Carbothermal synthesis of low-z β'-sialon from silica or elemental silicon in the presence and absence of Y_2O_3: an XRD and MAS NMR perspective

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Carbothermal formation of low-z β'-sialon ($z=0.5$) from halloysite clay has been carried out using two different forms of the necessary additional silicon, namely, finely divided SiO_2 (quartz) and elemental Si. XRD and solid-state ^{29}Si and ^{27}Al MAS NMR studies of the early stages of the reaction at 1000–1400 °C show that the SiO_2 forms both Si_3N_4, *via* a series of oxynitrides, and SiC. These then react with the mullite produced by thermal decomposition of the clay, to form β'-sialon. The addition of 3 mass% Y_2O_3 to the reaction mix does not change the reaction sequence, but facilitates the formation of both mullite and β'-sialon, in which it also promotes the formation of Al—N units. Using elemental Si, some SiC is formed, which reacts with the mullite and remaining Si to form O′-sialon, which may then react further with mullite to produce β'-sialon. The addition of Y_2O_3 forms transient $Y_2Si_2O_7$ at lower temperatures, but in the later stages facilitates the formation of β'-sialon with respect to O′-sialon.

Carbothermal synthesis is a convenient and cost-effective means of converting aluminosilicate minerals into β'-sialon, $Si_{6-z}Al_zO_zN_{8-z}$, in which z can vary between 0 (Si_3N_4) up to *ca.* 4.3. When the starting material is a kaolinite or halloysite clay in which the Si : Al ratio is typically *ca.* 1, the expected product composition has $z \approx 3$. For this reason, many of the previous carbothermal synthesis studies have been of sialons with $z=2.5$–3.[1] However, sialons of lower z value are of practical interest, since a decreasing Al content is balanced by an increase in N content, with physical properties approaching those of Si_3N_4, but combined with the sintering benefits of the Al. The present work was therefore directed towards the carbothermal synthesis of a low-z sialon (nominally $z=0.5$), the additional Si being supplied either by silica or elemental silicon.

Another potentially very useful class of compounds is the α-sialons, which typically contain structural yttrium or lanthanide atoms and occur in a stability region adjacent to the low-z β'-sialons; the latter may therefore represent suitable precursor phases for preparation of the α-sialons, provided a suitable method can be found for incorporating the yttrium into the precursor. A parallel series of experiments was therefore also carried out in which 3 mass% Y_2O_3 was added prior to the synthesis to evaluate the effect of such additional constituents on the reaction sequence. A combination of XRD and solid-state MAS NMR, which has provided useful information on the reaction sequences in other sialon studies,[1,2] was used to monitor the present reactions in the temperature range (<1400 °C) below that at which carbothermal sialon formation normally goes to completion.

Experimental

The starting materials were halloysite (NZ China Clays Ltd.), carbon (Degussa lampblack), SiO_2 (Superfine Silica, $d_{50}=1.45\ \mu m$, Commercial Minerals Ltd.), elemental Si powder (Permascand 4D) and Y_2O_3 (H. C. Starck, grade C). The halloysite contains 9% of residual crystalline SiO_2, which was taken into account when formulating the mixtures. These were blended in the correct proportions (incorporating 10% excess carbon), ball milled in ethanol for 24 h, dried in a rotary evaporator and extruded into rods of *ca.* 4 mm diameter. Firings were carried out in small alumina boats under flowing purified N_2 (50 ml min^{-1}). The samples were heated at 10 °C min^{-1} to the specified temperature, held for 2.0 h then cooled under N_2 at 10 °C min^{-1}. After crushing, the samples were examined by XRD (Philips PW 1700 automatic diffractometer) and by ^{27}Al and ^{29}Si MAS NMR at 11.7 T using a Varian Unity 500 spectrometer and 5 mm Doty high-speed probe spun at 10–12 kHz. The spectrometer conditions were: ^{27}Al, 1 µs $\pi/10$ pulse for solution, recycle delay of 5 s, referenced to 1 M aqueous $Al(NO_3)_3$; ^{29}Si, 6 µs $\pi/2$ pulse, recycle delay typically 300 s to allow for the presence of slow-relaxing species sometimes encountered in sialon systems.[1] The ^{29}Si were referenced to tetramethylsilane (TMS).

