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Silicothermal Synthesis and Densification of X-sialon in the Presence of Metal Oxide Additives

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Abstract

The effect is reported of seven inorganic oxide additives on both the formation mechanism and the densification of X-sialon prepared by a silicothermal process. The oxides were added to the starting mixture of halloysite clay, alumina and elemental silicon at a level of 1 wt% of the calculated final product, and fired in nitrogen at 1200–1500°C. The formation of X-sialon was monitored by thermal analysis, powder XRD and ^{27}Al *and* ^{29}Si *solid state MAS NMR. The effects of the additives are temperature dependent, and influence the various stages of the reaction by differing degrees. The oxides which best promote the formation of crystalline X-sialon (*Y_2O_3*, CaO and MgO) are also those which facilitate the conversion of initially-formed* Si_3N_4 *to* SiO_2N_2 *and* SiO_3N *units, the latter being particularly enhanced by* Y_2O_3*,* Fe_2O_3 *enhances the initial nitridation of Si but suppresses X-sialon formation by stabilising the preceding mullite phase. Densification is most enhanced by* Y_2O_3*, CaO and* CeO_2*; MgO exerts its maximum effect on sintering at lower temperatures. The beneficial influence of MgO and* Y_2O_3 *on both X-sialon formation and sintering is due to the formation of liquid phases. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: sialon, clay, Al_2O_3, silicon, sintering.

1 Introduction

X-sialon ($Si_{12}Al_{18}O_{39}N_8$) has a structure similar to mullite ($Al_6Si_2O_{13}$) and exists as a solid solution between mullite and Si_3N_4. In a previous paper[1] we reported a single-step silicothermal reduction method for producing sintered X-sialon ceramic bodies from kaolinite, dehydroxylated $Al(OH)_3$ and elemental silicon powder. Y_2O_3 is a well-known sintering aid and the addition of 3 wt% of this oxide to the silicothermal reaction mixture was found not only to assist densification but also to facilitate the silicothermal synthesis reaction without altering the reaction sequence.[1,2] Since other additives are also known which promote the formation of β, α and O-sialon,[3–6] the question arises how these might influence the silicothermal formation or sintering of X-sialon. This paper reports a systematic study of the effect of a low concentration (1 wt%) of MgO, CaO, BaO, Fe_2O_3, Y_2O_3, ZrO_2 and CeO_2 in the temperature range 1200-1500°C, using a combination of thermogravimetry, powder XRD and solid state MAS NMR to monitor the reaction sequence, and water absorption to monitor the bulk density and open porosity of the sintered bodies. The results are compared with those for additive-free control samples prepared under the same conditions.

2 Experimental

The starting materials were halloysite clay, $Al_2Si_2O_5(OH)_4.2H_2O$, (NZ China Clays Ltd.), elemental silicon powder (Permascand 4D) and $Al(OH)_3$ (British Drug Houses, reagent grade). Prior to batching, the $Al(OH)_3$ was dehydroxylated to γ-Al_2O_3 by heating at 800°C for 3·5 h. The mixture was batched to give the composition $Si_{12}Al_{18}O_{39}N_8$, ball milled for 20 h in hexane, using Si_3N_4 milling media, and the solvent removed by vacuum rotary evaporation before drying. A series of mixtures were then made from this feedstock with the additives MgO, CaO, BaO, Fe_2O_3, Y_2O_3, ZrO_2 and CeO_2, containing 1 wt% of the oxide based on the calculated yield of the X-sialon. Ca and Ba were added as the carbonates in an amount corrected for decomposition to the oxide. After hand grinding under ethanol, the homogenised

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*To whom correspondence should be addressed mixtures were dried at 100°C, granulated and uniaxially pressed at 140 MPa into 10 mm dia. 0·25 g pellets. Firings were carried out in a laboratory horizontal tube furnace under flowing nitrogen (100 ml min^{-1}) at a heating rate of 5°C min^{-1} to 1100°C, then 2°C min^{-1} to the maximum temperature (1200–1500°C). The furnace was cooled immediately on reaching the maximum temperature. Separate 10 mm discs were prepared for examination by thermogravimetry in flowing purified nitrogen, using a Mettler model 21 thermobalance and the same heating rate regime as for the tube furnace experiments but with a holding period of 4 h at the maximum temperature (1450°C).

