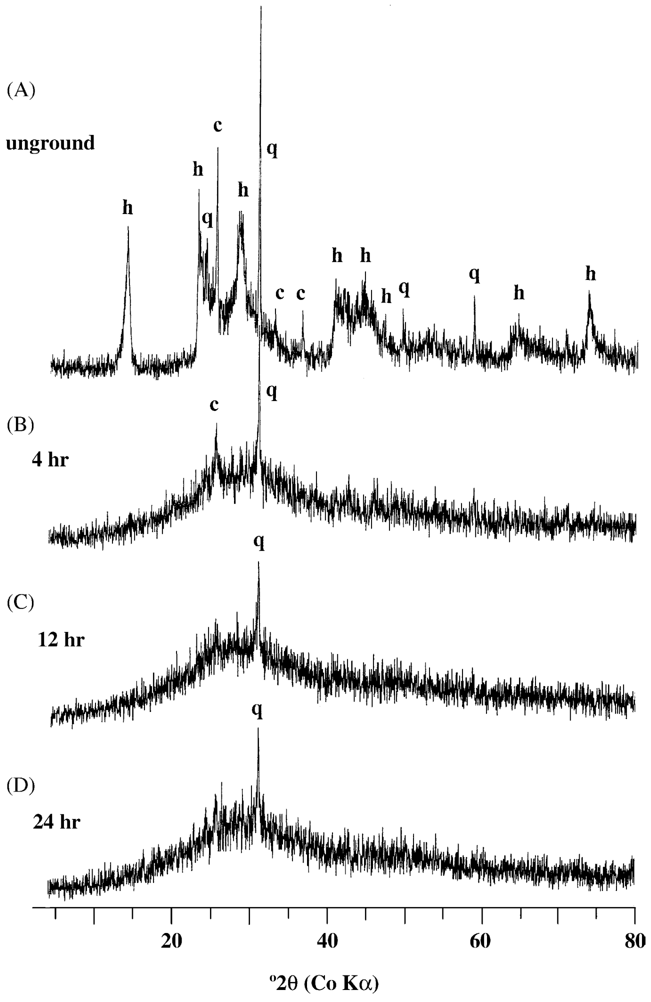

Fig. 1. XRD patterns of the carbothermal reaction starting mixture, unground and ground for periods as marked. Key: h: halloysite (JCPDS no. 9-453), q: quartz (JCPDS no. 33-1161), c: cristobalite (JCPDS no. 11-695).

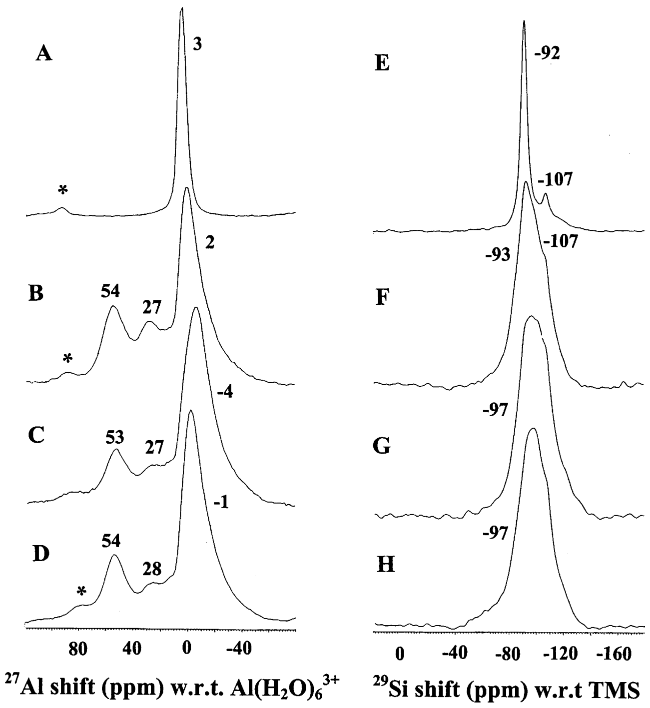

Fig. 2. (A–D) 11.7T ^{27}Al MAS NMR spectra, (E–H) ^{29}Si MAS NMR spectra of the carbothermal reaction starting mixture. (A, E) Unground. (B, F) Ground 4 h. (C, G) Ground 12 h. (D, H) Ground 24 h. Asterisks denote spinning side bands.

associated with the Q^3 units of the halloysite, together with a small sharp peak at −107 ppm arising from the crystalline quartz and cristobalite impurities which cannot be distinguished in this spectrum. Grinding results in a significant broadening of the Si spectra, which are displaced to more negative values and resemble the spectra of glasses even after 4 h treatment (Fig. 2F). The ^{29}Si NMR spectra provide no evidence of the formation of Si–N bonds (expected at about −48 ppm),[5] Si–O–N bonds (expected at about −62 ppm)[5] or Si–C bonds (expected at about −6 to −22 ppm).[5] Thus, the combined XRD and NMR evidence shows that the ground sialon precursors have become typically non-crystalline, with changes in the Al and Si atomic environments similar to those experienced by a halloysite clay ground in air in the absence of carbon. In particular, there is no evidence of the formation of new compounds at this stage of the processing.