Results and Discussion

Reaction sequence with SiO_2 (quartz)

XRD detection of the various phases occurring during the early stages of reaction in this system in the absence and presence of Y_2O_3 after firing for 2 h is shown semi-schematically in Fig. 1A and B, respectively. Because of the amorphous nature of many of the phases occurring in this temperature range (1000–1400 °C), the XRD traces typically consisted of a broad background hump on which were superimposed sharp peaks of the developing crystalline phases, which, apart from the quartz reactant, were of low intensity. For this reason, even semi-quantitative XRD estimates of the phase composition were not possible, but the semi-schematic representation in Fig. 1 summarises the changes occurring as the reaction proceeds, based on the peak height of the major XRD reflection of each phase.

Fig. 1A indicates that in the absence of Y_2O_3, mullite appears >1150 °C. This phase is insufficiently crystalline to permit a lattice parameter measurement, from which its composition could be deduced; previous experience with mullite derived from clay minerals[3] suggests however that in its initial stages its composition should be alumina-rich. The next phases (Si_3N_4 and SiC) appear at >1250 °C, formed by action of the carbon on the free silica present. The latter is present in two forms, the reactive amorphous silica resulting from thermal decomposition of the clay, and the added quartz, which has begun to convert to cristobalite at about 1300 °C (Fig. 1A). β'-Sialon first appears in this system above 1350 °C, presumably forming *via* alumina-rich precursors which are not sufficiently crystal-

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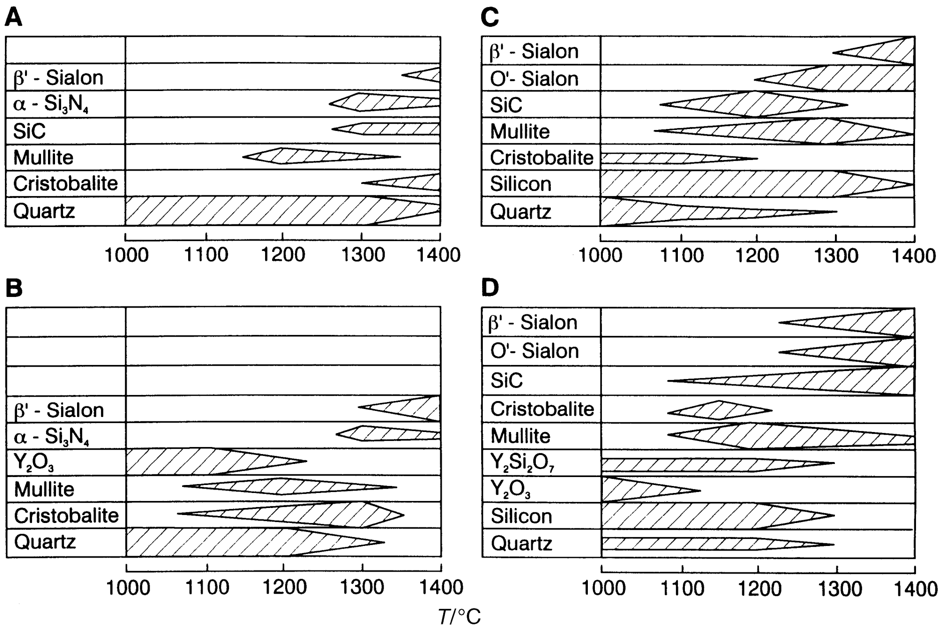

Fig. 1 Schematic representation of the phases detected by XRD during carbothermal reaction of (A,B) SiO_2–clay mixtures, (C,D) elemental Si–clay mixtures. Systems B and D also contain 3 mass% Y_2O_3.

line to be detected by XRD. The z-values of the β′-sialon in all the well reacted (1400 °C) samples, estimated from the XRD patterns, ranged from 0.45 to 0.70, spanning the target composition of the batched starting mixtures.

