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A New Silicothermal Route to the Formation of X-Phase Sialon: The Reaction Sequence in the Presence and Absence of Y_2O_3

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Abstract

A new method is described for the preparation of essentially monophase X-phase sialon, $Si_{12}Al_{18}O_{39}N_8$*, by silicothermal reduction of mixtures of kaolinite,* γ-Al_2O_3 *and elemental Si in purified nitrogen at 1450–1500°C. Powder X-ray diffraction and solid state* ^{29}Si *and* ^{27}Al *MAS-NMR of reaction mixtures heated to 1200–1570°C suggest that the reaction proceeds in several parallel steps, including the nitridation of the elemental Si to* Si_3N_4*, thermal decomposition of the kaolinite to mullite and amorphous silica, reaction between the amorphous silica and* γ*-alumina, and reaction between silicon nitride and the aluminosilicate phase. Two forms of O'-sialon also appear as minor phases, possibly formed in the early stages by nitridation of the silica or aluminosilicate. The addition of up to 3 wt% of* Y_2O_3 *to the reaction mixture increases the rate of all the reactions occurring above 1100°C without changing the reaction sequence, but the X-phase product formed in the presence of* Y_2O_3 *retains a high proportion of* SiO_2N_2 *groups, by comparison with X-phase formed without* Y_2O_3*, in which* SiO_3N *groups predominate. XRD and MAS-NMR show the fully reacted silicothermal product to be comparable with reputable X-phase sialon prepared by a two-stage carbothermal method. © 1997 Elsevier Science Limited. All rights reserved.*

Introduction

X-phase sialon exists over a narrow solid solution between Si_3N_4 and mullite, $Al_6Si_2O_{13}$. It has a structure similar to mullite, in which columns of AlO_6 octahedra are cross-linked by SiO_4 and AlO_4 tetrahedra, but the larger unit cell of X-phase results from an increase in the proportion of tetrahedral : octahedral units compared with mullite.[1] X-phase sialon has been assigned various compositions ranging from $SiAlO_2N$ to $Si_{16.9}Al_{22.7}O_{48.8}N_{11.6}$.[2]

Several methods have been reported to form essentially monophase X-phase sialon: hot-pressing mixtures of Si_3N_4–Al_2O_3–SiO_2 at 1650°C,[2] (such reaction mixtures may also include AlN)[3] hot-pressing at 1650°C a mixture containing Si_3N_4 and a gel of mullite composition derived from organometallic reactants,[2] and carbothermal reduction of kaolinite plus α-Al_2O_3 at 1500°C.[4]

During sialon synthesis experiments involving thermal reduction and nitridation of reaction mixtures containing elemental Si, it was observed that, in the absence of carbon, X-phase sialon is a major product. The present work was therefore carried out to investigate the reaction mechanism and to establish the optimal temperature range for preparing a monophase product by this route. Additions of Y_2O_3 are often made to assist post-synthesis sintering of sialons, and other experiments have shown that if the Y_2O_3 is added prior to carbothermal synthesis, its presence also exerts a beneficial effect on β'-sialon formation (to be published). On this basis, the silicothermal X-phase synthesis reaction was also studied in the presence of up to 3 wt% Y_2O_3. The progress of the reaction was monitored by thermal analysis, X-ray powder diffraction and solid-state MAS-NMR. The latter technique has previously proved useful in providing complementary information about the carbothermal synthesis of β'-sialon.[5]

Experimental

The starting materials were kaolinite (BDH 'Light' grade), silicon powder (Permascand 4D) and $Al(OH)_3$ (BDH, reagent grade). The $Al(OH)_3$ was dehydroxylated to form γ-Al_2O_3 by heating at 800°C for 3·5 h prior to batching. The particle size distributions of the reactants were: kaolinite:

10%<1·9 μm 50%<5·5 μm 90%<20.0 μm, silicon: 10%<1·0 μm 50%<4·6 μm 90%<17·7 μm, γ-Al_2O_3: 10%<43 μm 50%<70 μm 90%<126 μm. Mixes containing α-Al_2O_3 were not sufficiently reactive to give good yields of X-phase sialon under the present reaction conditions. The reactants were batched to the composition 49 wt% kaolinite, 40 wt% γ-alumina, 10 wt% Si, to give the stoichiometry $Si_{12}Al_{18}O_{39}N_8$, then ball milled for ≈20 h in hexane, using Si_3N_4 milling media. After removal of the solvent using a vacuum rotary evaporator, the mixture was passed through a 300-μm sieve then pressed in 0·5-g aliquots into 10-mm diameter discs (140 MPa) and fired in a laboratory tube furnace under 55 ml/min flowing nitrogen (oxygen-free instrument grade, further purified by passing through a molecular sieve column). To monitor the effect of temperature on the course of the reaction, firings were made at 1200–1570°C with zero holding time at the top temperature. The heating rate was 10°C/min to 1100°C, then 2°C/min to the top temperature, with cooling at the natural rate of the furnace (about 15°C/min down to 1000°C, 3·5°C/min down to 600°C). Parallel series of experiments were also made with mixtures containing 0·2–3·0 wt% Y_2O_3. The thermal behaviour of the various mixtures was examined by thermogravimetry (Mettler model 21 thermobalance, heating rate 2°C/min above 1100°C, in flowing purified nitrogen, 100 ml/min).

