JOURNAL OF MATERIALS SCIENCE 27 (1992) 2180–2186

# Synthesis of "SiMON" ceramics from various clays and different sources of carbon

F. BERGAYA, F. KOOLI, J. F. ALCOVER
*CNRS, CRSOCI, 1B, rue de la Férollerie, 45071 Orleans Cedex 02, France*

The preparation of β-SiMONs by the thermal treatment (1373–1773 K) under nitrogen of various mixtures of clays and organic molecules (acrylonitrile) or carbon (charcoal) or graphitic oxide, was investigated. Cation ($Na^+$, $Y^{3+}$, $C_6$-amine$^+$) exchanged smectites (montmorillonite or hectorite) and kaolinite were used. With charcoal mixtures, a threshold of carbon content was found for each clay in the formation of β-SiMONs: 23% for montmorillonite, 14% for hectorite and 21% for kaolinite. This threshold was not reached in the case of polyacrylonitrile or graphitic oxide–smectite precursors and carboreduction under nitrogen of these precursors did not yield β-SiMONs. The thermal evolution of the carbon phases at low temperature, before contact with clays, influenced the formation of β-SiMONs which appears at 1673 K if the carbon content is greater than the threshold, but always with other minor phases.

## 1. Introduction

### 1.1. Advantages of SiAlONs

Structural ceramics are required to replace metals in high-temperature applications. A considerable interest has been shown in the last few years in silicon nitride ceramics due to their potential use in high-temperature engineering. Among them, the "SiMONs" family and, more particularly, the "SiAlONs" family show valuable properties (Table I; [1]) as well as advantages as compared with other advanced ceramics:

(i) better corrosion resistance than β-$Si_3N_4$;

(ii) a densification temperature lower than that of SiC.

These desirable properties, which are generally obtained with fully densified silicon nitride, do not result from simple firing of β-$Si_3N_4$ or SiC, as occurs with oxide or silicate ceramics.

### 1.2. Structural characteristics of SiMONs

"SiMONs" are generally obtained by the reaction between $Si_3N_4$ and various densification aids, such as $Al_2O_3$, MgO, $Y_2O_3$, [2–7] . . . . Jack and Wilson [3] reported that $Al_2O_3$ dissolves in β-$Si_3N_4$ at 1973 K under flowing nitrogen with aluminium and oxygen atoms replacing silicon and nitrogen atoms, respectively. The substitutional solid solution obtained is referred to as β-SiAlONs and its general formula is $Si_{(6-z)}Al_zO_zN_{(8-z)}$, where $z$ is the number of oxygen atoms replacing nitrogen, with $z \leqslant 4.2$.

These substitutions modify the β-$Si_3N_4$ lattice parameters as observed by Jack [8] who studied the evolution of the $a$ and $c$ parameters with $z$ by X-ray diffraction (XRD). The neutron diffraction study by Gillott *et al.* [9] of β-SiAlONs allowed them to conclude that there is no fundamental change in the crystalline structure of the initial β-$Si_3N_4$ in spite of the increases in $a$ and $c$ of the hexagonal lattice which were observed. We can note that the other phases present (not always well known) did not elicit a great interest, the effort being mainly centred on the preparation of SiAlON ceramics.

### 1.3. Preparation of SiMONs

Wild [10] tried to obtain β-SiAlON by nitruration of metakaolin at 1673 K by $NH_3$ and $H_2$ but he only obtained AlN and β-SiAlON very poor in aluminium ($z < 1.8$). Lee and Cutler [11] were the first to start from cheap raw materials as a source of silicon and aluminium and to obtain SiAlON from carboreduction of kaolins under a nitrogen flow, but the SiAlON was always admixed with other compounds. Other workers [12–14] used this method, but the results have not been reproduced [15]. Sugahara *et al.* [16] obtained SiAlONs starting from liquid acrylonitrile (AN) intercalated in amine montmorillonites polymerized *in situ* and carboreduced under a nitrogen flow.

In our work, we have tried to obtain SiAlONs by thermal treatment of various mixtures of clays with organic molecules, or carbon, or graphitic oxide; in the first case, we used the fact that the formation of intercalation compounds allows the preparation of mixtures at the molecular level. Clays are sources of silicon and aluminium (montmorillonite, kaolinite) or silicon and magnesium (hectorite). The choice of the exchangeable cations used in these syntheses is not innocent. In addition to sodium cation exchange, which is the first step in the purification of the starting material, hexylamine cation exchange was performed

TABLE I Selected properties of SiAlON ceramics (after Trigg [1])

| | |
|---|---|
| Rupture modulus[a] | 828 MPa |
| Weibull modulus | 15 |
| Tensile strength[a] | 400 MPa |
| Compressive strength[a] | > 3.5 GPa |
| Young's modulus[a] | 300 GPa |
| Hardness (VPN 0.5 kg load)[a] | $1800\,\mathrm{kg\,mm^{-2}}$ |
| Fracture toughness | $5\,\mathrm{MN\,m^{-3/2}}$ |
| Density | $3.2\,\mathrm{g\,cm^{-3}}$ |
| Thermal expansion coefficient (0–1000 °C) | $3.2 \times 10^{-8}\,°\mathrm{C}^{-1}$ |
| Thermal shock resistance[b] | 510 °C |

[a] Measured at room temperature.