In the presence of Y_2O_3, a similar sequence of events occurs (Fig. 1B), but at temperatures which are modified by the yttria. The appearance temperatures of mullite and cristobalite detectable by XRD are lowered by about 100 and 250 °C respectively, but the appearance temperature of Si_3N_4 is unaffected by the Y_2O_3 (Fig. 1B). In this system, cristobalite formation clearly begins with the silica separated from the clay, but above 1200 °C, the quartz has also begun to transform. Another consequence of the early removal of the more reactive silica is the apparent lack of SiC formation, but MAS NMR results (see later) indicate that SiC is in fact present. The system proceeds directly to β′-sialon about 50 °C lower than in the absence of Y_2O_3, which also appears to increase the rate of β′-sialon formation.

Typical ^{29}Si MAS NMR spectra of the reacting system containing quartz, both with and without Y_2O_3, are shown in Fig. 2.

The spectrum of the unheated material (Fig. 2A) shows the expected peaks for halloysite at about −91 ppm and quartz at −108 ppm. Reaction at 1000–1100 °C results in a shift of the clay peak to about −104 ppm (Fig. 2B), corresponding to the destruction of the layer lattice by removal of the structural water.[4] The single broadened peak envelope also contains, in addition to the original quartz resonance, a contribution from the amorphous free silica resulting from the thermal decomposition of the clay. In samples containing Y_2O_3, a small peak at about −84 ppm which appears at 1100 °C (Fig. 2C) suggests the presence of mullite, consistent with the XRD result. Mullite formation is not detected by XRD at this temperature in the absence of Y_2O_3 (Fig. 2F).

In the ^{29}Si spectra of samples containing Y_2O_3, heating to higher temperatures <1400 °C produced little further change, apart from the appearance of a small feature at about −55 ppm which may indicate the incipient formation of the β′-sialon at 1300 °C (Fig. 2D). The shift of this peak is somewhat away from the normal position for β′-sialon (−48 ppm), but is close to the position of melilite ($Y_2Si_3O_3N_4$) (about −57 ppm) suggesting the possible transient formation of this phase; this

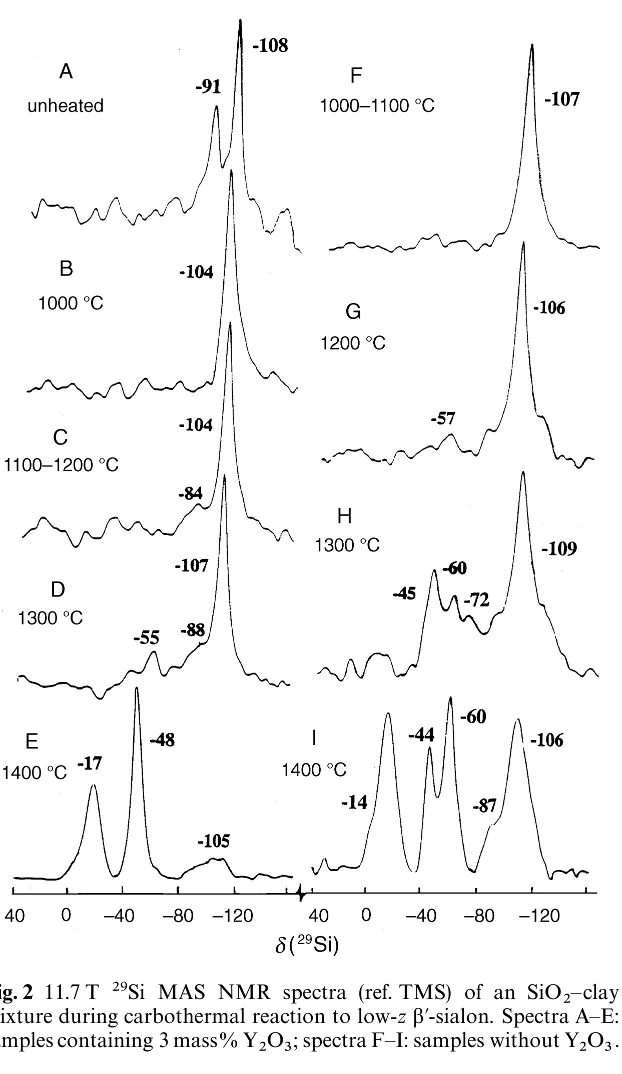

Fig. 2 11.7 T ^{29}Si MAS NMR spectra (ref. TMS) of an SiO_2–clay mixture during carbothermal reaction to low-z β′-sialon. Spectra A–E: samples containing 3 mass% Y_2O_3; spectra F–I: samples without Y_2O_3.