After firing, the pellets were ground and examined by X-ray powder diffraction (Philips PW 1700 automatic diffractometer with Co *Kα* radiation and graphite monochromator). The solid state ^{29}Si and ^{27}Al MAS-NMR spectra were acquired at 11·7 T using a Varian Unity 500 spectrometer and a Doty high-speed 5-mm MAS probe (spinning speed ≈ 12 kHz) under the following conditions:

^{29}Si: 6 μs π/2 pulse, recycle delay of 300 s, shifts referenced to tetramethylsilane (TMS).

^{27}Al: 1 μs π/10 pulse for solution, recycle delay of 5 s, referenced to 1M aqueous $Al(NO_3)_3$ solution.

For NMR reference purposes, essentially monophase X-phase sialon was prepared by two methods: (1) the new single-stage silicothermal method, in which the above reactant mixture without Y_2O_3 was heated at 2°C/min to 1450°C, held at this temperature for 4 h, then cooled at 10°C/min, (2) two-stage carbothermal reaction of BDH kaolinite with 7·5% lampblack in a carbon pot, heated in a graphite resistance furnace under purified nitrogen at 10°C/min to 1530°C, held at this temperature for 8 h, then cooled at the same rate. The resulting product, containing X-phase sialon and mullite in the approximate ratio 60 : 40, was pressed into 10-mm dia. pellets at 350 MPa using 5% oleic acid binder and re-heated in a carbon pot at 1580°C for 2 h under purified nitrogen in a BN powder bed, then cooled at 10°C/min.

Results and Discussion

The TG traces of the reaction mixtures both with and without Y_2O_3 are shown in Fig. 1. Below 1100°C, the form of both TG curves is similar, with a low-temperature mass loss of adsorbed moisture (6·6–7·5%) up to a slight inflection in the curve which marks the onset of dehydroxylation of the clay at about 400°C. The dehydroxylation mass loss of 6·6% agrees well with the theoretical loss based on the known structural water content of the clay (13 wt%). The onset temperature of the subsequent mass-gain reactions (1100°C) is identical both in the presence and absence of Y_2O_3, the magnitudes of the mass gains also being similar (8·1% and 8·6% in the samples with and without Y_2O_3 respectively). If the reaction is assumed to form X-phase of composition $Si_{12}Al_{18}O_{39}N_8$, the theoretical mass gain corresponding to the nitridation of the Si present in the original mix is 7·7%, in good agreement with the observed gains.

In the absence of Y_2O_3, the TG curve (Fig. 1(a)) indicates that the nitridation reactions above