The surfaces of the pellets fired in the tube furnace were lapped on a diamond wheel and examined by XRD (Philips PW1700 series automatic diffractometer with CoKα radiation and graphite monochromator). Bulk densities and open porosities were measured by the water absorption method. The pellets were then ground for examination by solid state ^{27}Al and ^{29}Si MAS NMR. All spectra were acquired at 11·7 T using a Varian Unity 500 spectrometer and a Doty high-speed 5 mm MAS probe (spinning speed 10–12 kHz) under the following conditions: ^{29}Si: 6 μs $\pi/2$ pulse with a recycle delay of 100 s, spectra referenced to tetramethylsilane (TMS), ^{27}Al: 1 μs $\pi/10$ pulse for solution with a recycle delay of 5 s, spectra referenced to 1 M aqueous $Al(NO_3)_3$ solution.

3 Results and Discussion

3.1 Thermogravimetric analysis

The TG curves of the various reaction mixtures all show an initial mass loss of about 10% below 600°C, corresponding to the removal of hydration and structural water from the halloysite clay component. Mass gains due to nitridation reactions begin at about 1100°C and continue up to 1350–1400°C, when in most mixtures the weight gain slows or stops. The high-temperature portions of the TG curves are shown in Fig. 1. In previously studied mixtures containing kaolinite[1] the nitridation weight gain in the absence of oxide additives occurred in two distinct steps; the first, of about 3%, was attributed to the formation of Si_3N_4 from the elemental Si which reaches a plateau with the formation of a gas-impermeable product layer but continues again when the layer is disrupted by the formation of X-sialon. By contrast, in the present halloysite-containing control mixture the weight gain occurred in one continuous step. The halloysite clay contains an excess (~9%) of free silica (both quartz and cristobalite) and the nitridation of this silica to silicon oxynitride may mask the two step nitridation of the silicon. The formation of the oxynitride from silica (from either excess silica in the clay or the decomposition of the clay) provides a mechanism for the production of X-sialon alternative to the one suggested earlier.[1]

$$\underset{\text{excess silica}}{2SiO_2} + 6Si + 4N_2 \rightarrow \underset{\text{silicon oxynitride}}{4Si_2N_2O} \qquad (1)$$

$$\underset{\text{siliconoxynitride}}{4Si_2N_2O} + 3Al_2O_3 \underset{\text{mullite}}{+2Al_6Si_2O_{13}} \rightarrow \underset{\text{X-sialon}}{Si_{12}Al_{18}N_8O_{39}} \qquad (2)$$

The nitridation reactions proceed in one continuous step for all the additives studied in this work (Fig. 1). This was also found for Y_2O_3 in the previous study.[1]

The effect on nitridation was generally similar for all the oxides except Fe_2O_3, which markedly facilitates the reaction by accelerating the nitridation without lowering the onset temperature. Since the initial formation of Si_3N_4 is only part of the overall reaction sequence and (as will be shown below) must be followed by the formation of silicon oxynitride, the accelerating effect of iron on this initial step is not in itself desirable, especially if the stability of the Si_3N_4 product is such as to interfere with the subsequent stages in the reaction sequence.

3.2 X-ray diffraction of the fired products

A previous XRD study[1] indicated a reaction sequence which involves (i) the removal of elemental silicon by nitridation, (ii) the formation of mullite both by thermal decomposition of the clay component and by solid-state reaction between the

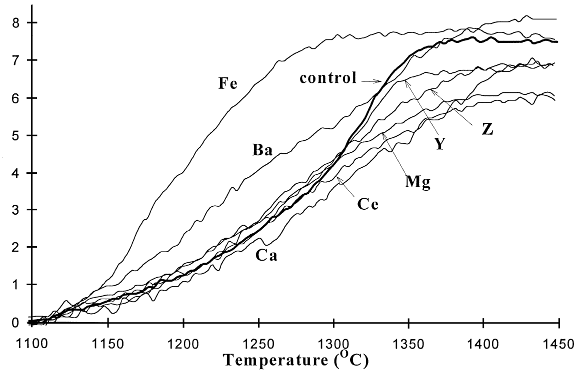

Fig. 1. TG mass-gain curves for pressed pellets of the silicothermal X-sialon mixture containing 1 wt% of the indicated metals as their oxide. Atmosphere: purified N_2, Heating rate: 2°C/min. above 1100°C. Heavy line indicates the additive free control sample.

γ-Al_2O_3 and the amorphous silica from the clay decomposition and (iii) the appearance of X-sialon.