could not however be confirmed by XRD. Between 1300 and 1400 °C, the spectrum undergoes a sudden change, with the appearance of the characteristic β′-sialon resonance at −49 ppm[1] and a broad SiC peak at −17 ppm (Fig. 2E). Thus, in the presence of Y_2O_3, the sialon-forming reaction occurs very rapidly and directly between 1300 and 1400 °C, consistent with the XRD results.

By contrast, the ^{29}Si spectra of mixtures without Y_2O_3 contain a number of new resonances at 1300 °C (Fig. 2H). In addition to the −45 ppm peak in the region of β′-sialon, other features at −60 to −70 ppm indicate the presence of oxynitride species; the peak at −60 ppm corresponds to Si_2N_2O,[1] whereas resonances further upfield may indicate more highly oxygenated oxynitrides. A good deal of free silica persists in this sample, evidenced by the major feature at −109 ppm with a broad underlying band (Fig. 2H). The major change in the ^{29}Si spectrum on heating this sample to 1400 °C is the appearance of a strong but broad SiC peak at −14 ppm (Fig. 2I) and the growth of the oxynitride peak at −60 ppm with a concomitant decrease in the free silica resonance. The origin of the slight shoulder on the SiC peak (Fig. 2I) is presently unknown. Thus, these spectra suggest that in the absence of Y_2O_3, the β′-sialon forms *via* oxynitride intermediates which become progressively more nitrogen rich as the reaction proceeds. The presence of Y_2O_3 may either suppress the formation of these oxynitride intermediates, or affect their reaction rate so that they form and disappear extremely rapidly over a very short temperature interval. That the formation of oxynitride intermediates and SiC in the absence of Y_2O_3 was detected by MAS NMR but not by XRD is not surprising in view of the large amount of interfering non-crystalline material which obscured the more crystalline phases in the XRD traces; this is a good example of the usefulness of MAS NMR in providing information unavailable to XRD.

Some typical ^{27}Al MAS NMR spectra are shown in Fig. 3, which includes samples derived from both SiO_2 and elemental Si (see below), with and without Y_2O_3.

Because of the low Al contents of these samples, the ^{27}Al spectra were all weak and rather noisy, and were processed by subtracting the broad background spectrum arising from the probe. The spectra of the unheated mixes (Fig. 3A) all show the typical sharp octahedral resonance of halloysite clay at about 4 ppm. The spectra of the partially reacted mixtures (Fig. 3B–D) indicate the presence of both octahedral and tetrahedral Al sites in the early stages of the reaction, with the tetrahedral component, estimated by spectral integration, increasing with heating temperature both in the presence and absence of Y_2O_3 (Fig. 4A). The general features of the lower temperature spectra are consistent with the formation of mullite,[1] but the resolution is not sufficiently good to detect the presence of a second tetrahedral peak thought to arise from the sites in which Al is coordinated to only three oxygen atoms.[5] In samples reacted at 1000–1200 °C, the proportion of tetrahedral sites is less than expected for well crystallised mullite measured at 11.7 T (52–53%[1]) but this characteristic mullite site distribution is established between about 1200–1300 °C, consistent with the XRD results. As with the ^{29}Si spectra, the ^{27}Al spectrum of the Y_2O_3-containing sample undergoes a sudden change at 1400 °C (Fig. 3F), with the appearance of a typical Al—N resonance at 115 ppm and the loss of most of the octahedral intensity; this spectrum contains the characteristic features of β′-sialon, which contains both Al—N and Al—O tetrahedral units.[1] As was found for carbothermal synthesis of higher-*z* β′-sialon at higher temperatures,[1] the Al—N bonds become established at a late stage in the reaction. In the absence of Y_2O_3, the formation of the Al—N units is delayed, with no evidence of the characteristic nitride peak at 1400 °C; all the ^{27}Al spectral intensity in this sample is concentrated in the broad tetrahedral β′-sialon resonance centred at about 60 ppm.