[b] Quenched into cold water.

to compare with Sugahara's results. Yttrium cation exchange was also used which could lead to better mechanical properties of the products obtained [5].

## 2. Experimental procedure

### 2.1. Precursor compounds

The clays used in the present study were montmorillonite (Mt) from Upton, Wyoming, hectorite (Ht) from Hector, California, and kaolinite (Ka) from Charente, France. The three clays were purified by sodium ion-exchange and when necessary, the two smectites were further exchanged with the yttrium or hexylammonium cations (Y and $C_6$-amine, [17]). Hectorite was decarbonated before purification by successive treatments with 0.1 N HCl and N NaOH.

The intercalation of acrylonitrile in smectites and its *in situ* cyclization at 493 K for 4 h were followed by adsorption isotherms, X-ray diffraction (XRD) and infrared spectroscopy. The detailed preparations of the polyacrylonitrile-smectite (PAN-smectite) precursors have already been reported [17].

The charcoal (Prolabo) which was used, contained 83% C with a specific surface area of $830\,\mathrm{m^2\,g^{-1}}$, and a basal spacing equal to 0.337 nm. Mixtures of charcoal with water suspensions of the appropriate clay were pelletized (1–2 mm) and dried at 363 K.

The colloidal graphitic oxide (GO) compound was obtained by oxidizing 4 g natural Madagascar graphite (40–60 μm) with 44 g potassium chlorate in a nitric–sulphuric acid mixture (70 ml $H_2SO_4$ (95%) and 36 ml $HNO_3$ (69%)). The detailed preparation of the colloidal GO–smectite mixture has been given previously [18].

In certain preparations, 1% Fe was added to the samples in the form of $Fe(NO_3)_3$ solution (Merck).

### 2.2. Heat treatment under nitrogen

About 0.5 g powder sample was heated in a carbon boat (8 mm × 10 mm × 100 mm) in a tube furnace under nitrogen gas ($2.5\,\mathrm{l\,min^{-1}}$) at temperatures between 1473 and 1773 K for 2–4 h. The temperature was measured with an optical pyrometer and manually regulated every 3 min. The heating rate was $20\,\mathrm{K\,min^{-1}}$, the cooling rate was not controlled.

### 2.3. Analytical techniques

The crystallographic characteristics of the heated products were investigated by XRD (Siemens diffractometer) on powder samples with $\mathrm{Cu}K_\alpha$ radiation.

Infrared spectra of KBr pellets were recorded in the $4000–400\,\mathrm{cm^{-1}}$ range (Perkin–Elmer 180 IR spectrometer).

Chemical analyses of the various elements in the mixtures were performed using X-ray fluorescence for the heavier elements and gas chromatography for carbon, hydrogen and nitrogen. The oxygen content was obtained by coulometry.

Scanning electron microscopy (Cambridge Stereoscan 100) was used to examine the surface morphology of the powdered products.

## 3. Results and discussion

### 3.1. Thermal transformation of pure clays in a nitrogen atmosphere

As a first step, the thermal transformations (1473–1673 K) under a nitrogen flow of the three clays (Mt, Ht and Ka) without any admixture, were investigated. The results are summarized in Tables IIa–c

TABLE II Principal crystalline phases obtained with various montmorillonites, hectorites and kaolinites heated under nitrogen at different temperatures

(a) Montmorillonites (Mt)

| Temperature (K) | Na–Mt [19] | Amine–Mt [19] | Amine–Mt [20] | $(M^{n+})$–Mt[a] |
|---|---|---|---|---|
| 1273 | Crist > Mu > Sp | Silica O > Mu | | |
| 1373 | | | Crist ≫ Mu, Sp | |
| 1473 | Mu ≫ Cord | Crist > Cord > Mu | Mu > Sp | Crist > Cord ≫ Sp |
| 1573 | | | Mu > Cord | Cord > Crist |
| 1673 | | | Mu | Cord |

(b) Hectorites (Ht)

| Temperature (K) | $(M^{n+})$–Ht[a] |
|---|---|
| 1473 | Enst > Crist |
| 1573 | Enst > Crist |
| 1673 | Enst |

(c) Kaolinites (Ka)

| Temperature (K) | Ka[a] |
|---|---|
| 1473 | Mu > Crist |
| 1573 | Crist > Mu |
| 1673 | Crist > Mu |

Enst, enstatite; Crist, cristobalite; Mu, mullite; Sp, spinel; Cord, cordierite.