The present XRD data show that the presence of oxide additives can influence each of these stages to varying degrees. The removal of elemental silicon, deduced from intensity measurements of the 3·13Å 111 reflection is most enhanced in the presence of Fe, Ce and Zr [Fig. 2(A)]. By 1400°C the Si reflection has disappeared from all samples, including the additive-free control. The formation of a small amount of Fe_3Si was observed in the Fe-containing sample at 1200°C but this phase was short lived, having disappeared from the XRD trace by 1250°C.

The formation of mullite, monitored by intensity measurements of the 5·39Å 110 reflection is also influenced by the present additives [Fig. 2(B)] being suppressed and its appearance delayed in the presence of Zr and Fe. Additives which favour the early formation of significant quantities of mullite under the present reaction conditions are Mg and Ca. Of more significance for the formation of X-sialon is the degree to which the mullite is removed at highest temperatures; this occurs most strongly with Y, Ca and Mg and least in the presence of Fe, which maintains a high mullite concentration at 1500°C, possibly due to its incorporation in the mullite structure.

These results bear some relationship to the growth in X-sialon, monitored by the intensity of the 3·62Å 100 reflection [Fig. 2(C)]. This shows that at 1400°C the greatest amount of crystalline X-sialon is formed in the presence of Y and Mg, followed by Ce. At 1400°C the least X-sialon is formed in the additive-free control. The beneficial effects of Y and Mg are probably due to the formation of liquid phases at the reaction temperature, which facilitate the atomic movements, bond breaking and reforming necessary to progress from mullite to X-sialon.

3.3 ^{29}Si MAS NMR spectroscopy

The ^{29}Si NMR spectra show considerable differences with the different additives but because of the broadness of the spectra their interpretation is confined here to a consideration of the changes with temperature of several characteristic spectral regions as the samples progress from 1200°C [Fig. 3(A)] towards the spectrum reported for X-phase[1] of silicothermal origin [Fig. 3(C)].

At 1200°C the ^{29}Si spectra [Fig. 3(A)] all contain a typically strong, broad but occasionally partly resolved feature at about −50 to −70 ppm corresponding to various Si–O–N units, a weaker band at −80 to −95 ppm (typically associated with framework aluminosilicates) and another weak band in the region of free silica (−105 to −115 ppm). The

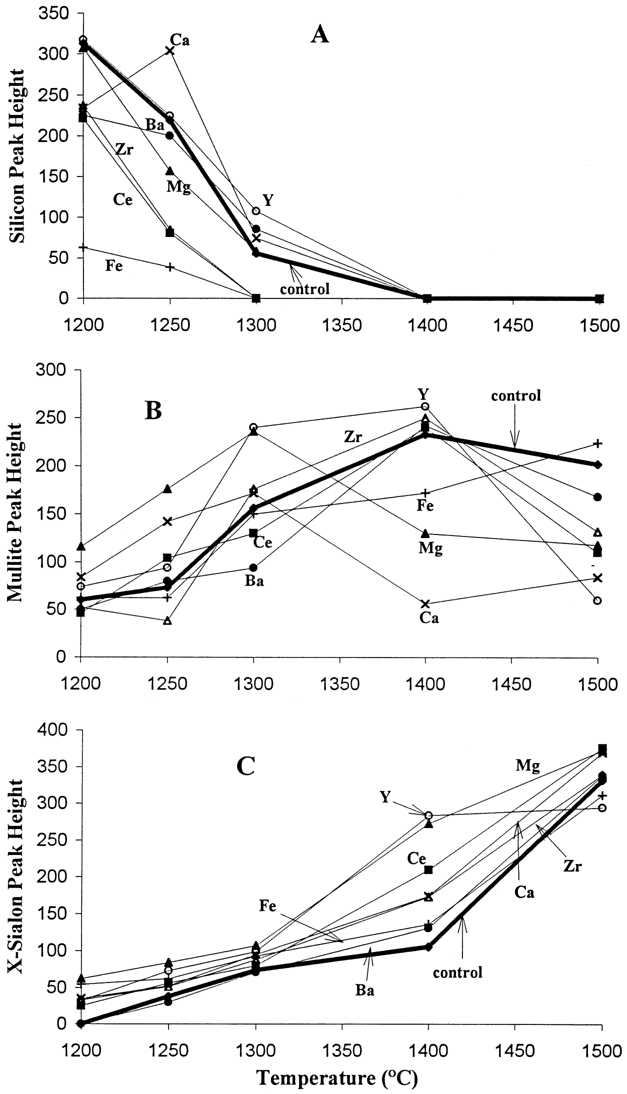

Fig. 2. Changes in XRD peak intensity with heating temperature for X-sialon mixtures containing the indicated oxide additives. A. Elemental Si (d = 3·13 Å), B. Mullite (d = 5·39 Å), C. X-sialon (d = 3·62 Å). Heavy lines indicate the additive free control sample.