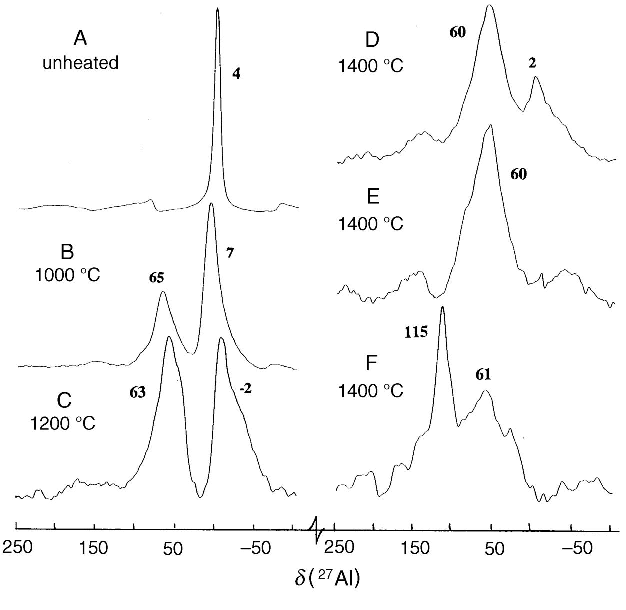

Fig. 3 Typical 11.7 T ^{27}Al MAS NMR spectra [ref. $Al(H_2O)_6^{3+}$] of low-*z* β′-sialon-forming mixtures during carbothermal reaction. Spectra A,B,D,E: elemental Si–clay mixtures; spectra C,F: SiO_2–clay mixtures. Samples A,C,E and F contain 3 mass% Y_2O_3.

Reaction sequence with elemental Si

The XRD results of Fig. 1C and D show that both in the presence and absence of Y_2O_3, the formation of β′-sialon is accompanied by the appearance of O′-sialon, which in the

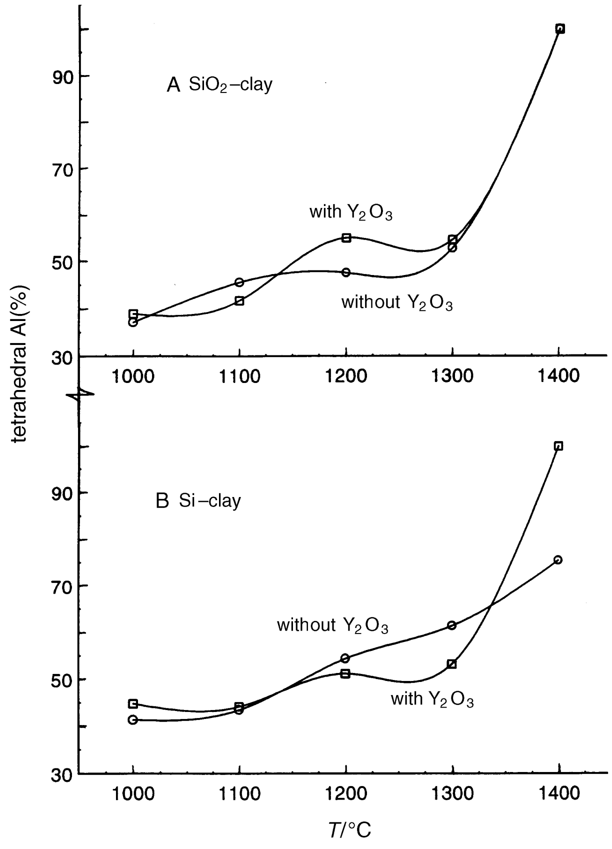

Fig. 4 Tetrahedral ^{27}Al MAS NMR site population as a function of temperature during carbothermal formation of low-*z* β′-sialon in the presence and absence of Y_2O_3. The 1400 °C point for the sample containing SiO_2–clay with Y_2O_3 does not take into account the presence of the Al–N resonance in this spectrum.