[a] Present results ($M^{n+}$ = Na, Y or $C_6$-amine).

with the $Na^+$-exchanged clays as an example. The results for all clays are the same, and independent of the nature of the exchanged cation: in the absence of carbon and up to 1673 K, the thermal transformation of clays under nitrogen does not lead to a silicon oxynitride compound.

### 3.1.1. Thermal transformation of montmorillonite (Table IIa)

Cordierite appears at 1473 K, with cristobalite as the major phase and spinel as a minor phase which disappears when the temperature increases. Cordierite becomes the major phase at 1573 K. The formation of cordierite at 1473 K was reported by Oya *et al.* [19] in the presentation of their results with $C_6$-amine Mt, but Sugahara *et al.* [20] found mainly a mullite phase persisting up to 1673 K. The sapphirine phase cited by Brown *et al.* [21] was not detected in our studies.

We should add that cordierite did not appear when montmorillonite was heated in air, this treatment leading to cristobalite as the major phase.

### 3.1.2. Thermal transformation of hectorite (Table IIb)

Enstatite was the major phase at all temperatures (1473–1673 K). Cristobalite was also detected but decreased when the temperature was increased or the solid phase was heated for longer periods. Heating hectorite in air rather than in nitrogen produced forsterite instead of enstatite [22].

### 3.1.3. Thermal transformation of kaolinite (Table IIc)

The thermal transformation of kaolinite in air has been thoroughly studied [23–25]. At 773 and 1273 K, metakaolinite and mullite are formed, respectively. The results under nitrogen are not very different, with mullite formed as the major phase at 1473 K with small amounts of cristobalite, but the latter increases and becomes the major phase with increasing temperature.

## 3.2. Thermal carbonitride synthesis of ceramics from PAN–smectite complexes

### 3.2.1. Thermal transformation of PAN–smectite complexes

Surprisingly, the PAN–smectite precursors heated under nitrogen between 1373 and 1673 K for different lengths of time do not lead to β-SiAlON or β-SiMgON. The resulting compounds are always cristobalite and cordierite in the case of PAN–Mt, and enstatite as major phase in the case of PAN–Ht, independently of the exchanged cations.

The products obtained at 1373 K have a granular aspect and are strongly attached to the surface of the carbon boat, but heating to 1673 K produces a vitreous mass also strongly adhering to the boat. Examination by SEM of the interface and of the vitreous surface shows that the linkage with the carbon boat is due to fibres rich in silicon and that the sample is surrounded by an amorphous phase (Fig. 1).

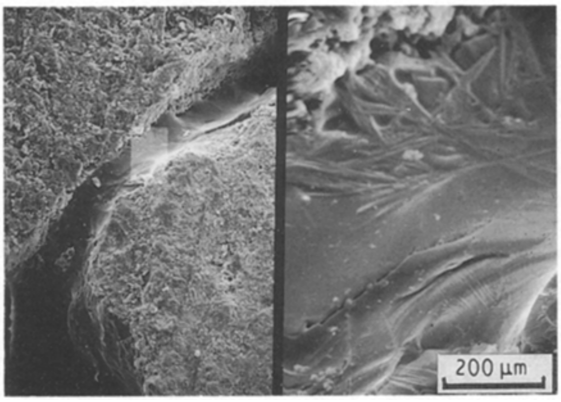

*Figure 1* SEM examination of the vitreous surface of the PAN–smectites complexes heated at 1673 K under nitrogen and also of the interface between the vitreous phase and the carbon boat.

The precursors prepared by intercalation of liquid AN in $C_6$-amine smectite (Sugahara's method) gave the same results as the precursors obtained by intercalation of AN vapour. No SiAlONs were obtained; this is in disagreement with Sugahara [16, 20] who observed the formation of β-SiAlON at relatively high temperature (1473 K), in quantities increasing with temperature up to 1673 K. Other phases were simultaneously formed in Sugahara's preparation [16]. These observations induced us to try to elucidate the role of the chemical and physical states of PAN and its aptitude to permit carboreduction of the smectite.

### 3.2.2. Behaviour of PAN–smectite complexes at temperatures between 573 and 1173 K

A chemical analysis of the heated products indicates a very low carbon content with respect to the amount originally introduced as AN. Examination of the microstructural evolution as a function of temperature of pure PAN (which gives an intense reflection at $d = 0.558$ nm at room temperature, in the bulk state) shows a formation of stacks of graphitic aromatic planes (0.35 nm) (at relatively high temperature $\simeq 973$ K). To obtain more information on the microstructural evolution of this intercalated carbon phase, we followed the behaviour of the PAN–smectite complexes heated between 573 K (temperature of preparation of the precursors) and 1173 K (final treatment temperature).