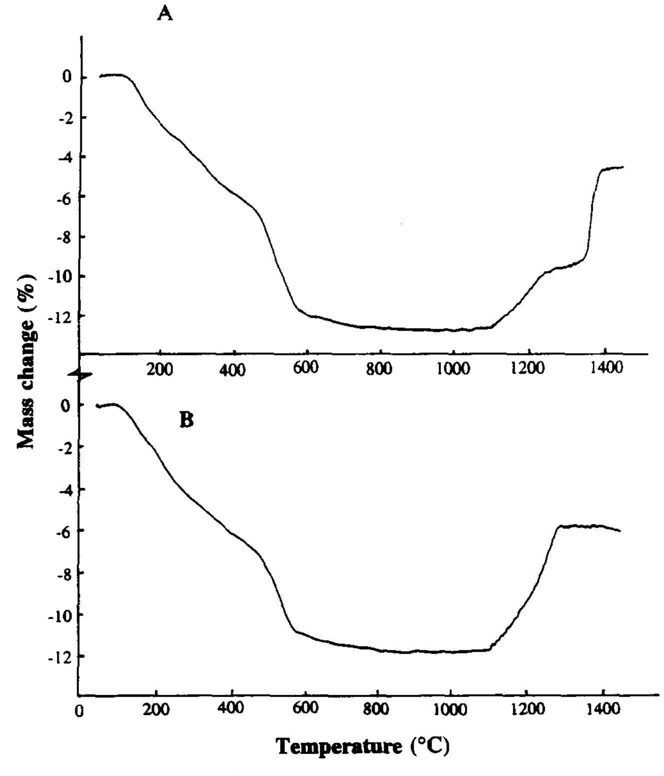

Fig. 1. Thermogravimetric curves for silicothermal reaction mixture containing kaolinite, γ-Al_2O_3 and elemental Si to X-phase stoichiometry $Si_{12}Al_{18}O_{39}N_8$. Heating rate 2°C/min above 1100°C, in purified nitrogen (100 ml/min). (a) Without Y_2O_3, (b) with 2·7 wt% Y_2O_3.

1100°C proceed in two steps. The first, at 1100–1240°C, corresponds to a mass gain of 3%, and is associated with the formation of Si_3N_4 which, according to XRD analysis (below), is the initial nitridation product. Between 1240 and 1350°C, the nitridation reaction becomes markedly slower, possibly due to the formation of a gas-impermeable product layer around the partially reacted Si grains. Above 1350°C, further rapid nitridation occurs, halting abruptly at 1390°C with a mass gain of 5·6%. This stage corresponds to the rapid increase in the amount of X-phase sialon shown by XRD to occur in the later stages of the reaction. Differences between the temperatures of these TG events and the XRD results (below) which are displaced to higher temperatures, probably arise from differences in gas flow rates, furnace geometry, and gas flow patterns.

In the presence of Y_2O_3 (Fig. 1(B)), the nitridation reactions proceed in one continuous step, concluding abruptly at about 1280°C. XRD results (below) indicate the early onset of X-phase sialon formation, which precedes the appearance of Si_3N_4, and continues throughout the reaction. Thus, the action of Y_2O_3 is to enhance the early formation of X-phase sialon at the expense of Si_3N_4, and to accelerate the overall nitridation, bringing the mass-gain reactions to a conclusion 110°C lower, under the present experimental conditions.

The changes in the phase assemblage of the reaction mixture during the weight-gain step >1100°C are shown semi-quantitatively in terms of XRD peak heights for samples without and with Y_2O_3 in Figs 2(a) and (b) respectively. The XRD peaks used for this purpose were: mullite (PDF no. 15-776) 5·39 Å (110), silicon (PDF no. 27-1402) 3·13 Å (111), γ-Al_2O_3 (PDF no. 10-425) 1·98 Å (400), Si_3N_4 (PDF no. 9-250) 6·69 Å (100), X-phase sialon (PDF no. 36-832) 3·62 Å (100), O′-sialon (PDF no. 42-1492) 4·44 Å (200). For comparison, the peaks were scaled to 100% on the basis of their tabulated relative intensities. The new form of O′-sialon was monitored using its peak at 4·63 Å, corrected for a contribution from the (110) O′-peak at 4·67 Å by using the known relative intensities of the (110) and (200) O′-peaks.

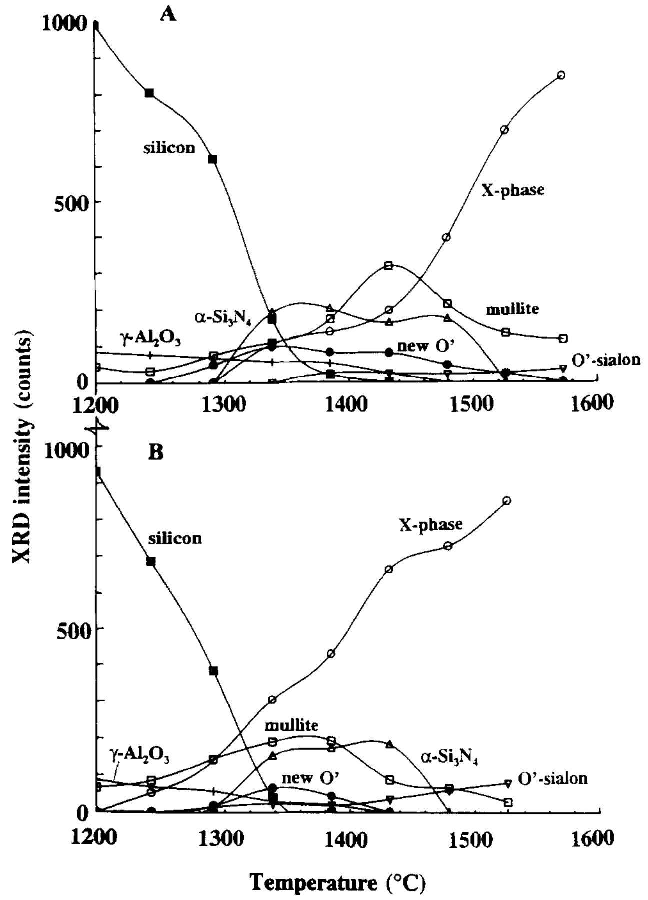

Fig. 2. Evolution of the crystalline phases with reaction temperature in silicothermal mixture of X-phase stoichiometry, from semiquantitative powder XRD measurements. (a) Samples without Y_2O_3, (b) samples containing 2·7 wt% Y_2O_3.