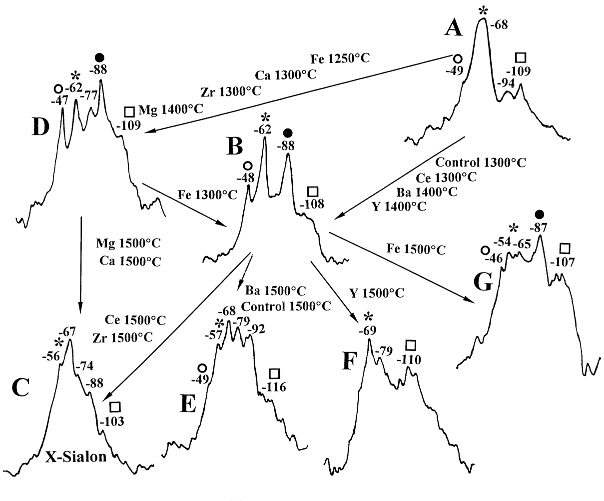

Fig. 3. Typical 11·7 T ^{29}Si MAS NMR spectra of the intermediate phases and product in reacting X-sialon silicothermal mixtures, illustrating the effect of the various metal oxides on the spectra. Key: * = silicon oxynitrides ○ = Si_3N_4 □ = SiO_2 ● = mullite.

latter two bands are as expected from the decomposition products of the clay mineral (mullite and free silica), while the major band arises from the nitridation products of silicon and silicates. During the course of the silicothermal reaction the ^{29}Si NMR spectrum progresses towards the spectrum of X-sialon [Fig. 3(C)], consisting of an envelope of peaks at about −56, −67 (the most intense), −74 and −88 ppm.[1] In this spectrum the shoulder at −56 ppm is associated with SiO_2N_2 units, whereas the major resonance at −67 ppm and the shoulder at −74 ppm are more typical of SiO_3N units.[1] The shoulder at −88 ppm arises from the tetrahedral Si(Al)-O unit of mullite.[1] Under the present reaction conditions only the samples containing Mg, Ce, Zr and Ca achieve the typical X-sialon spectrum at 1500°C, although the essential elements of the spectrum are exhibited by all the other samples.

The changes in the ^{29}Si NMR spectra over the range 1200–1500°C were monitored from curve-fitted estimates of the relative amounts of ^{29}Si contributing to the various regions of the spectra. The results are summarised as follows:

(a) Non-additive control. A high initial concentration of Si_3N_4 (−49 ppm) progressively decreases on heating to 1500°C. Silicon oxynitride (−62 ppm) remains low until 1400°C, when it increases abruptly and shifts to become the major X-sialon band at −68 ppm. The mullite-like Al–O resonance is of low intensity, and remains so until about 1400°C, when it abruptly increases in intensity. The intensity in the SiO_2 region (−110 ppm) remains significant up to 1300°C, when it abruptly increases [Fig. 3(B)] before rapidly decreasing. The spectrum at 1500°C [Fig. 3(E)] differs from that of pure X-sialon in showing higher proportions of Si_3N_4, mullite-like resonance and uncombined silica; it therefore corresponds to an under-reacted X-sialon mixture.

(b) Y-containing samples. By comparison with the control, the presence of Y favours the formation of silicon oxynitride at the lower temperatures but facilitates more rapid removal of an initially high concentration of Si_3N_4. The behaviour of the mullite-like resonance is similar to that of the control, abruptly intensifying at 1400°C [Fig. 2(B)] but dropping to the expected X-sialon level at 1500°C. Uncombined SiO_2 remains comparatively low the throughout the reaction but increases abruptly at 1500°C [Fig. 3(F)], at which temperature the ^{29}Si NMR spectrum is of well-developed X-sialon plus a large amount of unreacted silica.

(c) Zr-containing samples. These samples initially contain only a small amount of Si_3N_4 but a larger amount of silicon oxynitride; the former reaches maximum intensity at 1300°C and slowly decreases, whereas the latter remains reasonably constant throughout the temperature range. The mullite-like band behaves similarly to the control with an abrupt increase in intensity at 1400°C [Fig. 3(B)]. Uncombined SiO_2 starts at an initially high level but progressively decreases during the reaction. The spectrum at 1500°C contains all the X-sialon features [Fig. 3(C)], with small additional shoulders corresponding to Si_3N_4 and SiO_2.