(i) In the case of PAN–Mt, the interlayer distance is 1.38 nm up to 673 K. Between 673 and 973 K, this distance decreases to 1.08 nm, which is close to the value reported by Kyotani *et al.* [26] who found 1.10 nm for a pregraphitic carbon–montmorillonite interstratified material obtained by heating to 973 K under nitrogen, a γ-irradiated PAN–Mt complex. After 973 K, the clay material was destroyed and it was difficult to follow the evolution of the carbon phase.

(ii) in the case of PAN–Ht, the interlayer distance remains at 1.24 nm up to 1173 K; hectorite, which is a trioctahedral smectite, is stabler than the dioctahedral smectite in this range of temperature.

X-ray diffraction is therefore unable to give an explanation of the low carbon content observed.

### 3.2.3. Thermal transformation of mixtures of prepyrolysed PAN and smectites

Mixtures of PAN prepyrolysed at various temperatures and smectites, were heated to temperatures in the 1673–1773 K range. The results (Table III) showed that the composition of the products varied with the temperature of pretreatment of PAN. Only in the case of prepyrolysed PAN was β-SiAlON obtained.

The β-SiAlONs were identified from the XRD diagrams by the main peaks at 0.68, 0.38, 0.34, 0.266, 0.249 nm, and by infrared spectroscopy which showed the progressive replacement of the Si–O bands of the clays at $\simeq 1080$ and $\simeq 475\,\mathrm{cm}^{-1}$ by Si–N broad bands at $\simeq 1030$, $900\,\mathrm{cm}^{-1}$ and 570, $430\,\mathrm{cm}^{-1}$, respectively.

β-SiAlON appears when the concentration of PAN is sufficient, and is promoted by (i) prepyrolysis at 1673 K rather than at 673 K, (ii) a higher treatment temperature (1773 K) of the mixture, (iii) the nature of the interlayer cation: for example, yttrium in PAN–Y–Mt favours the formation of β-SiAlON at high temperatures. It is obvious then that the formation of β-SiAlONs is closely related to the thermal evolution of the carbon phase. The difference between our results and those of Sugahara *et al.* is probably due to the thermal history of our samples, which is related to the carbon content at the temperature of ceramization, and, more particularly, to the degree of cyclization of the PAN.

### 3.2.4. Summary of the results with PAN–smectite complexes

1. The thermal treatment between 1473 and 1773 K of the PAN–smectite complexes does not lead to β-SiMON. The PAN–Mt complexes essentially yield cordierite and cristobalite, whereas PAN–Ht complexes essentially yield enstatite.

2. The preparation method (liquid or gas phase) of the AN–smectite precursor does not influence the result.

3. Chemical analysis of the 973 K pyrolysed PAN–smectites shows that this negative result is due to a surprisingly large loss of carbon during the low-temperature phase of the thermal treatment. This was verified by (i) prepyrolysing pure PAN, (ii) mixing the pyrolysed polymer with a smectite, and (iii) finally heating this mixture at high temperature (1673–1773 K) under nitrogen in which case β-SiMON was obtained.

4. It seems that the nature of the exchangeable cations is important: Y cation favours SiAlON and $C_6$-amine favours SiMgON.

### 3.3. Thermal carbonitride synthesis of ceramics from charcoal–clay mixtures

Mechanical mixtures of charcoal and smectite clays were used to try to determine the conditions needed for the obtention of β-SiAlON. Kaolinite, which does not swell and has already been largely studied as cheap raw material for the preparation of β-SiAlONs [11, 27] was also used.

The components were mixed at the micronic rather than at the molecular level, as was the case with PAN–smectite complexes. β-SiAlONs were obtained but never as single phases, other minor phases appearing dependent on structural and kinetic effects (type of clays, temperature of ceramization, time of heating). XRD diagram of charcoal–Y–montmorillonite is given as an example in Fig. 2.

The products were studied as a function of temperature and carbon content.

(i) At 1573 K, under nitrogen there was no formation of β-SiAlON (Table IVa), which appears at 1673 K. Its formation was favoured by increasing temperatures and heating times (indication of a kinetic effect).

(ii) Table IVb shows the influence of the carbon content; the formation of β-SiAlON is related to a sufficiently high carbon content.

By plotting the absolute intensity of the first SiAlON peak at 0.68 nm versus the concentration of carbon in the initial mixtures (Fig. 3), we see the occurrence of a threshold in the synthesis of the nitride phase. This threshold, estimated from the half height of the step in the diagram, is at about 23% for montmorillonite, 14% for hectorite and 21% for kaolinite. Before discussing these thresholds, we note:

(i) among the interlayer cations which were studied (Na, Y, $C_6$-amine), $Y^{3+}$ gives the best result with montmorillonite at high temperature and $C_6^+$ is the best with hectorite (greater yield of β-SiAlON or β-SiMgON at 1773 K),

(ii) addition of 1% Fe favours the formation of the nitride phase, as shown by Lee and Cutler [11].