3.2. *Effect of heating these carbothermal precursors*

Fig. 3 shows a schematic diagram of the crystalline phases identified by powder XRD in the unground and ground precursors after heating in nitrogen at various temperatures. In the unground precursors, the silica polymorphs persist to high temperatures (>1300 °C for cristobalite and >1200 °C for quartz). Mullite (JCPDS no. 15-776), the normal thermal decomposition product of halloysite, is formed <1200 °C and persists to >1300 °C, at which temperature it is gradually replaced by a small amount of β-sialon (JCPDS no. 48-1616). 21R sialon (JCPDS no. 42-0162), a polytypoid structurally related to AlN, appears at 1400 °C.

Grinding for 4 h does not change the formation sequence of these phases, but produces changes in their temperature range; cristobalite and quartz have disappeared from the XRD trace by 1200 °C and corundum appears below 1300 °C (Fig. 3). However, grinding for 12 h significantly lowers the temperature interval over which mullite is present, confining it to around 1200 °C, above which it is replaced by β-sialon and α-Al_2O_3 (corundum, JCPDS no. 10-173) (Fig. 3). A similar result is found for the precursor ground for 24 h. The *z*-values of the β-sialon formed in all these samples, estimated from the XRD lattice spacing, is about 2, lower than the theoretical value deduced from the Al content of the starting clay mineral. The additional Al is the source of the corundum in the XRD pattern. Grinding for 48 h results in the formation

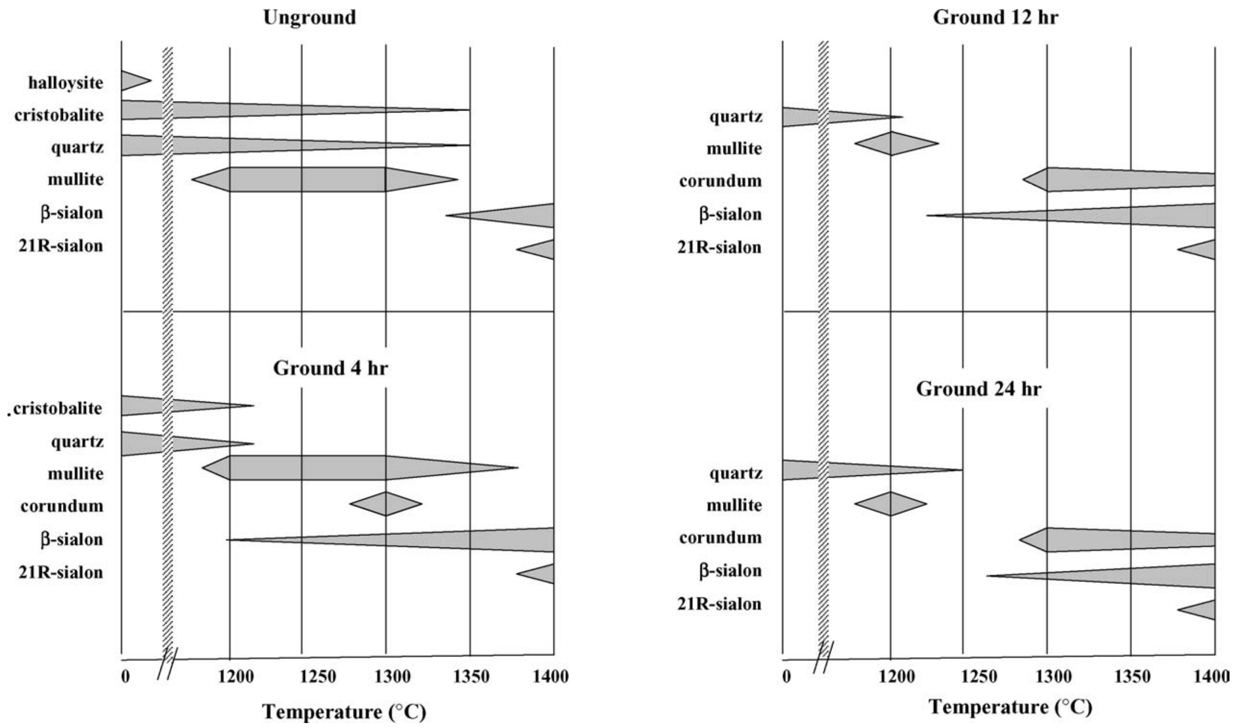

Fig. 3. Schematic representation of the crystalline phases formed from the ground and unground CRN precursors after firing for 4 h in flowing purified nitrogen, as a function of the firing temperature.