absence of Y_2O_3 precedes the β′-sialon by about 100 °C. SiC and mullite appear >1100 °C; in the absence of Y_2O_3, both are transitory phases, but in the presence of Y_2O_3 the SiC shows no sign of diminishing even at 1400 °C (Fig. 1D). The Y_2O_3 reactant itself has disappeared by 1100 °C, having been replaced by $Y_2Si_2O_7$, probably formed at lower temperatures by reaction with the reactive amorphous SiO_2 resulting from the thermal decomposition of the clay to form mullite. The $Y_2Si_2O_7$ persists to <1300 °C, by which temperature both Si and quartz have also disappeared. In the absence of Y_2O_3 (Fig. 1C), the behaviour of the quartz is similar, but the elemental Si is fully consumed at a higher temperature (<1400 °C).

Fig. 5 shows typical ^{29}Si MAS NMR spectra of the carbothermal system containing elemental Si, with 3 mass% Y_2O_3 (Fig. 5A–D) and without Y_2O_3 (Fig. 5E–I).

The spectrum of the unheated mixture (Fig. 5E) shows the expected halloysite resonance at −92 ppm and the elemental Si resonance at −80 ppm. The small amount of residual quartz from the clay is detectable as a broad peak at −109 ppm (Fig. 5E).

On heating with Y_2O_3 at 1000–1100 °C, the Si resonance broadens and its centre of gravity shifts downfield and approaches the position of Si_2N_2O (−63 ppm[1]), although neither this phase nor its Al-containing analogue O′-sialon are sufficiently well ordered to be detected by XRD at this temperature. ^{29}Si MAS NMR confirms the presence of SiC (−14 ppm) in these samples at 1200 °C; this resonance continues to increase with increasing reaction temperature, in agreement with the XRD results (Fig. 1D). The continued presence of elemental Si is denoted by the persistence to 1300 °C of the resonance at about −70 ppm (Fig. 5C), the slight downfield shift from the position of this resonance in the unheated mixture suggesting the incorporation of some nitrogen, possibly as a surface nitride layer. By 1300 °C, the presence of O′-sialon can be discerned as a shoulder on the downfield side of the broad central band of Si—O—N resonances (Fig. 5C), which can be resolved in the sample heated at 1400 °C into peaks at −43 and −56 ppm (Fig. 5D). These peaks can be identified with β′-sialon and O′-sialon respectively,[1] although both are about 5 ppm downfield of the tabulated positions for these phases (*ca.* −48 and −61 ppm respectively[1]). The present ^{29}Si spectra show no clear indication of $Y_2Si_2O_7$, of which the γ-polytype appears at −92.8 ppm.[6] This resonance, if present, may be obscured by the broad SiO_2 peak centred at −110 to −106 ppm; alternatively, this phase could have a long relaxation time[6] which would militate against its detection under the present conditions.