TABLE III Principal crystalline phases obtained with mixtures of prepyrolysed PAN and montmorillonites (Mt) heated under nitrogen at two different temperatures

| 1673 K | | 1773 K | |
|---|---|---|---|
| $C_6$Mt + PAN (673 K) | $C_6$Mt + PAN (1673 K) | $C_6$Mt + PAN (673 K) | YMt + PAN (673 K) |
| Cord > β-SiAlON, $Si_2N_2O$, Sp | β-SiAlON, α-$Si_3N_4$, Sp | β-SiAlON, α-$Si_3N_4$ > Sp, AlN (traces) | β-SiAlON ≫ Sp, AlN (traces) |

Cord, cordierite; Sp, spinel.
The amount of PAN in the mixtures corresponds to 27% Carbon.
PAN is obtained by ultraviolet polymerization of liquid AN.

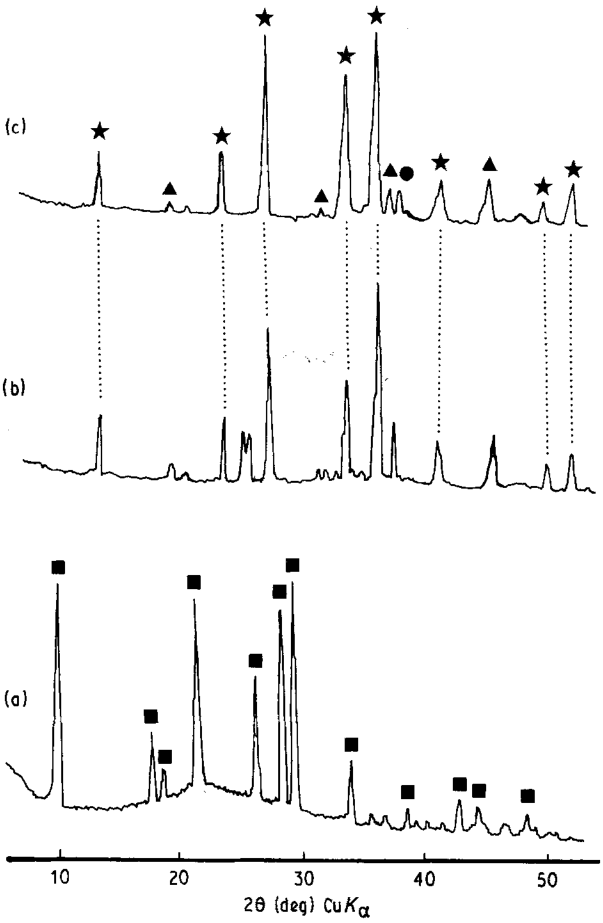

*Figure 2* XRD diagrams of mixtures of the Y–Mt, (b) with charcoal, (c) with PAN prepyrolysed at 673 K, both heated at 1773 K under nitrogen. (a) The XRD of pure Y–Mt without source of carbon heated at 1573 K is given for comparison. (★) β-SiAlON, (▲) spinel, (●) AlN, (■) cordierite.

### *3.3.1. Theoretical and experimental thresholds*

We now compare the experimental thresholds obtained for each clay with the known theoretical values of $z$ which correspond to the Al/Si ratio obtained by chemical analysis, namely $z = 2$ for montmorillonite, $z = 0$ for hectorite, and $z = 3$ for kaolinite [28] and from the following general equation [15]:

$$z/2\,Al_2O_3 + (6 - z)SiO_2 + (8 - z)/2\,N_2 + (12 - 3z/2)C \rightarrow Si_{(6-z)}Al_zO_zN_{(8-z)} + (12 - 3z/2)CO \quad (1)$$

The calculated and experimental thresholds are similar for smectites, but not for kaolinite (Table V). To check whether the values of $z$ are correct, we can calculate its value from experimental crystallographic data using the method given by Jack [8] who related $z$ to the lattice parameter, $a$, obtained from the XRD data. For montmorillonite, the value $z = 2.3$ thus obtained is slightly superior to Baldo's calculated value ($z = 2$). The difference is probably due to the presence of the mixture of phases. For kaolinite, $z$ increases with the charcoal content, from $z = 2.3$ for 20% C content to $z = 3$ for 40% C content. The theoretical value was taken as $z = 3$. The increase of $z$, we have observed, could be related to the decrease of the mullite phase which gives alumina.