(d) Mg-containing samples. These contain initially high Si_3N_4 intensity which rapidly falls off with reaction temperature [Fig. 3(D)]. Spectral intensity in the silicon oxynitride region remains high throughout the reaction but the peak splits and adopts X-phase characteristics at 1300°C. The mullite-like resonance behaves similarly to the control samples but the uncombined SiO_2 remains a significant component up to 1500°C. At 1500°C this sample shows an excellent X-phase spectrum with some additional SiO_2.

(e) Ce-containing samples. As with Zr the presence of Ce suppresses the formation of Si_3N_4 at lower temperatures but facilitates the formation of silicon oxynitride, which remains at high intensity throughout the reaction until it becomes the major X-sialon peak at 1500°C. The mullite-like resonance behaves similarly to the control samples, reaching maximum intensity at 1400°C [Fig. 3(B)] and the uncombined SiO_2 resonance reaches its maximum intensity at a 1250°C then drops to a low value. The spectrum at 1500°C [Fig. 3(C)] is of a good X-sialon with a small amount of uncombined SiO_2.

(f) Fe-containing samples. The presence of Fe produces significant spinning side bands in the ^{29}Si spectra even at the 1 wt% level. Its effect on the formation and behaviour of Si_3N_4 and silicon oxynitride is similar to that of Zr and Ce, except that at 1500°C the silicon oxynitride resonance does not become the major X-sialon peak at −65 ppm but its intensity is more equally divided between this and the −54 ppm peak [Fig. 3(G)]. Both the mullite and uncombined SiO_2 resonances become disproportionately intense at higher temperatures, resulting in a spectrum at 1500°C which contains the elements of X-sialon but with the incorrect intensity ratios and additional peaks corresponding to Si_3N_4 and SiO_2 [Fig. 3(G)].

(g) Ca-containing samples. The intensity of the silicon oxynitride resonance in these samples is favoured over that of Si_3N_4, which behaves similarly to the control sample. Although the silicon oxynitride peak is more significant at lower temperatures than in the control spectrum, in all other respects it behaves similarly, increasing in intensity at 1400°C before shifting to −67 ppm and becoming the major X-sialon peak. Up to 1400°C the mullite-like and SiO_2 resonances also behave similarly to the control spectrum but at 1500°C the

relative intensities of the X-sialon spectra are suddenly achieved [Fig. 3(C)], with the loss of the Si_4N_4 peak and a decrease in both the mullite-like and SiO_2 resonances. Thus, this additive appears to achieve its maximum effectiveness at higher temperatures.

(h) Ba-containing samples. Samples containing this additive behave similarly to those with Zr with respect to the Si_3N_4 and silicon oxynitride intensities but the behaviour of the mullite-like and SiO_2 resonances is more like that of the control, resulting in a spectrum at 1500°C which differs from the characteristic X-sialon in showing a Si_3N_4 shoulder and over-intense mullite-like and SiO_2 resonances [Fig. 3(E)]. These are all characteristics of an under-reacted sample and suggest that unlike Ca, Ba does not exert a high-temperature effect on the reaction sequence.

To summarise, the reaction sequence, as deduced from the ^{29}Si spectra, is as follows:

(i) At lower temperatures, silicon nitridation products (Si_3N_4 and Si_2N_2O) are formed, the amount of nitride decreasing with respect to oxynitride as the reaction proceeds. An accompanying decrease in the amount of uncombined silica suggests this is the primary source of the oxynitride. By comparison with the control samples, the low-temperature formation of oxynitride is facilitated by all the present additives. Additionally, the initial formation of Si_3N_4 is suppressed by Zr and Ce.

(ii) At about 1400°C the amount of oxynitride suddenly increases prior to a change in its atomic environment at 1400–1500°C, becoming less N-rich, as evidenced by its ^{29}Si NMR resonance shift to -67 ppm. This change towards Si–O–N units more typical of X-sialon is accompanied by the appearance of other minor peaks typical of X-phase (SiO_2N_2 units at -57 ppm and SiO_3N at -75 ppm). The additives which facilitate the high-temperature changes in the oxynitride units to the typical X-sialon configuration are Mg, Ce, Ca and Zr. Y and Ba favour the disproportionate formation of the SiO_3N units giving rise to the peak at -79 ppm but this is suppressed by Fe in favour of the SiO_2N_2 units at -54 ppm.

