

# The effect of reaction atmosphere on the early stage carbothermal reduction of kaolinite: an XRD, $^{29}\text{Si}$ and $^{27}\text{Al}$ MAS NMR study

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Phase formation in kaolinite heated at 1200 °C in eight different reaction atmospheres in the presence and absence of carbon has been studied by solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) and X-ray powder diffraction. Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and amorphous  $\text{SiO}_2$  are the principal products in all atmospheres. The amount of mullite formed is generally greater under vacuum and in reducing atmospheres, but the precise effect of the atmosphere is also modified by the presence of carbon. Vacuum and reducing atmospheres generally produce mullites of alumina:silica composition nearer 3:2 than 2:1 (estimated from unit cell measurements) and containing a higher proportion of  $\text{Al}^*$ , i.e. tetrahedral aluminium associated with an oxygen defect (estimated by  $^{27}\text{Al}$  NMR measurements). The result of most significance to sialon formation is the detection by  $^{29}\text{Si}$  NMR of silicon oxynitride formation at 1200 °C in systems containing either nitrogen or ammonia, in the presence of carbon. The preferential formation of Si–O–N bonds at such an early stage of the reaction under carbothermal conditions was confirmed by thermodynamic calculations, which also clarify other details of the complex interactions between the aluminosilicate, carbon, and the various gas atmospheres.

## 1. Introduction

The initial stage in the carbothermal formation of sialon from kaolinite minerals involves the formation of mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and amorphous  $\text{SiO}_2$  from the clay [1]. Further reactions include the formation of SiC from the silica and carbon, and reaction with the mullite under nitriding conditions to form a series of sialons of increasing nitrogen content. The conventional view of the reaction, based on X-ray diffraction (XRD) observations, is that nitridation occurs at a relatively late stage; the main function of the nitrogen in the early stages is to protect the carbon from oxidation.

It is known, however, that the formation of mullite from kaolinite is influenced by the reaction atmosphere [2], the reaction at 1100 °C proceeding most fully in a static humid atmosphere, followed in order of decreasing mullite formation by vacuum, hydrogen, nitrogen, air, oxygen and carbon dioxide. Although these experiments suggest that the reaction atmosphere may also influence the early stages of the sialon-forming reaction by influencing the formation of the mullite precursor, the results cannot be applied directly because they involved static atmospheres rather than a flowing gas, and carbon was not present. For this reason, the present series of experiments was carried out, in which kaolinite was fired in flowing gas atmospheres, both with and without carbon. In addition to the usual phase analysis by X-ray diffraction,

solid-state nuclear magnetic resonance (NMR) was also used, because this technique has proved invaluable in detecting changes in the environment of the silicon and aluminium atoms in clay minerals during thermal reaction, in some cases well before sufficient long-range order has been established for the new phases to be detected by XRD [3].

## 2. Experimental procedure

The kaolinite used here (BDH Light) was an English china clay of low iron content and good crystallinity. Two series of heating experiments were carried out.

(a) The clay was heated in alumina boats in an electric tube furnace under various dynamic gas atmospheres ( $150 \text{ ml min}^{-1}$ ). The heating cycle included a slow drying phase up to 100 °C at  $0.6 \text{ °C min}^{-1}$ , followed by heating to 1000 °C at  $10 \text{ °C min}^{-1}$ . The final stage of heating, up to the holding temperature of 1200 °C, was at  $5 \text{ °C min}^{-1}$ , and the dwell time at top temperature was 10 min, followed by rapid cooling while maintaining the gas atmosphere. The gases used were air, oxygen, nitrogen, carbon dioxide, argon, hydrogen, ammonia and vacuum ( $1.3 \times 10^{-3} \text{ Pa}$ , obtained by continuous pumping of the furnace work tube).

(b) The clay was ball-milled with 25 wt % carbon (Degussa lampblack) under hexane for 16 h. This typical sialon-forming mix was then heated in a parallel set of experiments to (a) above.

After reaction, the samples were examined by X-ray powder diffraction (Philips PW 1700 computer-controlled diffractometer with graphite monochromator and  $\text{CoK}_\alpha$  radiation). The mullite cell parameters were calculated from measurements of the positions of at least 11 mullite peaks (excluding unresolved doublet peaks), corrected by use of an external silicon standard.

The  $^{29}\text{Si}$  and  $^{27}\text{Al}$  solid-state NMR spectra were obtained at 11.7T using a Varian Unity 500 spectrometer. The  $^{27}\text{Al}$  spectra were collected using a Doty high-speed magic angle spinning (MAS) probe spinning up to 12.2 kHz, with a  $15^\circ$  pulse of  $1\ \mu\text{s}$  and a recycle time of 1 s. The  $^{29}\text{Si}$  spectra were obtained at spinning speeds of about 8 kHz with a  $90^\circ$  pulse and a recycle delay time of 300 s to ensure the detection of any species with very long relaxation times, such as can be encountered in sialon-forming systems.

### 3. Results and discussion

Fig. 1 shows the weight losses of the samples after reaction in the various atmospheres at  $1200^\circ\text{C}$  for 10 min. As would be expected, the weight losses from all the samples without carbon are the same within experimental error, and correspond approximately to the dehydroxylation weight loss of this kaolinite (13.8%). Some of the samples containing carbon (those fired in hydrogen, nitrogen and argon) also show similar weight losses, indicating that under these

inert or reducing conditions, some weight loss over and above that of dehydroxylation has occurred, presumably from the carbon. However, the much greater weight losses from carbon-containing samples heated in oxygen and air indicate that virtually all the carbon has been lost. Slightly less carbon burn-out occurs in carbon dioxide, suggesting a somewhat oxidizing atmosphere, while the weight loss in vacuum and ammonia indicated comparatively less carbon burn-out over and above the dehydroxylation loss (Fig. 1).

X-ray diffraction indicates that the only crystalline phase in the samples is mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , with an amorphous (silica) phase showing up in most samples as a substantial hump centred at about  $d = 0.4\ \text{nm}$ .

Fig. 2 shows the relative amounts of mullite formed in these samples, estimated semi-quantitatively from the height of the major mullite X-ray diffraction peak at 0.34 nm (this diffraction feature is a doublet, but in most samples, the mullite was not sufficiently crystalline for this to be resolved). Because measurements of the areas under the mullite peaks were found to give virtually identical results to those obtained from the peak heights, the latter were deemed satisfactory for the present purpose.