Figure 2 shows that the removal of Si by nitridation is accompanied by a concomitant but more gradual removal of γ-Al_2O_3 and the early appearance of X-phase sialon. Mullite, the decomposition product of the clay, continues to increase in XRD intensity up to 1350–1450°C, reflecting an increase in crystallinity, before being progressively removed at higher temperatures. Other transient phases detected during the reaction include Si_3N_4 which appears at 1350°C, indicating that it is not the primary product of nitridation, and a previously unreported form of O′-sialon.[14] The more usual form of O′-sialon (PDF no. 33-1162) also appears during the reaction, and is particularly evident in the samples containing Y_2O_3 (Fig. 2(B)). The general sequence of the reaction is similar in both the presence and absence of Y_2O_3, but with Y present, the mullite is removed at lower temperatures, with the formation of correspondingly more X-phase sialon. Thus, the action of the Y_2O_3 is to increase the reaction rate without significantly changing the reaction sequence.

Considerable effort was put into synthesising pure X-phase sialon, by both carbothermal and silicothermal routes, to provide a reference material for the determination of the ^{29}Si MAS-NMR spectrum which is not well documented in the literature, and to compare the products of the two synthesis methods. X-ray powder diffraction (Fig. 3) shows the products of both syntheses to be very similar crystallographically, and to contain all the X-phase sialon peaks listed in PDF no. 36-832. The small additional peaks marked by asterisks in Fig. 3 may indicate the presence of traces of O′-sialon impurity, but it should be noted that these peaks are attributed to X-phase sialon in other reference diffractograms (e.g. PDF no. 42-166,

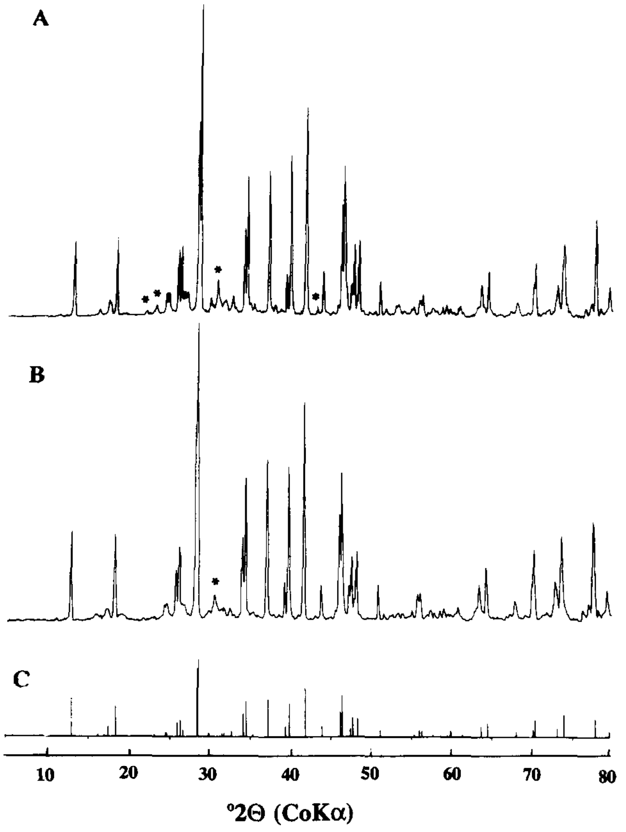

Fig. 3. X-ray powder diffractograms of essentially monophase X-phase sialon, prepared (A) by the two-stage carbothermal process, (B) by the one-stage silicothermal process. (C) PDF reference pattern no. 36-832 for X-phase sialon $Si_6Al_{10}O_{21}N_4$. Peaks marked by asterisks are common with O′-sialon (PDF no. 42-1492).