(iii) Also at 1400°C, the concentration of mullite-like Si(Al)–O units abruptly increases with an increase in the intensity of the NMR resonance at -88 ppm. In the subsequent development of the typical X-sialon spectrum these units become less significant, as evidenced by a decrease in the intensity of this peak; under the present experimental conditions this decrease does not occur at 1500°C in the absence of additives. By contrast, all the present additives except Fe, Ba and Y facilitate the changes at 1500°C in this part of the structure accompanying the formation of X-sialon. The maintenance of the Si(Al)–O structure is most marked in the presence of Fe, possibly due to a stabilising effect related to the known ability of this ion to substitute for Al in mullite.[7]

(iv) During the reaction, the concentration of uncombined SiO_2 from thermal decomposition of the clay mineral is progressively consumed by nitridation at lower temperatures to form oxynitride units or by reaction with γ-alumina to form mullite at higher temperatures. In the absence of additives some unreacted SiO_2 (-110 ppm) is still present at 1500°C. Lower amounts of unreacted SiO_2 remain at 1500°C in the presence of Mg, Ce and Ca, consistent with the more advanced state of X-sialon formation in these systems. The presence of Y exerts a different effect on the level of uncombined SiO_2, which remains reasonably low until 1500°C when its characteristic resonance suddenly becomes very large and broad, due to the formation of a significant amount of glass.

3.4 ^{27}Al MAS NMR spectroscopy

The ^{27}Al spectra of all the X-sialon samples heated at various temperatures with the various additives are superficially similar and contain one tetrahedral and one octahedral resonance. However, during the course of the reaction, changes occur in the positions of the tetrahedral and octahedral peaks and in their intensity ratios. At 1200°C the ^{27}Al NMR spectrum of the additive-free control sample shows the tetrahedral and octahedral resonances at 64 and 8 ppm respectively, with a tetrahedral:octahedral intensity ratio, estimated by spectral integration, of 0·54. These values are similar to those obtained for γ-Al_2O_3 at the same magnetic field and under identical conditions (tetrahedral peak at 66 ppm, octahedral peak at 7.6 ppm, tetrahedral:octahedral ratio 0.63). On heating to higher temperatures both the tetrahedral and octahedral peak positions progressively shift, levelling out at 1400°C to 59 and 0·8 ppm, respectively. The tetrahedral:octahedral intensity ratio increases almost linearly with temperature, taking the value of 1·33 at 1500°C. These high-temperature parameters are similar to both well-crystallized mullite and monophase silicothermal X-sialon, both measured under the same conditions (mullite;

58·8 and 0·3 ppm, Td:Oh ratio 1·15, X-sialon; 63 and 0·8 ppm, Td:Oh ratio 1·33). Well-crystallised mullite shows two partially-resolved tetrahedral resonances at 58·8 and 48 ppm, the latter being ascribed[8] to a distinctive oxygen-deficient tetrahedral Al-O tricluster unit. X-sialon shows no NMR evidence of such a feature; although the tetrahedral resonance is broad, it is also reasonably symmetrical.

In the presence of the additives the general behaviour of the octahedral and tetrahedral resonance positions and the tetrahedral:octahedral ratios are retained but their temperature dependence is changed. The changes in the octahedral resonance positions in the presence of Mg, Y, Ce and Fe occur at lower temperatures than in the control, Zr and Ca are similar to the control and the samples containing Ba lag behind the control. The positions of the tetrahedral resonances are also influenced by the additives [Fig. 4(A)]; all but the Mg-containing samples show smaller changes than in the control. In the initial stages of the reaction (below 1400°C) the tetrahedral shifts approach that of the non-defect tetrahedral mullite peak but by 1500°C, this peak position has moved back towards the value for X-sialon in samples containing Mg, Y, Zr, Ba and Ca.