As found previously [2], the reaction atmosphere has a considerable influence on the amount and crystallinity of the mullite formed, particularly in the clay without carbon, in which the greater mullite formation was found in vacuum, carbon dioxide, ammonia

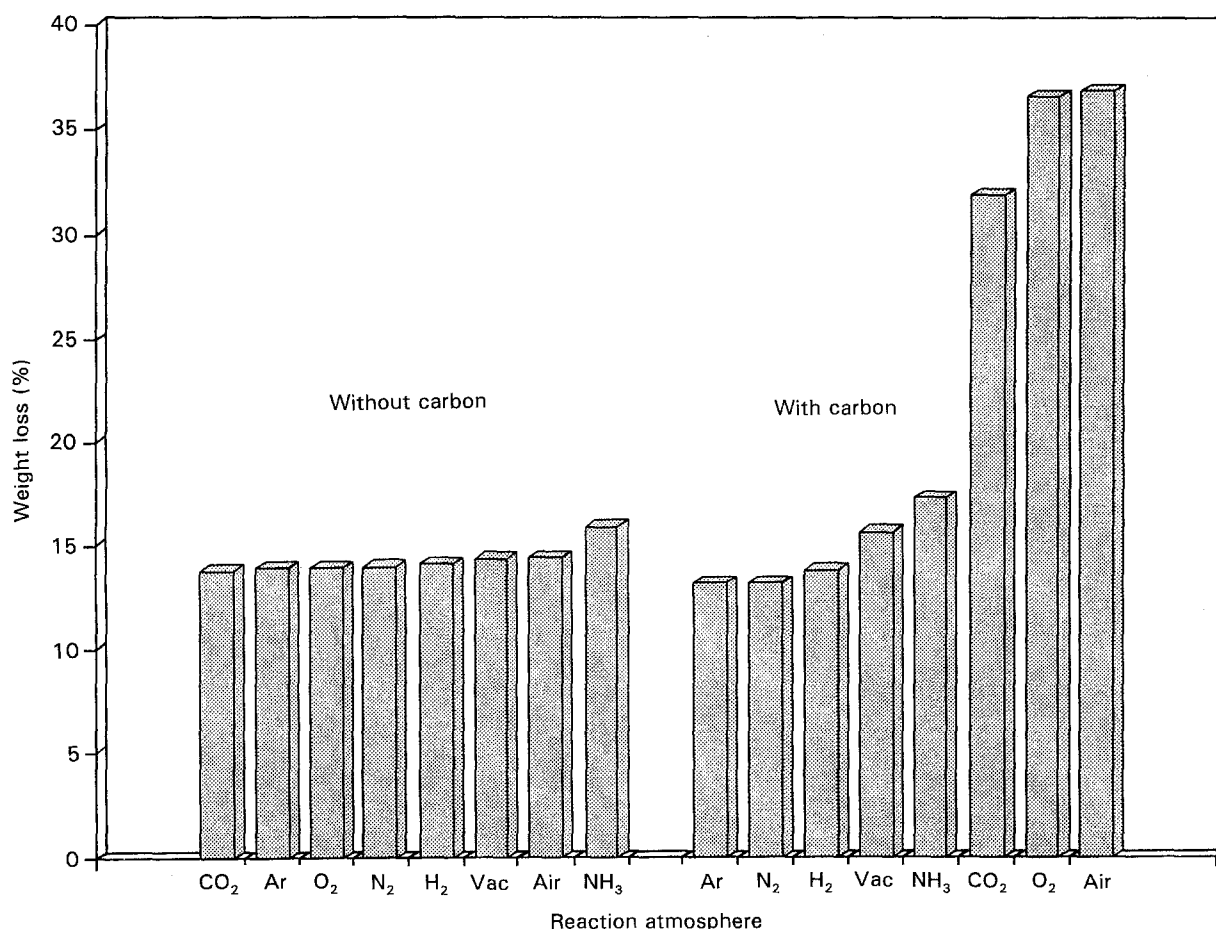


Figure 1 Weight losses in kaolinite after reaction at  $1200^\circ\text{C}$  for 10 min under various atmospheres in the presence and absence of carbon.

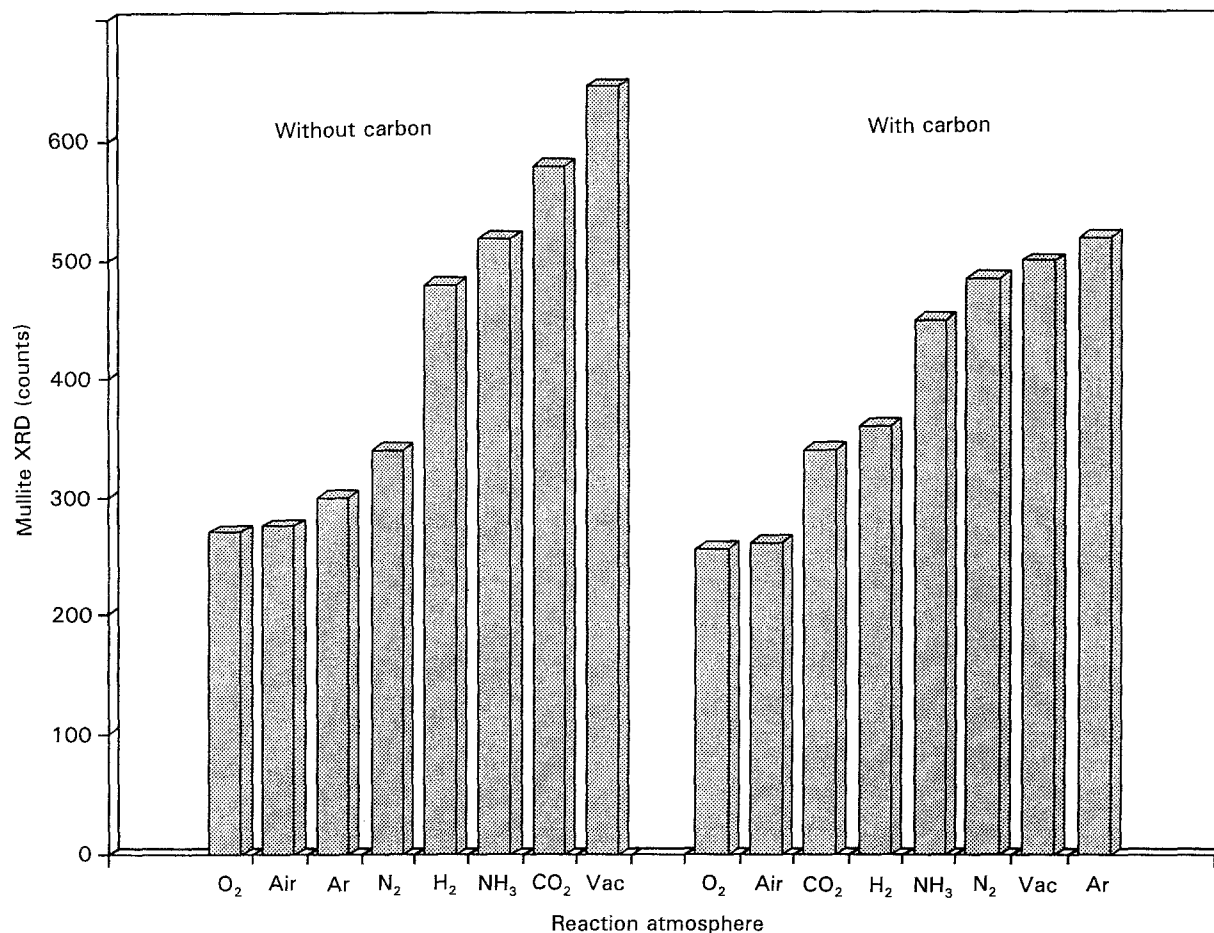


Figure 2 Degree of mullite formation in kaolinite after reaction at 1200 °C for 10 min under various atmospheres in the presence and absence of carbon.

and hydrogen. The oxidizing and inert atmospheres promote considerably less mullite formation. As far as a comparison is possible, the order of these results is similar to those previously reported [2]; the present experiments did not include humid atmospheres, which were previously found to exert the strongest beneficial effect, and the previous study did not include argon and ammonia.