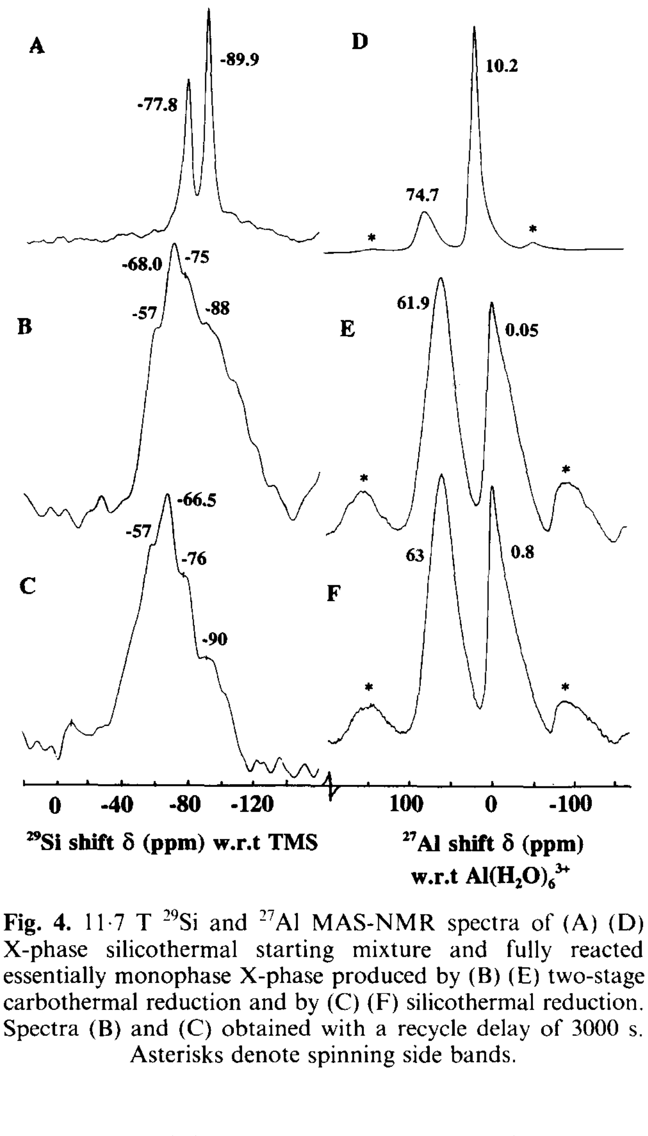

Fig. 4. 11·7 T ^{29}Si and ^{27}Al MAS-NMR spectra of (A) (D) X-phase silicothermal starting mixture and fully reacted essentially monophase X-phase produced by (B) (E) two-stage carbothermal reduction and by (C) (F) silicothermal reduction. Spectra (B) and (C) obtained with a recycle delay of 3000 s. Asterisks denote spinning side bands.

PDF no. 35-23, PDF no. 31-32). The XRD baseline profiles show little evidence of amorphous material.

Scanning electron microscopy of the X-phase reference powders showed that the carbothermal sample is composed of angular, 5–12-μm blocky grains, in some cases aggregated into 30-μm clumps. EDX analysis indicated an average Si : Al ratio of 0·58, in reasonable agreement with the composition $Si_{12}Al_{20}O_{42}N_8$ (Si : Al = 0·60). Point analyses of individual grains showed some compositional variation, down to a Si : Al ratio of 0·53. The silicothermal sample showed evidence of its lower firing temperature, with 1-μm grains aggregated into loose, powdery 5-μm clusters containing some denser-looking regions. The average Si : Al ratio, by EDX, was 0·66, in good agreement with the target composition $Si_{12}Al_{18}O_{39}N_8$, but as with the carbothermal sample, compositional differences were observed between individual grains; in general, the light, fluffy areas contained slightly less Si than the harder, denser-looking regions (typical Si : Al ratios 0·47 and 0·62 respectively). Thus, although both samples have the X-ray characteristics of monophase X-phase sialon, compositional differences exist within the individual grains, especially in the lower-fired silicothermal sample. The apparent bulk density of both the silicothermal and carbothermal fully reacted compacts was typically 3·0, the pycnometric density of the X-phase sialon prepared by the silicothermal synthesis being 3·15. These results indicate that the silicothermal method is capable of producing X-phase sialon of equal quality to that produced by carbothermal synthesis, but with possibly less O′-impurity. The silicothermal synthesis has the advantage of producing essentially monophase product in one step using significantly lower temperatures and shorter times than the two-stage carbothermal process; one disadvantage of the lower reaction temperature may, however, be the slightly greater variation in the composition of the individual particles.

The ^{29}Si and ^{27}Al MAS-NMR spectra of the fully reacted X-phase sialons produced by the carbothermal and silicothermal routes are shown in Fig. 4, which also includes the MAS-NMR spectra of the unreacted silicothermal mixture.