### *3.3.2. Summary of the results with charcoal clay mixtures*

1. For each clay (Mt, Ht, Ka), there is a threshold of carbon content (23%, 14% and 21%, respectively) for the formation of β-SiMON.
2. These experimental threshold values are in good agreement with the carbon/clay ratios calculated by Paris and Grollier–Baron's equation (Equation 1) using the $z$ values calculated from the X-ray diffraction data.
3. The yields of β-SiMON increase with increasing temperature and heating times.
4. The iron of the clay probably catalyses the reaction.

TABLE IV (a) Principal crystalline phases obtained with mixtures of charcoal and clays heated under nitrogen at different temperatures

| Temperature (K) | Y–Mt + charcoal (27%) | Y–Ht + charcoal (24%) | Ka + charcoal (24%) |
|---|---|---|---|
| 1473 | Crist > Cord | Enst > Crist | Mu > Crist |
| 1573 | Cord > SiC > Sp | Forst > SiC > $Si_2N_2O$ | Mu > SiC |
| 1673 | β-SiAlON, Sp, $Si_2N_2O$, X | β-SiMgON, Forst > SiC | β-SiAlON > Mu, α-$Al_2O_3$ |
| 1773 | β-SiAlON > Sp > $Si_2N_2O$, X | β-SiMgON > Forst > $MgSiN_2$ | β-SiAlON > Sp > α$Al_2O_3$ |

Crist, cristobalite; Cord, cordierite; Sp, spinel; Enst, enstatite; Forst, forsterite; Mu, mullite; X, unidentified phase; Mt, montmorillonite; Ht, hectorite; Ka, kaolinite.

TABLE IV (b) Principal crystalline phases obtained with mixtures of charcoal and clays heated at 1673 K under nitrogen

| Charcoal content (%) | Y–Mt | Y–Ht | Ka |
|---|---|---|---|
| 10 | Cord > Crist > Mu | Enst > Forst > $Si_2N_2O$ | Mu > Crist |
| 20 | SiC > Mu > Sp | β-SiMgON, Forst > $Si_2N_2O$ | Mu > β-SiAlON |
| 24 | – | β-SiMgON, Forst > SiC | β-SiAlON > Mu, $Al_2O_3$ |
| 27 | β-SiAlON, Sp, $Si_2N_2O$, X | – | – |
| 30 | β-SiAlON > Sp, X | β-SiMgON > Forst | β-SiAlON > α-$Al_2O_3$ > α-$Si_3N_4$ |
| 40 | β-SiAlON > AlN, α-$Si_3N_4$ | β-SiMgON > $MgSiN_2$ > α-$Si_3N_4$ | β-SiAlON > AlN > α-$Si_3N_4$ |

Cord, cordierite; Crist, cristobalite; Mu, mullite; Sp, spinel; Enst, enstatite; Forst, forstierite; Mt, montmorillonite; Ht, hectorite; Ka, Kaolinite.

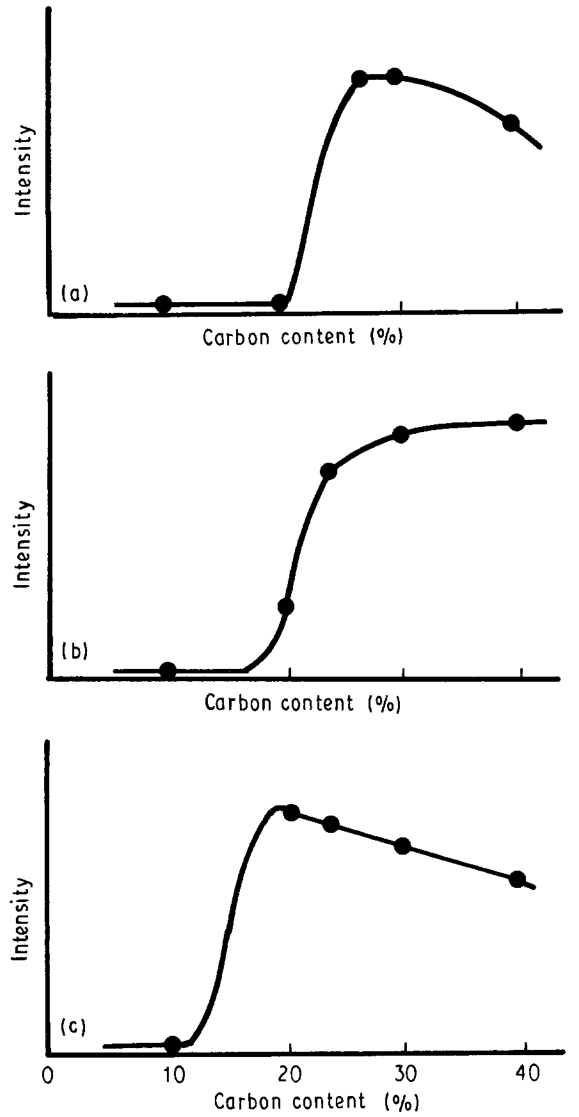

*Figure 3* The absolute intensity of the first SiMON peak at 0.68 nm versus the carbon content in the initial mixtures. (a) Mt–Y, (b) Ka, (c) Ht–Y.