The presence of carbon changes the degree of mullite formation in the various atmospheres, with argon and nitrogen now promoting a high degree of mullite formation, and hydrogen and carbon dioxide being less efficient promoters of mullite. The result with nitrogen is particularly significant for the carbothermal production of sialon, because the combination of carbon and nitrogen apparently favours mullite formation (Fig. 2).

The *a*-parameter of the mullite unit cell, refined from the measured positions of between 11 and 13 of the mullite diffraction peaks, was used to estimate the compositions of the mullites from the relationship of Cameron [4] (Fig. 3). Previous work [5] has shown that as mullite is progressively formed from kaolinite, its composition becomes less alumina-rich, passing through a 2:1 alumina/silica ratio (about 66.6 mol % alumina) to the preferred ratio of 3:2 (about 60 mol % alumina). The present samples show a wide composition range, from highly aluminous mullite formed in oxygen and air, through to other samples intermediate between 2:1 and 3:2 mullite, formed under neutral

and reducing atmospheres. Anomalous behaviour is again found in argon which, in the absence of carbon, forms a highly aluminous mullite, and hydrogen, which does so in the presence of carbon (Fig. 3). If the lowering of the alumina content is taken as an indicator of the progress of the mullite-forming reaction, then a relationship might be expected between the amount of mullite formed and its composition. In general, it appears that both in the presence and absence of carbon, the more highly aluminous (least reacted) mullites also occur in lowest concentrations (Fig. 4), but the scatter in this plot, and the presence of outliers suggests that under certain combinations of atmospheres and carbon, other factors may be operating, such as the removal of silica from otherwise well-developed mullite.

### 3.1. NMR spectroscopy

A selection of typical <sup>29</sup>Si MAS NMR spectra of samples reacted with and without carbon are shown in Fig. 5. The spectra show two major features; a broad peak centred at about -105 to -112 p.p.m. arises from the amorphous silica ejected when kaolinite forms mullite [5]. The other feature, present in most of the spectra, is a resonance at about -86 to -91 p.p.m. arising from mullite which has a major resonance at about -86.8 p.p.m. [6]. Two minor mullite resonances, which are sometimes observed at -90 and -94.2 p.p.m. in well-crystallized mullites

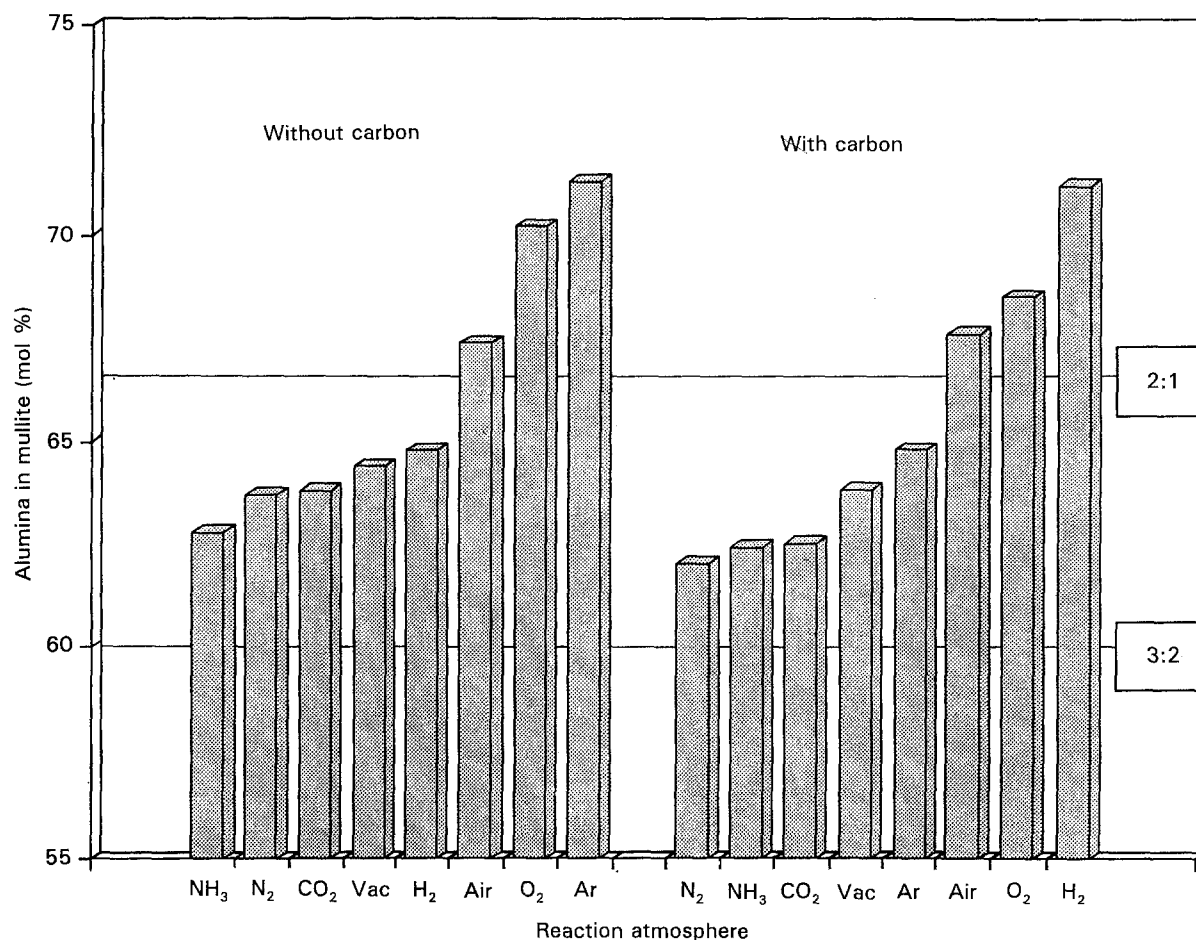


Figure 3 Variation in the alumina content of the mullite formed at 1200 °C under various atmospheres in the presence and absence of carbon.

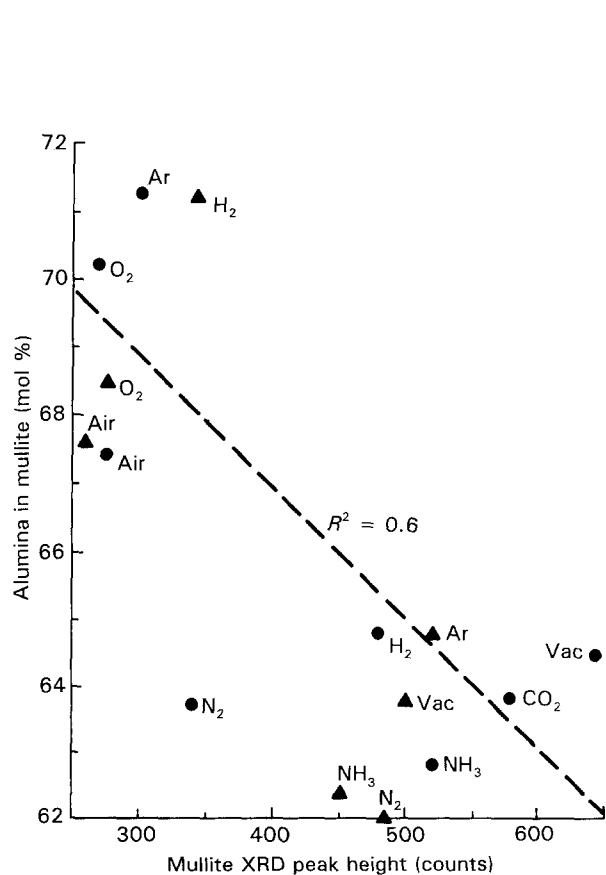


Figure 4 Relation between the amount of mullite formed at 1200 °C and its alumina content under various atmospheres in (▲) the presence and (●) absence of carbon.