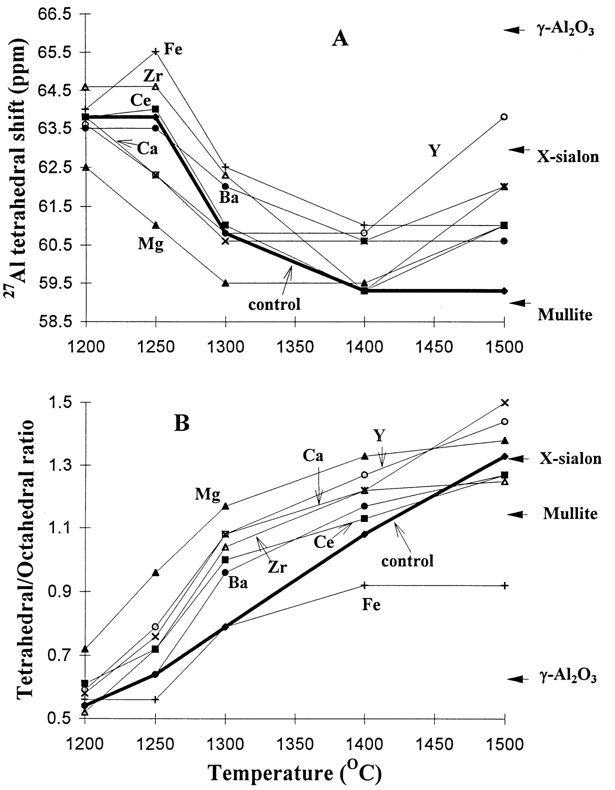

Fig. 4. Effect of reaction temperature on the ^{27}Al MAS NMR spectra of silicothermal X-sialon mixtures containing 1 wt% of various metal oxides. Heavy line indicates additive-free control sample. A. Tetrahedral Al peak position versus temperature. B. Tetrahedral:octahedral peak area ratio versus temperature.

The presence of all the additives except Fe produces a Td:Oh ratio which is greater (more like X-sialon) at each temperature than in the control [Fig. 4(B)]. The presence of Fe stabilises the ratio at a value intermediate between that of γ-Al$_2$O$_3$ and mullite. On the basis of both the tetrahedral Al peak position and the Td:Oh ratio, X-sialon formation is most advanced at 1500°C in the presence of Y, Ca and Mg; these conclusions are consistent with the XRD results for the conversion of mullite to X-sialon [Fig. 2].

These results suggest that the aluminous portion of the reacting system is most affected by Mg and Y, which lower the temperature at which changes in the octahedral units occur, produce a tetrahedral resonance close to that of X-sialon at 1500°C and secure the early establishment of an X-sialon Td:Oh intensity ratio. These effects may result from the formation by these additives of a low-melting liquid phase. Other additives exert an influence on more specific parts of the Al structure; the temperature at which X-sialon octahedral units are established is lowered by Ce and Fe, while Zr and Ca cause the tetrahedral resonance to most closely approach that of mullite below 1400°C and produce a more typical tetrahedral X-phase at 1500°C. All the additives facilitate the establishment of an X-sialon-like Td:Oh ratio, except Fe, which stabilises the mullite-like structure of the preceding phase.

3.5 Effect of additives on X-sialon densification

Figure 5 shows the effect of the various additives on the density of the fired X-sialon pellets as a function of firing temperature.

For most additives significant densification did not occur until 1500°C under the present conditions;

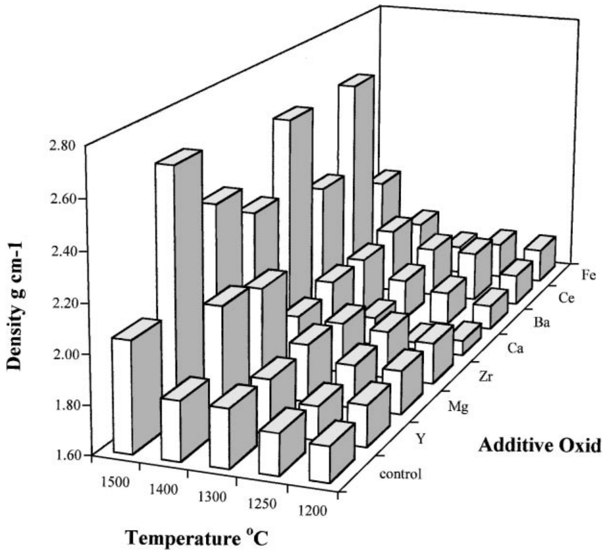

Fig. 5. Effect of reaction temperature on the bulk density of silicothermal X-sialon pellets containing 1 wt% of various metal oxide additives.

the exceptions are Y and Mg, which produced densities at 1400°C equivalent to that achieved in the additive-free control sample at 1500°C. The sintering behaviour in the presence of these two additives is probably due to the increased ionic mobility in the presence of liquid phases, as previously reported for the sintering of β-sialon.[9] By 1500°C all the additives except Fe have improved the densification over that of the control; at this higher temperature Y, Ca and Ce were the most effective sintering agents. These results were confirmed by the porosity measurements, which in all cases were inversely related to the density. Of all the additives studied here only Y, Ca and Ce exerted a beneficial influence on both the formation and densification of X-sialon under the present conditions.