below 1300 °C of a small amount of β-sialon with an even lower Al content ($z \approx 1$).

Fig. 4 shows a selection of ^{27}Al MAS NMR spectra of unground and 12-h ground samples heated in N_2 at various temperatures. On heating to 1200 °C, the unground precursor shows the typical spectrum of mullite (Fig. 4B), with an octahedral resonance at 0 ppm showing evidence of electric field gradient (EFG) interactions showing up as a tail to higher fields. The characteristic square-topped tetrahedral resonance at 43–57 ppm arises from the overlap of peaks from the regular tetrahedral sites and sites associated with tricluster defects in mullite.[7] The development of a shoulder at 13–14 ppm provides evidence of corundum formation, which becomes more pronounced in the sample heated at 1300 °C (Fig. 4C). Firing to 1400 °C produces a marked change in the unground spectrum (Fig. 4D), with the appearance of an intense Al–N resonance at 113 ppm and an increase in the intensity of the corundum peak at 14 ppm. A broad feature at about 69 ppm may be associated with the presence of a variety of Al–O–N units,[5] principally AlO_3N.

A similar development is seen in the 1200 °C spectrum of the sample ground for 12 h (Fig. 4F), with mullite being formed in good amount; however, by 1300 °C (Fig. 4G) this has been replaced by an intense corundum peak at 14 ppm and evidence of Al–N formation (113 ppm). Firing at 1400 °C results in a slight decrease of the corundum resonance and a marked increase in the intensity of the AlN peak (Fig. 4H). Thus, the NMR evidence is that all the necessary changes in the Al environment, particularly the replacement of Al–O units with Al–N are occurring at least 100 °C lower in the sample ground for 12 h. Whereas the samples ground for 24 h show very similar ^{27}Al MAS NMR spectra after heating, those ground for 4 h show evidence that the thermal formation of AlN is less advanced. These results suggest that grinding has a beneficial effect on the formation of Al–N bonds; however, it also facilitates the formation of corundum.

Fig. 5 shows the corresponding ^{29}Si MAS NMR spectra of the unground and 12-h ground samples heated in N_2 at various temperatures. Heating the unground mixture at 1200 °C (Fig. 5B) results in the appearance of a broad resonance at -90 ppm arising from the framework Al–O–Si resonance of mullite[7] and the intensification of the SiO_2 resonance at -109 ppm, reflecting the separation of silica associated with the thermal decomposition of halloysite. Both these resonances are still present after heating to 1300 °C (Fig. 5C), but the mullite peak has become dominant. Three small new peaks also appear at this temperature; one, at -49 ppm signals the formation of Si–N bonds, while another broad feature at about -70 ppm arises from the presence of a range of Si–O–N units.[5] The small peak at -18 ppm indicates the formation of a small amount of SiC, an intermediate in the CRN process in halloysite which is generally not detected by XRD.[4] Heating to 1400 °C (Fig. 5D) produces a broad spectral feature extending from the position of uncombined silica