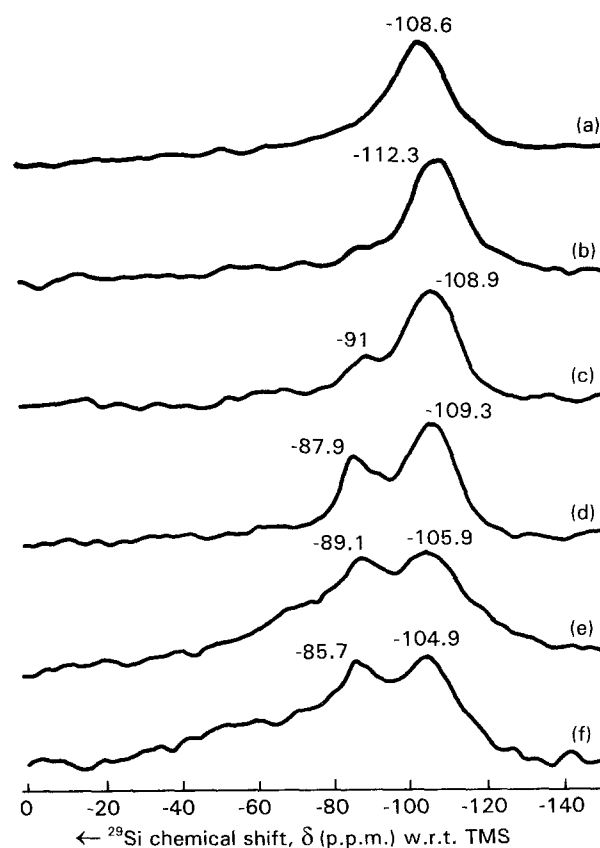


Figure 5 A selection of typical <sup>29</sup>Si MAS NMR spectra of kaolinite reacted at 1200 °C for 10 min under various conditions: (a) O<sub>2</sub>, without carbon; (b) air, with carbon; (c) Ar, without carbon; (d) vacuum, without carbon; (e) NH<sub>3</sub>, with carbon; (f) N<sub>2</sub>, with carbon.

[6], are not resolved in the present spectra. The relative amounts of silicon present in mullite and as amorphous silica were estimated by using a curve-fitting procedure to fit a broad peak to each of these two resonances. The amounts of silicon in mullite correlate reasonably well with the amount of mullite estimated by XRD (Fig. 6).

Two other features of the  $^{29}\text{Si}$  MAS NMR spectra require comment.

(i) A progressive change in the chemical shift of the amorphous silica resonance from about  $-112$  to  $-105$  p.p.m. occurs as the amount of silica in the mullite increases. This occurs in all samples, but is most noticeable in those containing carbon, suggesting that mullite formation is proceeding by reaction of the free silica, forming aluminosilicate phases with chemical shifts downfield of silica.

(ii) In the carbon-containing samples reacted in nitrogen and ammonia, a long tail is observed, extending down into the region of silicon-nitrogen resonances (Fig. 7a, b). Most of the area of this tail occurs in the region between  $-40$  and  $-80$  p.p.m., suggesting that a continuum of species is present, including a range of silicon oxynitrides (typically,  $\text{Si}_2\text{N}_2\text{O}$  appears at  $-63$  p.p.m. [7], whereas the fully nitrated compound has a chemical shift of  $-47$  to  $-50$  p.p.m. [7]). These compounds are not sufficiently crystalline to be detected by XRD. A similar tail in this spectral region is found in the sample without carbon fired in ammonia (Fig. 7c, d), but there is less evidence for such a feature in the sample without carbon fired in nitrogen.

A typical  $^{27}\text{Al}$  spectrum is shown in Fig. 8a. All the samples, both with and without carbon show these typical mullite spectra, consisting of an octahedral

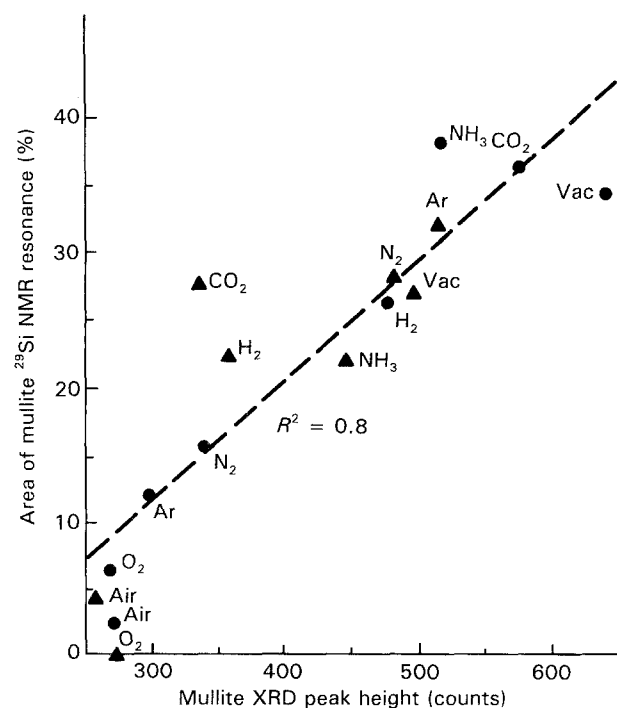


Figure 6 Relation between the amount of mullite formed at  $1200^\circ\text{C}$  under various conditions (estimated by X-ray diffraction) and the relative area of the  $^{29}\text{Si}$  MAS NMR peak of mullite, ( $\blacktriangle$ ) with and ( $\bullet$ ) without carbon.