4 Conclusions

1. Metal oxide additives at 1 wt% concentration influence the silicothermal formation of X-sialon at 1200–1500°C by affecting to varying degrees the different stages of the synthesis reaction. The effect of the different additives is also temperature-dependent.
2. Initial nitridation of the elemental Si is facilitated by all the oxides used here but especially by Fe_2O_3, which also forms a small amount of transient Fe_3Si at 1200°C. Reaction of the clay and γ-Al_2O_3 to form mullite is promoted by Y_2O_3 and ZrO_2 but delayed by CaO and MgO. The conversion of this mullite to X-sialon at higher temperatures is most marked in the presence of Y_2O_3, CaO and MgO, but is suppressed by Fe_2O_3, which enters and stabilises the mullite structure. The beneficial effects of Y_2O_3 and MgO are probably related to their formation of liquid phases at the reaction temperature. The XRD results are confirmed by measurements of the ^{27}Al MAS NMR tetrahedral peak position and the intensity ratio of the tetrahedral:octahedral ^{27}Al NMR peaks.
3. ^{29}Si MAS NMR shows that the conversion of Si_3N_4 to the silicon oxynitride units of X-sialon (SiO_2N_2 and SiO_3N) is facilitated by MgO, CaO, CeO_2, and ZrO_2. The formation of SiO_3N is disproportionately enhanced by BaO and Y_2O_3, whereas Fe_2O_3 enhances the formation of SiO_2N_2. The formation of X-sialon also involves changes in the Si(Al)–O portions of the mullite structure, which are enhanced over the additive-free samples by all the present oxides except BaO, ZrO_2 and Fe_2O_3.
4. The consumption of uncombined SiO_2 during the course of the silicothermal reaction is facilitated by MgO, CaO and CeO_2, which produce samples with ^{29}Si MAS NMR spectra typical of well-reacted X-sialon. A high level of uncombined SiO_2 present at 1500°C in the Y_2O_3 containing sample arises from the formation of a significant concentration of glass.
5. Under the present conditions, the greatest densification was promoted by Y_2O_3, CaO and CeO_2. Thus, the most favourable additives for promoting both X-sialon formation and densification are Y_2O_3, CaO and CeO_2, followed by MgO.

References

1. Sheppard, C. M., MacKenzie, K. J. D., Barris, G. C. and Meinhold, R. H., A new silicothermal route to the formation of X-phase sialon: The reaction sequence in the presence and absence of Y_2O_3. *J. Eur. Ceram. Soc.*, 1997, **17**, 667–673.
2. Sheppard, C. M., MacKenzie, K. J. D. and Ryan, M. J., The physical properties of sintered X-phase sialon prepared by silicothermal reaction bonding. *J. Eur. Ceram. Soc.*, 1998, **18**, 185–191.
3. Ekström, T. C, White, G. V, Brown, I. W. M, Barris, G. C. and Sheppard, C. M., Effects of yttria on carbothermal reduction and nitridation to form β, O′ and X-phase sialons. *Proc. IPENZ Ann. Conf. Wellington*, 1997, **2**, 408–410.
4. Higgins, I. and Hendry, A., The mechanism of formation of β'-sialon from oxides. *Proc. Brit. Ceram. Soc.*, 1986, **39**, 163–178.
5. Narciso, F. J. and Rodriguez-Reinoso, F., Synthesis of β-SiAlON from clays: Effect of starting materials. *J. Mater. Chem.*, 1994, **4**, 1137–1141.
6. Kokmeijer, E., Scholte, C., Blömer, F. and Metselaar, R., The influence of process parameters and starting composition on the carbothermal production of sialon. *J. Mater. Sci.*, 1990, **25**, 1261–1267.
7. Schneider, H. and Rager, H., Iron incorporation in mullite. *Ceram. Int.*, 1986, **12**, 117–125.
8. Merwin, L. H., Sebald, A., Rager, H. and Schneider, H., ^{29}Si and ^{27}Al MAS NMR spectroscopy of mullite. *Phys. Chem. Minerals*, 1991, **18**, 47–52.
9. MacKenzie, K. J. D. and Meinhold, R. H., Additive-assisted pressureless sintering of carbothermal β'-sialon: An X-ray and solid-state MAS NMR study. *J. Mater. Chem.*, 1996, **6**, 821–831.