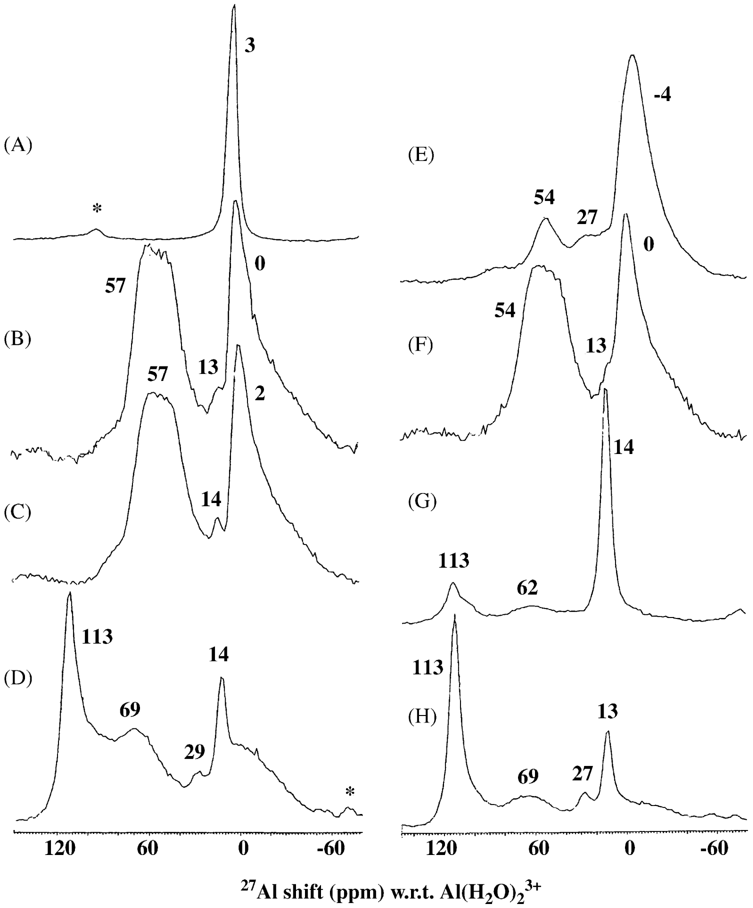

Fig. 4. Representative 11.7T ^{27}Al MAS NMR spectra of the CRN precursors fired for 4 h in flowing purified nitrogen. (A–D) Unground, (A) unheated, (B) 1200 °C, (C) 1300 °C and (D) 1400 °C. (E–H) ground 12 h. (E) Unheated, (F) 1200 °C, (G) 1300 °C and (H) 1400 °C. Asterisks denote spinning side bands.

at −115 ppm to about −60 ppm, with inflexions at the positions of Al–O–Si groups (−90 ppm) and Si–O–N groups (−62 to −75 ppm). These features are typical of the ^{29}Si spectrum of X-sialon[8] and of the AlN polytypoid sialons (unpublished results). The formation of Si–N bonds such as occur in Si_3N_4 and β-sialon is evidenced by the sharp peak at −48 ppm.

Heating the precursor ground for 12 h at 1200 °C indicates that the reaction sequence is already more advanced than in the unground control, the ^{29}Si NMR spectrum (Fig. 5F) showing good development of the mullite resonance at −90 ppm and a reduction in the intensity of the uncombined SiO_2 peak (−108 ppm) and the peak due to the presence of SiC (−20 ppm). A small feature at −48 ppm in this spectrum provides an initial indication of the formation of Si–N bonds. Both the Si–N and Si–C peaks increase significantly in intensity on heating at 1300 °C (Fig. 5G), with the concomitant development of the broad peak characteristic of polytypoid sialon extending from about −110 to −60 ppm. Heating to 1400 °C largely removes the SiC peak, but the spectrum (Fig. 5H) is otherwise unchanged. The spectra of the heated precursor ground for 4 h (not shown) show differences from this behaviour only with respect to the temperature of first appearance of Si–N bonds (1300 °C) and in a greater intensity of the SiC peak appearing at 11,300 °C. The ^{29}Si NMR spectra of heated precursors ground for 24 h are identical to those ground for 12 h (Fig. 5), but grinding for 48 h appears to have arrested the reaction processes, with the Si–N resonance appearing only at 1400 °C, at which temperature ample SiC is also still evident. Thus, grinding for 12–24 h has the beneficial effect of facilitating the formation of both the intermediate SiC phase and the necessary Si–N bonds. However, the formation of the range of Si–O–N units typical of sialons other than β-sialon is also facilitated by the grinding, probably reflecting an increased reactivity of the mullite for the Si_3N_4 formed at an earlier stage than in the unground precursors. This 21R polytypoid sialon is apparently rather stable, and, being Al-rich, it may represent a decomposition product of β-sialon rather than an intermediate which can be converted to β-sialon by more prolonged grinding or thermal reaction. Overgrinding may also present a problem by producing an apparently less-reactive form of SiC which persists to higher temperatures.