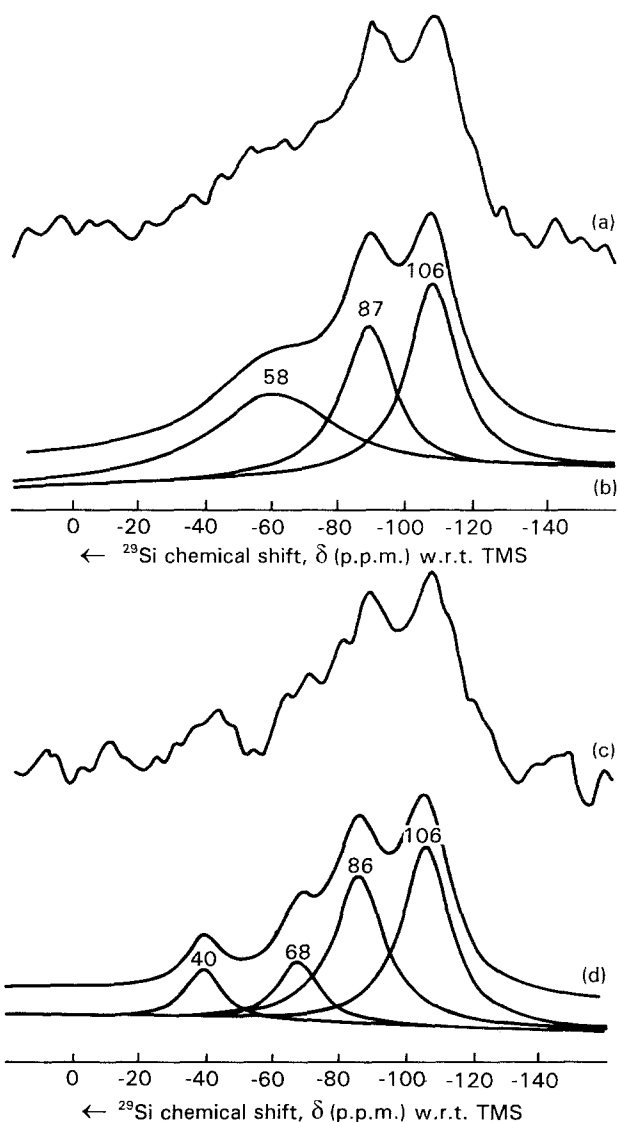


Figure 7 Observed and simulated  $^{29}\text{Si}$  MAS NMR spectra. (a) Kaolinite plus carbon heated at  $1200^\circ\text{C}$  in nitrogen, (b) simulation of this spectrum. (c) Kaolinite heated at  $1200^\circ\text{C}$  in ammonia, (d) simulation of this spectrum.

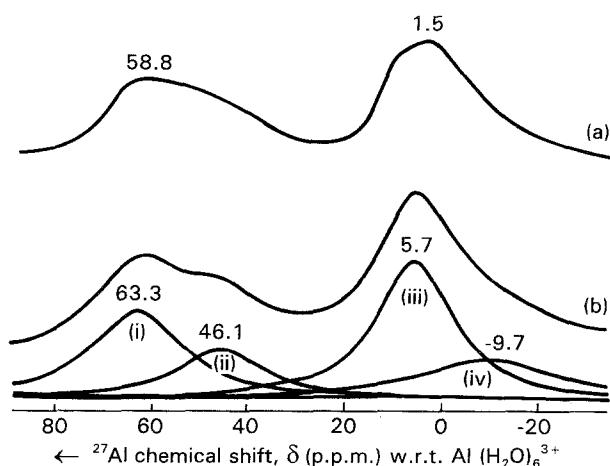


Figure 8 (a) Typical  $^{27}\text{Al}$  MAS NMR spectrum of kaolinite heated at  $1200^\circ\text{C}$  for 10 min with carbon in  $\text{H}_2$ ; (b) simulation of this spectrum.

feature at about  $-13$  to  $+4$  p.p.m. and a broad resonance in the tetrahedral region ( $44$  to  $64$  p.p.m.). The octahedral resonance shows a pronounced tail in most samples, and the broadness and asymmetry in

the tetrahedral peak in several of the samples suggests that this is composed of at least two overlapping peaks.

Curve-fitting procedures indicate that these spectra can be satisfactorily resolved into two tetrahedral components and an octahedral peak (Fig. 8b), the latter having a broad tail (iv) which probably arises from Electric Field Gradient (EFG) effects. The relative areas of the tetrahedral components vary considerably from sample to sample, as does the octahedral to tetrahedral ratio. Two tetrahedral components have previously been reported in the 11.7T  $^{27}\text{Al}$  MAS NMR spectra of well-crystallized mullites [6]. In these spectra, resonance (i) at 58 to 63 p.p.m. is assigned to the regular tetrahedral aluminium sites, whereas peak (ii) at 42 to 48 p.p.m. is attributed to aluminium tetrahedra in triclusters, i.e. where one oxygen atom is shared by three surrounding aluminium tetrahedra, giving rise to a more distorted aluminium site designated  $\text{Al}^*$  [6].

In all the samples, the proportion of total tetrahedral aluminium varies between 40% and 60% (Fig. 9), but within the tetrahedral envelope, the distribution between the regular and distorted ( $\text{Al}^*$ ) sites varies considerably (Fig. 9). There is, however, a degree of correlation between the number of distorted tetrahedral  $\text{Al}^*$  sites and the amount of mullite estimated by XRD (Fig. 10), suggesting that the  $\text{Al}^*$  sites are a characteristic of well-developed mullite, in which the alumina:silica ratio is within the range 2:1 to 3:2. The

correlation between the proportion of distorted tetrahedral sites and the composition of the mullite as deduced from the unit-cell measurements, is poorer; the less well-formed mullites of highest aluminium content have the smaller numbers of distorted tetrahedral sites.

### 3.2. Thermodynamic analysis of the aluminosilicate–gas system with and without carbon

The reaction chemistry occurring in the present experiments is clearly quite complex, and a consideration of the chemical thermodynamics of the various possible reactions can provide useful insights into their relative feasibility. However, because the thermodynamic calculations refer to equilibrium conditions and the present experiments were conducted under dynamic gas flows, predictions based on thermodynamics must be treated with caution. For the purpose of these calculations, the system is treated as anhydrous, because the water evolved from the kaolinite is removed from the system well before the final reaction temperature is reached. According to previous work [5], the product at about 1000 °C can be a mixture of a poorly formed mullite-like phase,  $\gamma$ -alumina and amorphous silica; reaction between the latter two components leads to further mullite. The thermodynamic feasibility of various reactions between these