TABLE V Threshold (minimum carbon content) for the appearance of β-SiMON

| Clays | Carbon content (%) | |
|---|---|---|
| | Theoretical | Experimental |
| Mt | 23 | 23 |
| Ht | 13 | 14 |
| Ka | 31 | 21 |

## 3.4. Thermal carbonitride synthesis of ceramics from graphitic oxide–clay colloidal suspensions

To try to understand why the threshold was not reached in PAN–smectite complexes, a precursor, intermediate between the two previous ones, was studied: a mixture of clay and GO obtained by mixing and stirring the two suspensions and evaporating to dryness. The non-stochiometric mixtures are similar to clays. They have a lamellar structure, which swells in polar solvents, and have a high CEC. Their XRD patterns show a basal distance of 0.8 nm at room temperature; this distance decreases to 0.6 nm under vacuum.

As in the case of the mixtures with charcoal, the formation of β-SiAlON is dependent on the initial GO content, which is always at least 25% (Table VI). Generally, the yield of β-nitride ceramic phases is less important compared to that given by the previous precursor (charcoal–clay mixture).

### 3.4.1. *Thermal evolution of pure GO*

At room temperature, the XRD pattern of GO shows a peak at 0.8 nm, but after thermal treatment to 1173 K, this peak comes close to 0.337 nm, which is typical of a disordered graphitic structure. However, even after the heat treatment at this temperature (1173 K) a broad band also exists close to 0.6 nm.

### 3.4.2. *Thermal evolution of the colloidal GO–clay mixtures*

With increasing temperature, the XRD pattern of the clay–GO mixtures changes and the two peaks which exist in the XRD pattern before the thermal treatment gradually disappear, but the superposition of the 0 0 3 peak of clays and the 0 0 1 peak of graphite prevents the study of the thermal evolution of the mixture by this method.

The more surprising result concerns the carbon content which, from the initial value of 25%, drops to 13% after heating at 1173 K. This suggests that the different behaviour of these preparations is due to the carbon content effectively present at the temperature of the reactions between the solids.

### 3.4.3. *Thermal transformation of prepyrolysed GO–smectite mixtures*

The influence of the thermal pretreatment of the precursor on the nature of the products obtained was studied by heating the prepyrolysed GO–smectite mixtures (Table VII). Although β-SiAlON was obtained in both cases, the major phase was strongly dependent on the thermal pretreatment, confirming the importance of the thermal history of the carbon in its initial environment.

TABLE VI Principal crystalline phases obtained with mixtures of GO and Y-clays heated under nitrogen at 1673 K

| GO content (%) | Y-montmorillonite | Y-hectorite |
|---|---|---|
| 10 | Cord > Crist | Enst > Forst |
| 20 | Cord > Mu ≫ α-$Si_3N_4$ > β-SiAlON > Sp | Forst > α-$Si_3N_4$ > β-SiMgON |
| 40 | Cord > α-$Si_3N_4$ > β-SiAlON > Sp | Forst > β-SiMgON > α-$Si_3N_4$ |

Cord, cordierite; Crist, cristobalite; Mu, mullite; Sp, spinel; Enst, enstatite; Forst, forsterite.

TABLE VII Principal crystalline phases obtained by thermal treatment at 1773 K of different mixtures (first line of the table). Temperatures in parentheses are pretreatment temperature of the precursor which is given in brackets

| [Y-Mt + G0] (873 K) | Y-Mt + [G0] (873 K) |
|---|---|
| Sp > β-SiAlON, $\alpha$-$Si_2N_2O$ | β-SiAlON, $\alpha$-$Si_3N_4$ > $Si_2N_2O$, Mu, Sp |

Sp, spinel; Mu, mullite; Mt, montmorillonite, Ht, hectorite.

### 3.4.4. Summary of the results with GO–smectite complexes

The yield of SiAlON is smaller than with charcoal; this can be assigned to the loss of carbon during the low-temperature thermal treatment.

## 4. Mechanisms and conclusion

On the basis of these results we propose the following reaction mechanisms for the carboreduction of the three clays.

For montmorillonite three important steps occur.

(i) decomposition of the montmorillonite under nitrogen in cordierite and cristobalite independently of the carbon sources.

(ii) Reduction of cristobalite to silicon carbide and of cordierite to mullite and spinel.

(iii) Complete reduction and nitridation of mullite by SiC and carbon to give β-SiAlON and AlN.

For hectorite, again three important steps occur.

(i) Decomposition of the hectorite under nitrogen in enstatite and cristobalite.

(ii) Reduction of enstatite to forsterite and of cristobalite to silicon carbide.