The unreacted mixture shows the expected ^{29}Si peaks (Fig. 4(A)) corresponding to elemental Si

(−77·8 ppm) and kaolinite (−89·9 ppm).[6] The corresponding ^{27}Al spectrum (Fig. 4(d)) is dominated by the octahedral/tetrahedral signature of γ-Al_2O_3 but with an additional octahedral component from the kaolinite giving about 80% octahedral intensity rather than about 70% as expected for pure γ-Al_2O_3.[7]

Earlier MAS-NMR work on X-phase sialon[8] reported the ^{27}Al NMR spectrum, but not the ^{29}Si spectrum, which has a long relaxation time. More recently, Smith[9] has reported the ^{29}Si spectrum of a mixture containing X-phase, SiC and β-Si_3N_4, and by applying a process of elimination, deduced that X-phase is distinguished by a resonance at −56·5 ppm. The ^{29}Si MAS-NMR spectra of our essentially monophase X-phase sialons prepared both by carbothermal reduction and silicothermal reduction (Figs 4(B) and (C) respectively), which were acquired with a recycle delay time of 3000 s, are very broad, with the maximum intensity component at −66·5 to −68 ppm and at least three shoulders which are probably real, since they appear at very similar positions in the two different samples. Both the major intensity and the shoulder at −75 to −76 ppm are in the region expected for SiO_3N groups, the former peak corresponding to a minor feature observed by Smith.[9] The shoulder at −57 ppm probably corresponds to the −56·5 ppm peak reported by Smith, and assigned to SiO_2N_2 groups.[9] The shoulder at −88 to −90 ppm corresponds to the major tetrahedral Si–O grouping in mullite.[10] Thus, the present spectra are consistent with a range of Si–O/N groupings, with the major contribution arising from SiO_3N, of which there are at least two different Si environments. The ^{27}Al spectra (Figs 4(E) and (F)) are consistent with previously published spectra,[8,9] consistent with one tetrahedral and one octahedral site, by contrast with mullite, in which two tetrahedral sites can often be distinguished.[10]

Typical ^{29}Si MAS-NMR spectra of partly reacted silicothermal X-phase preparations are shown in Fig. 5, both of mixtures containing Y_2O_3 (Figs 5(A)–(E)) and without Y_2O_3 (Figs 5(F)–(J)). These samples, which were prepared for the purpose of investigating the reaction sequence, correspond to the samples reported in Fig. 2, and differ from the fully reacted specimens of Fig. 4 in having been heated to the indicated temperature, then immediately cooled without a soaking period.

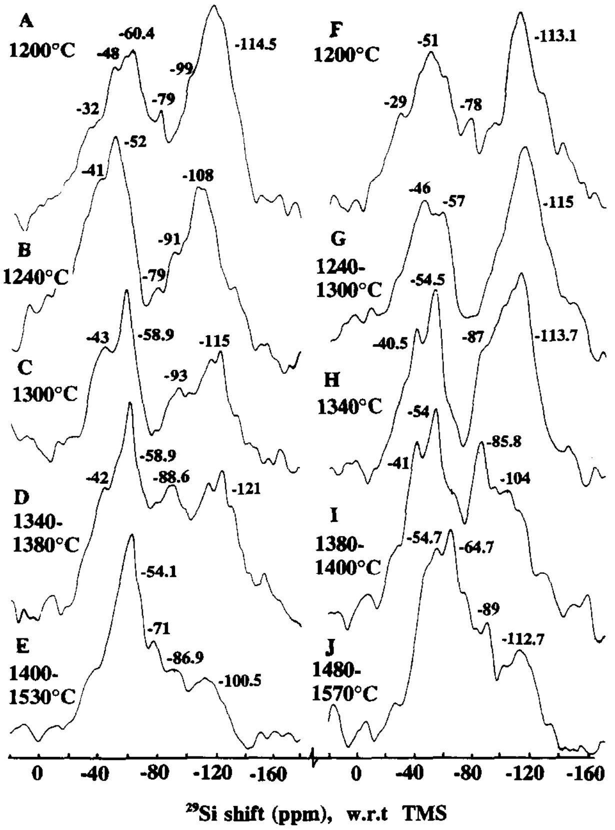

Fig. 5. Typical 11·7 29Si MAS-NMR spectra of partially reacted silicothermal X-phase mixtures: (A)–(E), mixture containing 2·7 wt% Y_2O_3, (F)–(J), mixture without Y_2O_3.