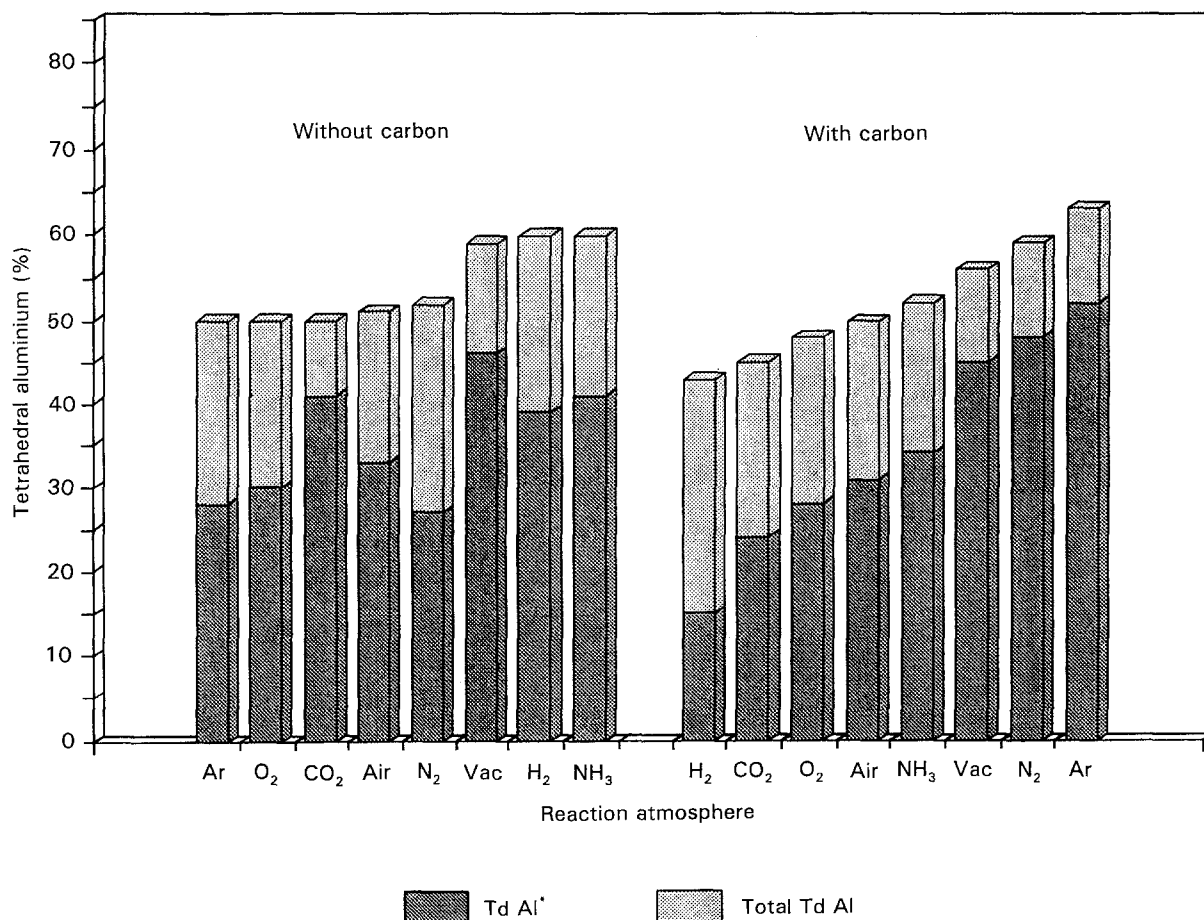


Figure 9  $^{27}\text{Al}$  NMR estimate of the tetrahedral (Td) aluminium content of mullites formed at 1200 °C under various atmospheres in the presence and absence of carbon.

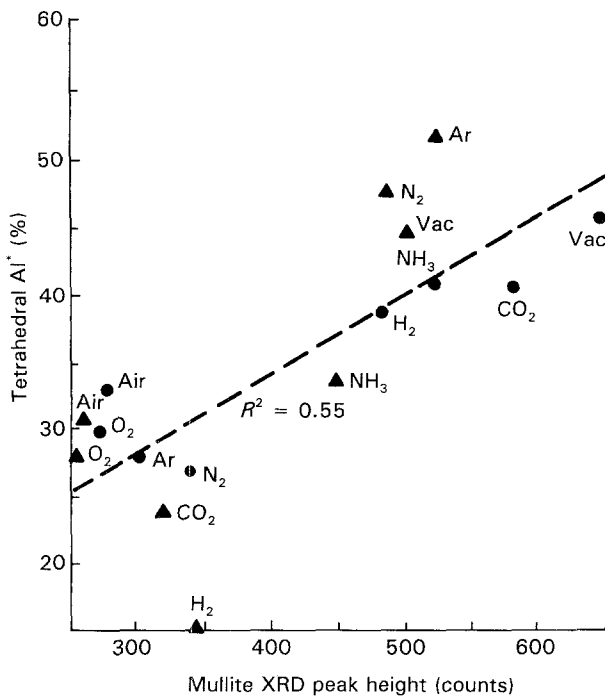


Figure 10 Relation between the amount of mullite formed at 1200 °C under various conditions and its tetrahedral Al\* content, estimated by  $^{27}\text{Al}$ NMR, (▲) with and (●) without carbon.

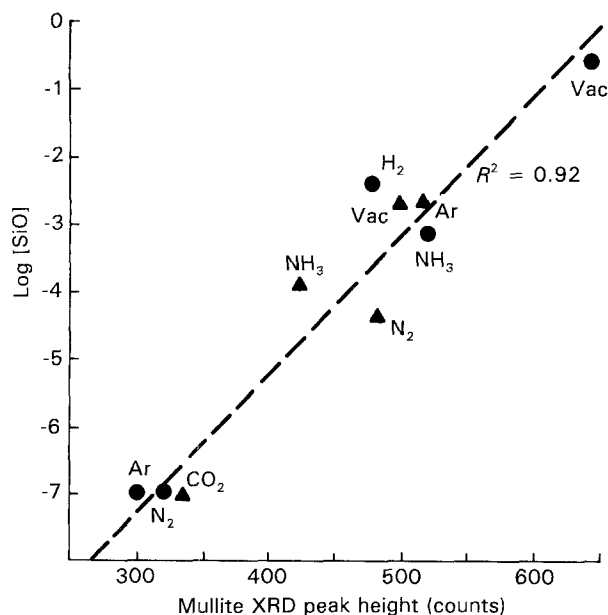


Figure 11 Relation between the amount of mullite formed at 1200 °C under various conditions and the concentration of SiO predicted by thermodynamic calculations, (▲) with and (●) without carbon.

phases and the reaction gas were examined, both in the presence and absence of carbon, using a computer program [8] which calculates from tabulated thermodynamic data the composition of the product assemblage as a function of the gas concentration and reaction temperature. Thermodynamic modelling of vacuum conditions can be approximated by extremely high concentrations ( $10^6$ – $10^9$  mol) of an inert gas such as argon, the dilution effect of which mimics the removal of gaseous species by pumping. The calculations also indicate that although  $\gamma$ -alumina is speci-

fied as a reactant, at the temperature of the present experiments,  $\alpha$ -alumina is the thermodynamically stable phase, which therefore appears throughout these calculations. The effect of temperature was also examined in these calculations, but the results discussed below were calculated for 1200 °C, thus relating closely to the temperature of the present experiments. For the purpose of these calculations, 100 mol reactant gas was assumed, except in the vacuum simulations, and in the calculations including carbon, an ample excess (10 mol) was assumed.

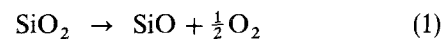
### 3.2.1. Reactions in the absence of carbon

Under these conditions, the experimental observations indicate that the greatest enhancement of mullite formation occurs under reducing atmospheres and  $\text{CO}_2$ , in the order

$$\text{vacuum} > \text{CO}_2 > \text{NH}_3 > \text{H}_2$$

Oxidising and inert atmospheres are less beneficial (Fig. 2).