(iii) Further reduction by SiC and carbon gives, β-SiMgON and $MgSiN_2$.

For kaolinite we observe a similar evolution to that of the two previous clays.

(i) Decomposition of kaolinite under nitrogen to mullite and cristobalite.

(ii) Reduction of cristobalite to silicon carbide.

(iii) Appearance of β-SiAlON and AlN by reduction of mullite by SiC and carbon.

In conclusion, our results have shown that the thermal history of the carbon phase in the low-temperature domain (below 1273 K) may be a key parameter, when complex carbon sources are used; the other parameter controlling the formation of β-SiMONs is the nature of the clays (chemical composition, nature of the exchangeable cation). The kinetic and catalytic effects are also apparent, but the most important result is the existence of a threshold of the carbon content specific to each clay.

From the practical point of view there is no doubt that clays are suitable cheap raw material for the preparation of SiMON as already shown [29] in the first preindustrial developments; In view of the sensitivity of the reaction to the composition of the reacting solids, it is also evident that each specific mineral requires a specific optimization procedure.

## Acknowledgement

The authors thank Dr R. Setton for helpful discussions.

## References

1. M. B. TRIGG, *J. Aust. Ceram. Soc.* **21** (1985) 24.
2. Y. OYAMA, *Jpn. J. Appl. Phys.* **11** (1985) 760.
3. K. H. JACK and W. I. WILSON, *Nature* **238** (1972) 28.
4. Y. OYAMA and O. KANIGAITO, *Yogyo Kyokai-Shi* **81** (1973) 290.
5. A. TSUGE, K. NISHIDA and M. KOMATSU, *J. Amer. Ceram. Soc.* **58** (1975) 323.
6. L. J. GLAUCKER, H. L. LUKAS and T. Y. TIEN, *Mater. Res. Bull.* **11** (1976) 503.
7. F. F. LANGE, *J. Amer. Ceram. Soc.* **61** (1978) 53.
8. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
9. L. GILLOTT, N. COWLAM and G. E. BACON, *ibid.* **16** (1981) 2263.
10. S. WILD, *ibid.* **13** (1976) 1972.
11. J. B. LEE and I. B. CUTLER, *Amer. Ceram. Soc. Bull.* **58** (1979) 869.
12. I. L. BOYARINA, E. V. DEGTYAFEVA, A. B. PUCHKOV, A. M. GAVRISH and N. V. GUL'KO, *Ognewporov. Moskova* **8** (1981) 33.
13. H. YOSHIMATSU, M. MITOMO and H. MIHASHI, S. OHMORI and T. YABUKI, *Yogyo Kyokai-Shi* **91** (1983) 442.
14. H. YOSHIMATSU, H. MIHASHI and Y. HISASHI, *ibid.* **94** (1986) 309.
15. R. A. PARIS and T. GROLLIER-BARON, Eur Pat. 23869, A1, 11 February 1981.
16. Y. SUGAHARA, K. KURODA and C. KATO, *J. Amer. Ceram. Soc.* **67** (1984) C-247.
17. F. BERGAYA and F. KOOLI, *Clay Minerals* **26** (1991) 33.
18. F. KOOLI and F. BERGAYA, in "Surfaces and Interfaces of Ceramic Materials", edited by L. C. Dufour *et al.* (Kluwer Academic, Dordrecht, 1989) p. 575.
19. A. OYA, M. SAITO and S. OTANI, *Appl. Clay Sci.* **3** (1988) 291.
20. Y SUGAHARA, K. KURODA and C. KATO, *J. Mater. Sci.* **23** (1988) 3572.
21. W. M. BROWN, K. J. D. MACKENZIE and R. H. MEINHOLD, *ibid.* **22** (1987) 3265.
22. J. M. GREEN, K. J. D. MACKENZIE and J. H. SHARP, *Clays Clay Miner.* **18** (1970) 339.
23. H. INSLEY and R. H. EWELL, *J. Res. Nat. Stand.* **14** (1935) 615.
24. G. W. BRINDLEY and M. NAKAHIRA, *J. Amer. Ceram. Soc.* **42** (1959) 319.
25. J. F. DUNCAN, K. J. D. MACKENZIE and P. K. FOSTER, *ibid.* **52** (1969) 74.
26. T. KYOTANI, N. SONOBE and A. TOMITA, *Nature* **331** (1988) 331.
27. Y. SUGAHARA, J. MIYAMOTO, K. KURODA and C. KATO, *Appl. Clay. Sci.* **4** (1989) 11.
28. J. B. BALDO, V. C. PANDOLFELLI and J. R. CASARINI, in "Ceramic Powders", edited by P. Vincenzini (Elsevier Scientific, Amsterdam, 1983) p. 437.
29. M. FERRETTI, *Sci. Techniq.* **22** (1986) 40.

*Received 7 January*
*and accepted 1 May 1991*