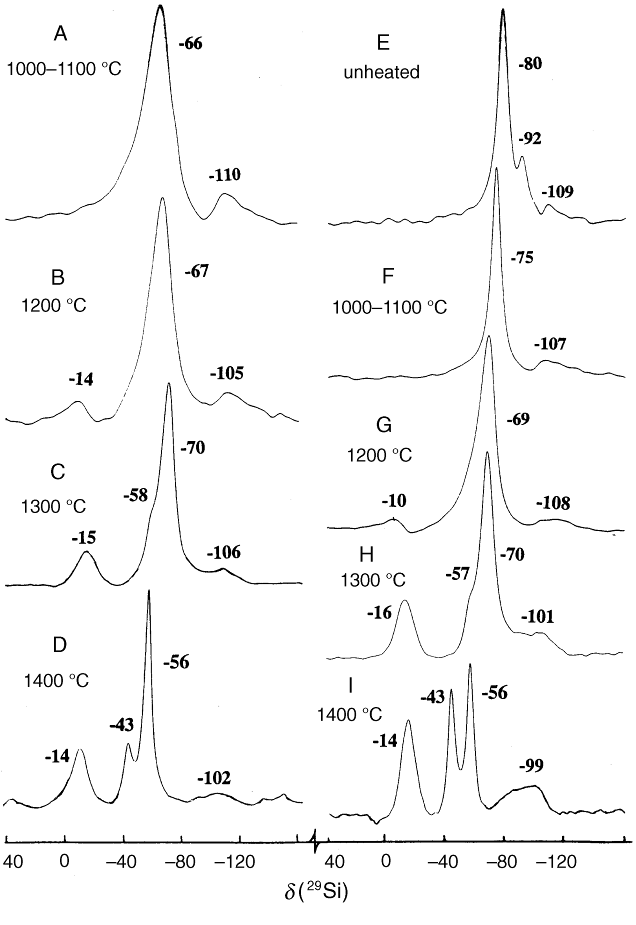

Fig. 5 11.7 T ^{29}Si MAS NMR spectra (ref. TMS) of elemental Si–clay mixtures during carbothermal reaction to low-z β′-sialon. Spectra A–D: samples containing 3 mass% Y_2O_3; spectra E–I: samples without Y_2O_3.

In the absence of Y_2O_3, the major elemental Si resonance shows a downfield shift to about −70 ppm as heating progresses (Fig. 5G), similar to the mixtures containing Y_2O_3, but without the early broadening shown by the latter. At 1300–1400 °C, the spectra of mixtures with and without Y_2O_3 show the development of similar features, but the mixture without Y_2O_3 heated at 1400 °C shows relatively more intense resonances of SiC and β′-sialon (Fig. 5I).

The ^{27}Al MAS NMR spectra of mixtures containing elemental Si heated below 1400 °C (Fig. 3) are very similar to those of the SiO_2-containing mixtures, but in the absence of Y_2O_3, a more gradual and progressive increase in the tetrahedral intensity with temperature is evident (Fig. 4B); residual octahedral sites are still present in these mixtures at 1400 °C (Fig. 3D). At this temperature, the sample containing Y_2O_3 no longer contains octahedral Al (Fig. 3E), but the Al—N units have not yet appeared at 115 ppm.

Implications for the mechanism of sialon formation

(*a*) **Carbothermal reaction with SiO_2/clay.** Both the XRD and NMR results indicate that the first reaction is the thermal decomposition of the clay to form mullite and amorphous SiO_2 [eqn. (1)].

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

The amorphous SiO_2, and possibly some of the quartz reactant, is then carbothermally reduced *via* a series of oxynitrides which become progressively more nitrogen-rich [eqn. (2) and (3)].

$$2SiO_2 + 3C + N_2 \rightarrow Si_2N_2O + 3CO \qquad (2)$$

$$Si_2N_2O + SiO_2 + N_2 + 3C \rightarrow Si_3N_4 + 3CO \qquad (3)$$

Concomitant with the formation of Si_3N_4, SiC also forms [eqn. (4)].

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (4)$$

β′-Sialon ($z = 0.5$) then forms by reaction between mullite, Si_3N_4 and SiC [eqn. (5)].

$$Al_6Si_2O_{13} + 19Si_3N_4 + 7SiC + 7N_2 \rightarrow 6Si_{11}AlON_{15} + 7CO \qquad (5)$$

In the presence of Y_2O_3, the reaction follows the same sequence, but the temperature of mullite formation is lowered by about 100 °C, the β′-sialon formation temperature is lowered by about 50 °C and the formation of the characteristic Al—N units in the β′-sialon is facilitated. These observations suggest that the action of the Y_2O_3 is to facilitate diffusion processes, not only by the formation of liquid at higher temperatures (≈1350 °C), but also in the solid state at mullite formation temperatures. The SiC which is formed in the presence of Y_2O_3 is detectable by NMR but not by XRD, suggesting that it is incorporated at higher temperatures in an amorphous or glassy phase which must also contain the silica which in the absence of Y_2O_3 is detectable in plentiful amounts both by NMR (Fig. 2I) and XRD.