3.2.1.1. *Vacuum conditions.* Calculations at high argon concentrations, approximating to vacuum conditions, indicate that if the silica and alumina are treated as separate components, the reactions

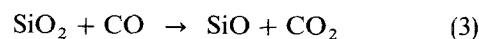


and



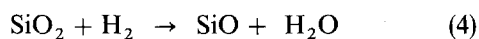
are both thermodynamically feasible at 1200 °C, but Reaction 1 is considerably favoured over Reaction 2, which occurs to only a very limited degree. When the starting phase is assumed to have the composition of metakaolinite, the products at 1200 °C are mullite and silica, with slight dissociation of the latter into SiO (Equation 1). At the higher argon concentration, approximating to a higher vacuum, silica decomposition is predicted to be considerably more extensive; by 1300 °C, dissociation of all the free silica is predicted, in addition to some decomposition of mullite itself, resulting in the appearance of a small amount of  $\text{Al}_2\text{O}_3$  (but no  $\text{Al}_2\text{O}$  as in Equation 2). Because the simulated vacuum cannot be directly related to an actual pressure, only the trend can be predicted; the calculated results may refer to lower pressures than used in the experiment ( $1.3 \times 10^{-3}$  Pa). Nevertheless, the calculations suggest that enhancement of mullite formation by vacuum conditions involves the disruption of the silica component rather than the alumina.

3.2.1.2. *Carbon dioxide atmospheres.* The thermodynamic calculations indicate that in carbon dioxide atmospheres at 1200 °C in the absence of carbon, a small but significant concentration of carbon monoxide is present. Calculations based on pure monoxide, and treating the silica and alumina as separate components, indicate that some reduction of silica will occur at 1200 °C, according to the reaction

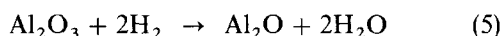


Although the calculations indicate that the concentration of CO present in CO<sub>2</sub> atmospheres at 1200 °C is insufficient for Reaction 3 to occur under the equilibrium conditions assumed, the situation may be quite different under the dynamic reaction atmospheres of the experiments, which could shift the CO<sub>2</sub>-CO equilibrium in such a way as to allow Reaction 3 to proceed. The calculations indicate that reduction of alumina is not thermodynamically feasible at 1200 °C. When metakaolinite is the starting phase, a small amount of CO is again predicted, but in insufficient quantity to decompose either the silica or the mullite present at 1200 °C; by the above reasoning, the concentration of CO may be sufficiently high to promote some reduction of the silica under the actual experimental conditions, but this will affect only the mullite subsequently formed by solid-state reaction, and should not alter the mullite formed directly from metakaolinite at 980 °C.

*3.2.1.3. Ammonia atmospheres.* Calculations on ammonia gas indicate that it dissociates completely into nitrogen and hydrogen at about 400 °C. Thus, the effect of this atmosphere should reflect both the reducing potential of the hydrogen and the nitriding effect of the nitrogen. The reactions of hydrogen with silica and alumina can be written

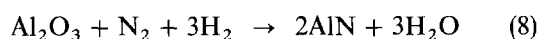
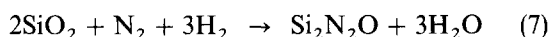
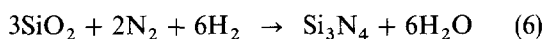


and



The calculations indicate that Reaction 4 is highly favoured over Reaction 5, which proceeds only negligibly at 1200 °C. Other possible lower oxide species such as AlO and Al<sub>2</sub>O<sub>2</sub> are even less thermodynamically favourable.

The additional reactions of silica and alumina with nitrogen introduce the possibility of nitride or oxynitride formation



The calculations indicate that with silica as the sole reactant, neither Reaction 6 nor 7 is thermodynamically favourable at 1200 °C, but Reaction 8 is predicted to proceed to a slight extent in alumina. Thermodynamic data for aluminium oxynitride phases were not available. By contrast, where metakaolinite is assumed as the starting material, some Si<sub>2</sub>N<sub>2</sub>O formation is predicted, at the expense of some of the available free silica, but not mullite which is also present in this system. Experimental confirmation that Reaction 7 occurs in metakaolinite starting material is provided by the <sup>29</sup>Si MAS NMR spectra which indicate the presence of significant concentrations of a range of oxynitrides (Fig. 7).

*3.2.1.4. Hydrogen atmospheres.* The calculations indicate that in hydrogen at 1200 °C, Reaction 4 occurs to some extent, but not Reaction 5. A similar result is

found when the starting material is metakaolinite; in this case, a small amount of the free silica is reduced, but the reduction does not extend to the mullite. With metakaolinite as the reactant, the degree of reduction of silica by hydrogen is greater than with ammonia, but in the latter gas, the total silica decomposed is slightly greater, due to the formation of some Si<sub>2</sub>N<sub>2</sub>O in addition to SiO.

*3.2.1.5. Nitrogen and argon atmospheres.* The calculations predict that the amount of SiO formed from silica at 1200 °C in nitrogen is extremely small, and oxynitride formation is similarly unfavourable. Likewise, the direct nitridation of alumina at 1200 °C is not predicted. A similar lack of reaction between the gas atmosphere and metakaolinite is also predicted. The calculations suggest that argon behaves similarly, producing almost no SiO from silica at 1200 °C, and showing no reaction with alumina or mullite.

*3.2.1.6. Oxidizing atmospheres.* The calculations show that silica, alumina and mullite are all thermodynamically stable phases in air and oxygen at 1200 °C.

### *3.2.2. Reactions in the presence of excess carbon*

In the presence of carbon, the experimentally observed effects after the reaction gases are changed with inert atmospheres, in addition to vacuum, exerting considerable enhancing effects on mullite formation (Fig. 2), in the order Ar > vacuum > N<sub>2</sub> > NH<sub>3</sub>. The effect of hydrogen and CO<sub>2</sub> is considerably decreased by comparison with the situation in the absence of carbon.

*3.2.2.1. Argon atmospheres.* In this case, the carbon is protected from oxidation by the inert atmosphere, and is thus able to react with both silica and the siliceous component of the mullite. At 1200 °C, the principal product is predicted to be SiC, with some SiO also occurring. Alumina is predicted not to react under these conditions, and remains as one of the products of mullite decomposition. Because neither alumina nor SiC were detected experimentally, the reaction must be less advanced than the equilibrium situation predicted by the thermodynamic calculations. This is not surprising, because the present samples were held at 1200 °C for only 10 min, and the formation of SiC is not observed at this temperature even after much longer heating times; furthermore, SiC is formed via gaseous SiO intermediates which are likely to be removed from the system by the dynamic gas flow of the present experiments. However, the thermodynamic calculations indicate that considerable scope exists in this system for modification of the siliceous component of the mullite.



3.2.2.2. *Vacuum conditions.* Where vacuum conditions are simulated by assuming very high concentrations of argon, the results are virtually identical with those described above for lower argon concentrations. The calculations suggest no reason why the simulated vacuum conditions should be less beneficial in promoting mullite formation, but the observed differences between these two atmospheres are quite small (Fig. 2), and the samples may be the same within experimental uncertainty.

3.2.2.3. *Nitrogen atmospheres.* The calculations predict that in nitrogen atmospheres, in the presence of carbon, full decomposition of both silica and the siliceous component of mullite will occur at 1200 °C, with the formation of the maximum amount of Si<sub>2</sub>N<sub>2</sub>O and a small amount of SiO. The formation of more SiO and SiC at the expense of the Si<sub>2</sub>N<sub>2</sub>O, is predicted to become significant only at higher temperatures (> 1500 °C). Alumina, present in its own right or resulting from the decomposition of the mullite, remains essentially unreacted at 1200 °C, with only a trace of AlN formation predicted; by 1300 °C, however, most of the alumina is predicted to be converted to AlN.