The ^{29}Si spectra are all broad and somewhat noisy, but indicate the evolution of several recurring groups of frequencies during the reaction sequence. Even at the lowest temperatures, the elemental Si (−79 ppm) is only just detectable, having been replaced by a group of frequencies in the region of silicon nitride (−48 to −51 ppm) and silicon oxynitride (−60 ppm).[5] A second broad but major feature at about −114 ppm arises from X-ray amorphous SiO_2, the product of thermal decomposition of the kaolinite. This decreases as the reaction progresses, but never completely disappears from the partly reacted samples. As the reaction proceeds at progressively higher temperatures, a feature in the region −86 to −88 ppm becomes more prominent (Figs 5(D) and (I)), then decreases (Figs 5(E) and (J)); this arises from the formation of mullite, and its behaviour is consistent with the XRD results (Fig. 2). A striking feature of the ^{29}Si spectra is the variation in the Si–O–N resonances in the region about −45 to −70 ppm during the course of the reaction, particularly the late development of the resonance at −65 ppm (Fig. 5(J)) which we found to be diagnostic for well-crystallised X-phase sialon (see above). This resonance is preceded by the earlier appearance of a major feature at about −54 to −58 ppm corresponding to Smith's major X-sialon peak.[9] The conversion of this SiO_2N_2 resonance to the SiO_3N resonance at −65 ppm (Fig. 5(J)) appears to be hindered in the presence of Y_2O_3 (Fig. 5(E)), even though samples both with and without Y_2O_3 show XRD evidence of ample, well-crystallised X-phase sialon. This difference in the O/N ordering of the product phase was the main consequence observed by ^{29}Si NMR of the addition of Y_2O_3 to the reaction mixture.

A selection of typical ^{27}Al MAS-NMR spectra of the partly reacted mixtures is shown in Fig. 6. The most notable feature of the ^{27}Al spectra is the growth of the tetrahedral resonance during the reaction, with only a slight change in the resonance position from 65·5 ppm to about 62 ppm. A hint of asymmetry in the tetrahedral resonance at 1300°C (Fig. 6(C)) may reflect the presence of increased mullite in this sample. A greater change in the position of the octahedral resonance is noted, from about 9 ppm at 1100°C, corresponding to virtually unreacted γ-Al_2O_3, to 1·6 ppm at 1350°C, most of the reaction of γ-Al_2O_3 occurring between 1250 and 1300°C (Fig. 6). The pronounced upfield tail on the octahedral resonance throughout most of the reaction is usually ascribed to electric field gradient (EFG) effects on the spin 5/2 nucleus.[5] Two other small features are worth noting; the shoulder at about 90 ppm in the samples in early stages of reaction (Fig. 6(A)) is in the region assigned by Smith[11] and Fitzgerald *et al.*[12] to AlO_2N_2 units. This feature becomes less evident during the course of the reaction (Fig. 6), probably due to a general broadening of the tetrahedral envelope rather than to the disappearance of these structural units.

Another small feature found only in the well-reacted Y_2O_3-containing samples at about 16 ppm (Fig. 6(E)) is somewhat obscured by the broadness of both the tetrahedral and octahedral envelopes; this does not arise from a Y-containing phase such as yttrium aluminium garnet, YAG (δ = 0·8 ppm),[13] but indicates the presence of a small amount of α-Al_2O_3, confirmed by careful inspection of the XRD traces. The X-phase composition formed in the presence of Y_2O_3 may thus be slightly Al-deficient.

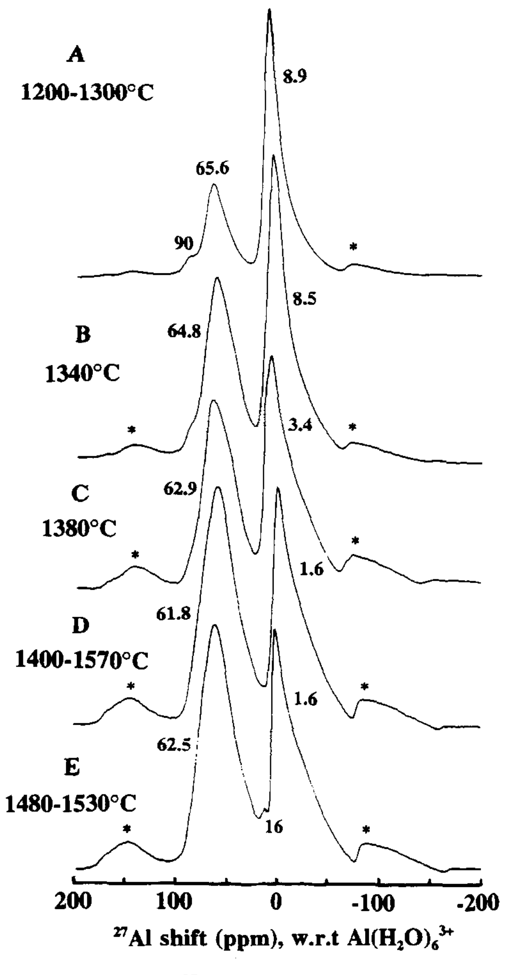

Fig. 6. Typical 11·7 T ^{27}Al MAS-NMR spectra of partially reacted silicothermal X-phase mixtures: (A)–(D) mixture without Y_2O_3, (E) mixture with 2·7 wt% Y_2O_3. Asterisks denote spinning side bands.