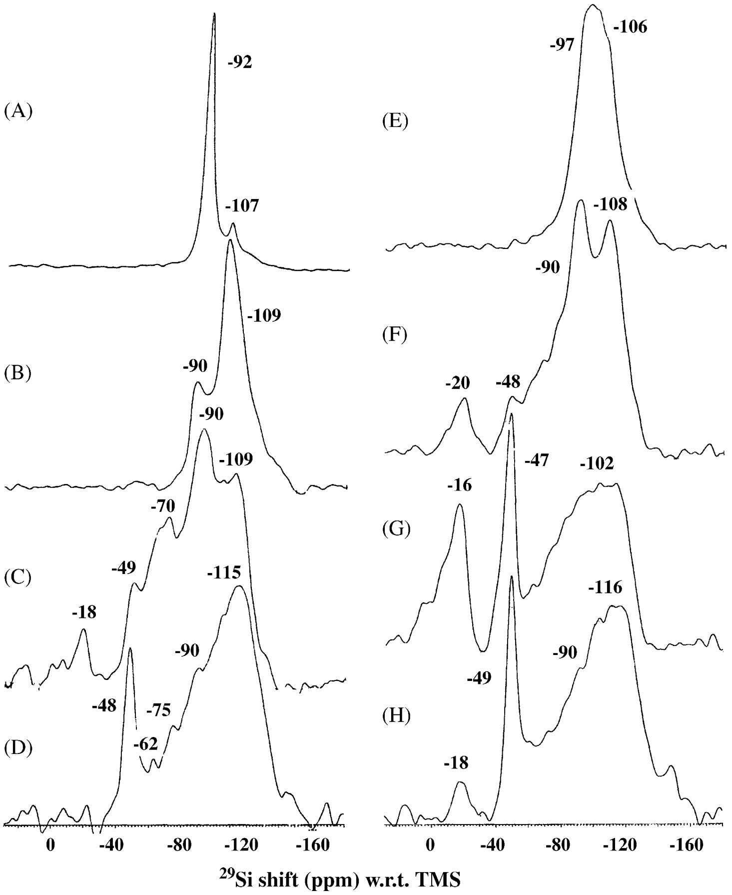

Fig. 5. Representative 11.7T ^{29}Si MAS NMR spectra of the CRN precursors fired for 4 h in flowing purified nitrogen. (A–D) Unground, (A) unheated, (B) 1200 °C, (C) 1300 °C and (D) 1400 °C. (E–H) ground 12 h. (E) Unheated, (F) 1200 °C, (G) 1300 °C and (H) 1400 °C.

4. Conclusions

Mixtures of the clay mineral halloysite with fine carbon powder were ground under flowing nitrogen in a planetary ball mill for varying periods of time. Grinding for 4 h destroys the XRD reflections of the halloysite, but the X-ray reflections of the SiO_2 impurity minerals persist for longer grinding times (>24 h in the case of quartz). The results indicate that grinding for 12 h satisfactorily enhances the desired sialon formation on subsequent heating under nitrogen.

^{27}Al MAS NMR shows that even after 4 h grinding, a proportion of the octahedrally coordinated Al of the original clay mineral is converted to four and five-coordination, but there is no evidence that Al–N bonds are formed by grinding. The corresponding ^{29}Si MAS NMR spectra show that grinding results in the formation of a broad range of tetrahedrally coordinated Si–O units, but there is no evidence of the formation of Si–N bonds.

When these CRN precursors are heated at 1200–1400 °C for 4 h in flowing purified nitrogen to convert them into sialon, marked differences are found between the crystalline products from the ground and unground mixtures. The unground mixture forms mullite as an intermediate phase, which, together with the quartz and cristobalite impurities, persists to >1300 °C. The sialon products (β-sialon and a small amount of 21R AlN polytypoid sialon) are formed between 1300 and 1400 °C. The ^{27}Al and ^{29}Si MAS NMR spectra of the heated samples confirm that the formation of Al–N, Al–O–N, Si–N and Si–O–N units associated with sialons appear only at the higher temperatures, and that the intermediate phase SiC (undetected by XRD) persists in high concentration even at 1400 °C.

By contrast, the thermal reactions of the samples ground for >4 h are comparatively more advanced at lower temperatures; mullite appears as a short-lived transient phase at 1200 °C, the crystalline silica impurities have disappeared by 1200 °C and β-sialon appears <1300 °C, but corundum is more persistent, forming at 1300 °C and being still present in good amount at 1400 °C. The z-value of the β-sialon formed in all these samples is about 2, reflecting the separation of some of the Al of the starting clay into corundum and 21R AlN polytypoid sialon.

These conclusions are confirmed by the ^{27}Al and ^{29}Si MAS NMR spectra, which additionally indicate that grinding produces a product containing relatively less Al–O–N units than that from the unground precursor, and that the formation of SiC (an intermediate phase) is facilitated by grinding.

Thus, mechanochemical activation of CRN precursors for 12 h lowers the temperature of subsequent β-sialon formation by at least 100 °C, but also brings about the separation of corundum and does not suppress the formation of the 21R AlN polytypoid sialon at higher temperatures.

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