3.2.2.4. *Ammonia atmospheres.* Irrespective of the presence of carbon, ammonia atmospheres behave as a combination of a reducing agent and a nitriding agent; in the presence of carbon, some of the hydrogen concentration is decreased by the formation of CH<sub>4</sub>, but this loss of reduction capability is compensated for by the presence of additional carbon. Thus, at 1200 °C, the calculations again predict complete decomposition of silica and mullite, with the formation of Si<sub>2</sub>N<sub>2</sub>O and a little SiO. Where alumina is present in its own right, or as a decomposition product of mullite, its concentration is decreased at 1200 °C by the formation of AlN, this reaction progressing to a greater extent than in the comparable nitrogen/carbon system (above).

3.2.2.5. *Hydrogen atmospheres.* The calculations indicate that up to 700 °C, complete reaction occurs between the carbon and hydrogen to form CH<sub>4</sub> which, however, progressively dissociates at higher temperatures



By 1200 °C, sufficient carbon is again present to remove virtually all the free silica by forming SiC and a small amount of SiO. Where mullite is also assumed to be initially present, this is also predicted to be decomposed fully at 1200 °C under these conditions, but the alumina component remains unchanged even at 1500 °C. The continued presence of mullite and the absence of SiC in the XRD trace of this experimental sample indicates that the system has not approached its predicted equilibrium situation, reflecting the short reaction time and the possible alteration of the system

composition by removal of gaseous components under the dynamic reaction conditions used.

3.2.2.6. *Carbon dioxide atmospheres.* In the presence of carbon, the formation of carbon monoxide is predicted to go to completion below 900 °C



The resulting removal of carbon from the system is apparently not compensated for by the reducing power of the CO produced at the carbon concentrations assumed in these calculations, because virtually no change is predicted in the concentrations of free silica or mullite at 1200 °C.

3.2.2.7. *Oxidizing atmospheres.* Under these conditions, all the carbon is predicted to oxidize to CO<sub>2</sub>, with no nett effect on the free silica or mullite contents at 1200 °C.

The thermodynamic calculations therefore indicate that the various gas atmospheres are most likely to react with the free silica component present. When this silica has been consumed, the mullite present will be progressively decomposed by similar reactions of its silica component. Depending on the nature of the gas atmosphere, and its possible modification by reaction with free carbon, the silica product is predicted to be the oxynitride, the carbide or the monoxide. Of these possible products, only the oxynitride has been detected in the experimental samples (by MAS NMR). SiC has not been detected in any of the samples either by XRD or MAS NMR, but if, as is commonly believed, this phase is formed via gaseous SiO intermediate, depletion of the latter by removal in the gas stream would militate against SiC formation. Similarly, removal of SiO from the hot zone of the furnace will decrease the silicon concentration of the sample, unless it is retained by undergoing reaction with the alumina-rich components to form further mullite. An indication that this might be the case is shown in Fig. 11, in which the calculated equilibrium SiO concentration is plotted against the observed degree of mullite formation. Although the thermodynamic calculations cannot accurately predict the amount of SiO produced under the experimental (dynamic gas) conditions, they provide an indication of the tendency towards silica reduction by the various atmospheres. Despite considerable scatter, Fig. 11 suggests that those atmospheres forming the most SiO (i.e. exercising the greatest disruptive effect on the Si-O bonds) give rise to samples containing the most mullite. This is, however, an over-simplification, because it takes no account of other reactions which decompose the mullite in the system (e.g. hydrogen in the presence of carbon, in which the mullite is predicted to be largely decomposed by 1200 °C).

Of particular interest are those reaction conditions under which sialons may form (nitrogen and ammonia atmospheres). Fig. 12 shows the temperature dependence of the various phases in these systems, predicted by the thermodynamic calculations and assuming a

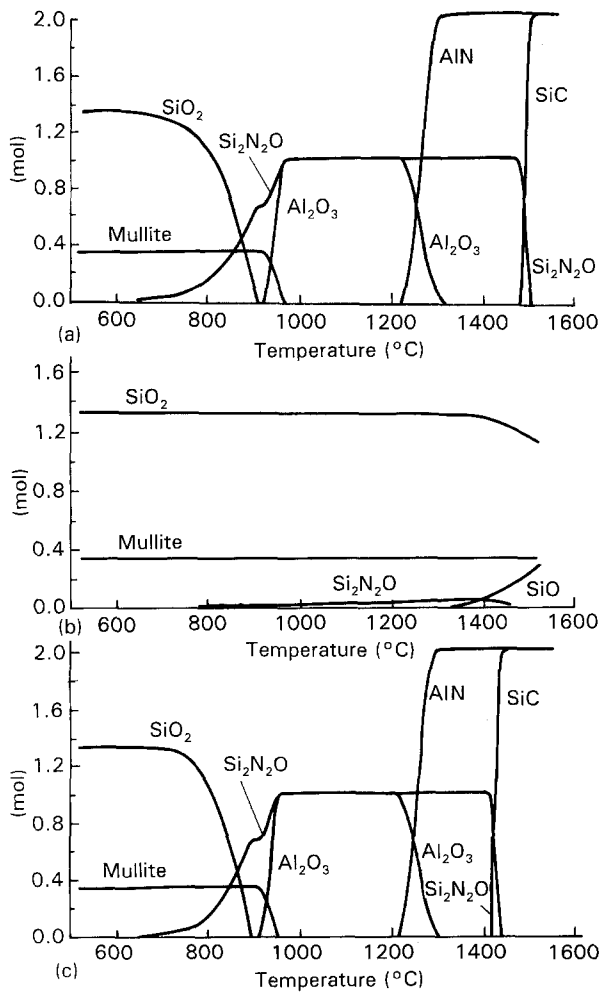


Figure 12 Phase assemblages as a function of temperature, predicted in sialon-forming systems by thermodynamic calculations, assuming 100 mol gas and 10 mol carbon. Thermodynamic data for the sialons were not available and thus are not included. (a) Aluminosilicate/ $N_2$ /C, (b) aluminosilicate/ $NH_3$ , (c) aluminosilicate/ $NH_3$ /C.

starting composition corresponding to metakaolinite. In the absence of carbon, nitrogen is almost totally inert towards mullite and silica at 1200 °C, but with the addition of carbon, both the silica and mullite are predicted to be thermodynamically unstable with respect to silicon oxynitride and alumina (Fig. 12a). Ammonia in the absence of carbon at 1200 °C exerts a slightly reducing effect on the free silica component, with which it forms a very small amount of silicon oxynitride and, at higher temperatures, some SiO, but the mullite remains intact (Fig. 12b). The addition of carbon to this system renders both the free silica and mullite unstable with respect to silicon oxynitride, alumina and AlN (Fig. 12c). Although the predicted silicon oxynitride is observed by NMR in these experiments, the other phases are not, suggesting that the reactions have not gone to completion under the present dynamic conditions which will remove gaseous intermediates such as SiO.

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