(***b***) **Carbothermal reaction with elemental Si/clay.** The initial reaction is again the formation of mullite from the clay [eqn. (1)]. Concomitant with mullite formation, SiC is formed from either or both of the Si sources [eqn. (4) and (6)].

$$Si + C \rightarrow SiC \tag{6}$$

Reaction between mullite, SiC and elemental Si then results in the formation of O′-sialon, $Si_{2-x}Al_xO_{1+x}N_{2-x}$. Although the XRD reflections from this and the other crystalline phases were too weak to permit sufficiently precise cell parameter measurements to determine the present O′-sialon composition, measurements on fully reacted mixtures of similar composition[7] suggest a degree of Al substitution (x) approaching 0.2; this was therefore assumed [eqn. (7)].

$$Al_6Si_2O_{13} + 23SiC + 29Si + 27N_2 \rightarrow 6Si_9AlO_6N_9 + 23CO \tag{7}$$

This reaction may either precede the formation of β′-sialon, or proceed in tandem with it, in the absence and presence of Y_2O_3 respectively. β′-Sialon formation may therefore proceed *via* O′-sialon [eqn. (8)], or directly from mullite [eqn. (9)].

$$Si_9AlO_6N_9 + 2SiC + 3C + 3N_2 \rightarrow Si_{11}AlON_{15} + 5CO \tag{8}$$

$$Al_6Si_2O_{13} + 7SiC + 57Si + 45N_2 \rightarrow 6Si_{11}AlON_{15} + 7CO \tag{9}$$

Under the present conditions, this reaction sequence is also followed in the presence of Y_2O_3, which however facilitates the formation of β′-sialon with respect to O′-sialon. By contrast with the SiO_2/clay system, the formation temperature of mullite is unchanged by the presence of Y_2O_3, probably because of the early formation of a transient $Y_2Si_2O_7$ phase, which renders the Y_2O_3 unavailable for the lower temperature reactions.

Conclusions

The course of carbothermal synthesis of low-z β′-sialon from SiO_2/clay mixtures, as revealed by XRD and MAS NMR, is similar to the reaction sequence for sialons of higher z-value, and involves the intermediate formation of mullite and α-Si_3N_4. SiC, which forms during the later stages of the reaction, was readily detected by ^{29}Si MAS NMR even when not apparent by XRD. The additional SiO_2, added in the form of fine quartz powder to adjust the composition of the final product, forms cristobalite during the course of the reaction; this is progressively consumed in the later stages. In the absence of Y_2O_3, sialon formation proceeds *via* a series of oxynitride intermediates, which become progressively more nitrogen rich during the reaction. These oxynitride species are detected by ^{29}Si MAS NMR but not by XRD.

Addition of 3 mass% Y_2O_3 to the reaction mixture results in a general increase of reactivity in the system, lowering the formation temperature of both mullite and cristobalite, and promoting the rapid formation of β′-sialon $>1300\,°C$ without the appearance of stable oxynitride intermediates. The presence of Y_2O_3 also facilitates the formation of the characteristic Al—N units in the β′-sialon. The Y_2O_3 concentration used here was too low to permit MAS NMR evidence of the formation of Y-containing phases, but all the results are consistent with a mechanism in which the atomic mobility of the system is increased by the presence of Y. Although the mechanism may involve the formation of a small amount of liquid phase at higher temperatures, the facilitation of mullite and cristobalite formation as low as 1050 °C suggests that the Y also assists solid-state diffusional processes.

Carbothermal reaction of mixtures containing elemental Si as the source of additional silicon constitutes a useful alternative route to low-z β′-sialons. The reaction proceeds *via* the formation of SiC, which, together with elemental Si, reacts with mullite formed by thermal decomposition of the clay to produce O′-sialon and β′-sialon. As with mixtures utilising SiO_2 as the Si source, the addition of Y_2O_3 facilitates the reactions at higher temperatures by liquid formation, but does not influence the lower temperature formation of mullite, probably because of the removal of available Y in the formation of transient crystalline $Y_2Si_2O_7$.

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Paper 6/07677G; *Received* 12*th November*, 1996