The Silicothermal Reaction Sequence

From the combined TG, XRD and MAS-NMR evidence, the reaction sequence involves the following steps, for which the equations are adjusted to the actual molar basis of the reactant mixture:

1. Thermal decomposition of the clay to form mullite and amorphous SiO_2, expected to be fully complete by 1100°C.

$$3\ Al_2Si_2O_5(OH)_4 \rightarrow Al_6Si_2O_{13} + 4\ SiO_2 + 6\ H_2O \quad (1)$$

2. Nitridation of the elemental Si. According to TG and ^{29}Si MAS-NMR, this begins at 1100°C, and is well advanced by 1250°C, although the Si_3N_4 does not become sufficiently crystalline to be detected by XRD <1300°C. TG indicates that in the absence of Y_2O_3, the reaction proceeds in two well-defined stages, possibly associated with the formation of a gas-impermeable nitride layer around the Si grains.

$$6\ Si + 4\ N_2 \rightarrow 2\ Si_3N_4 \quad (2)$$

3. Reaction between γ-alumina and the amorphous silica from (1). ^{27}Al MAS-NMR suggests that most of the reaction occurs between 1250 and 1300°C, with residual SiO_2 persisting to higher temperatures.

$$6\ \gamma\text{-}Al_2O_3 + 4\ SiO_2 \rightarrow 2\ Al_6Si_2O_{13} \quad (3)$$

4. Formation of X-phase sialon. In the absence of Y_2O_3, this phase forms slowly below 1450°C; the lower-temperature product contains comparatively more SiO_2N_2 groups, suggesting that the tri-coordinated anion sites in mullite are the first to be occupied by nitrogen. As the reaction proceeds at higher temperatures, in the absence of Y_2O_3, the regular tetrahedral sites of the mullite structure contain progressively more nitrogen,

evidenced by the increasing dominance of the SiO_3N NMR resonance.

$$3\ Al_6Si_2O_{13} + 2\ Si_3N_4 \rightarrow Si_{12}Al_{18}O_{39}N_8 \quad (4)$$

Although these equations account for the overall stoichiometry of the synthesis reaction, and are consistent with the temperature sequence of these events, they are over-simplified, in not accounting for the appearance of the O′ intermediates. These may result from a degree of early-stage nitridation of oxygenated phases, e.g. mullite, the clay-derived amorphous silica which can contain some Al,[15] or even the oxidised surface layer on the Si grains. The success of the silicothermal synthesis method is probably related to the concomitant formation of labile silicon nitride and aluminosilicate phases which react readily as they form. The addition of Y_2O_3 does not change the overall reaction sequence, but facilitates the various stages, especially (2) and (4).

Conclusions

1. Silicothermal reduction of kaolinite, with adjustment of the Al content by addition of γ-Al_2O_3, constitutes a novel and useful single-step method for the preparation of X-phase sialon, which proceeds to completion in a shorter time and 130°C lower than the comparable two-step carbothermal synthesis. The products of both synthesis methods are essentially monophase, according to XRD, but SEM/EDX measurements show the silicothermal product to have slightly more variability in the Si : Al ratio of the individual grains. The addition of 0·2–3·0 wt% Y_2O_3 to the silicothermal reactant mixture facilitates the formation of X-phase sialon by increasing the rates of the various reaction steps without changing the overall reaction sequence.

2. The reactions involved in silicothermal X-phase formation include formation of mullite and amorphous SiO_2 by thermal decomposition of the clay, nitridation of the elemental Si, reactions between the γ-Al_2O_3 and amorphous SiO_2, and reaction between Si_3N_4 and mullite. Although ^{29}Si MAS-NMR indicates that Si–N bonds are formed in the early stages of the reaction, Si_3N_4 becomes sufficiently crystalline to be detectable by XRD only >1300°C. Two forms of O′-sialon also appear as minor phases during the reaction, probably formed in the early-stage nitridation of the amorphous silica or aluminosilicate.

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