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Synthesis of Si_3N_4 using sepiolite and various sources of carbon

A. O. KURT*, T. J. DAVIES
Manchester Materials Science Centre, Grosvenor St., M1 7HS, Manchester, UK
E-mail: aokurt@mu.edu.tr

Sepiolite of Turkish origin was used as Si precursor in the syntheses of silicon nitride (Si_3N_4) powders by carbothermal reduction-nitridation (CRN) by mixing with several reducing agents i.e. charcoal, carbon black and petroleum coke as discrete particles and acrylonitrile as an intercalation medium. Purified sepiolite samples with a pre-determined C/SiO_2 ratio of 4 yielded Si_3N_4 powders after firing at temperatures 1300–1475°C under continuous nitrogen flow. The various sepiolite-reducing agent combinations were evaluated. The α/β ratio and secondary phase content of the powders after CRN were found to depend on temperature, time, heating rate and on the physicochemical properties of the precursor used such as, surface area and mixing of the reactants. © *2001 Kluwer Academic Publishers*

1. Introduction

1.1. Synthesis of Si_3N_4 ceramics

Despite of their low impact resistance and low fracture toughness, advanced ceramics, such as nitrides and oxides, have increasingly been used due to their characteristics in exhibiting high hardness, good thermal and corrosion resistance, and retention of strength at elevated temperatures. Silicon nitride (Si_3N_4) and its derivatives, such as the SiAlONs have excellent thermal shock resistance with a high thermal conductivity making them suitable candidates for adiabatic engine components. Although a large number of powder preparation methods have been researched to produce ultra-fine, high-purity Si_3N_4 powders; such as imide decomposition [1], polymer pyrolysis [2], laser-synthesis [3, 4], plasma techniques [5] for example, only a few of these have received detailed attention because of uncertainties about cost-effectiveness and bulk production controls.

Commercially, silicon nitride is produced via direct nitridation and imide decomposition methods. In both techniques, final product is obtained after several intermediate steps. In the former case, pre-formed silicon compact is reacted (at 1300 to 1500°C) with iron as catalyst (used to enhance the reaction rate [6] with nitrogen gas forming Si_3N_4 pellets) [7]. To obtain fine particles this has to be crushed and milled. In the imide decomposition methods, volatile silicon halides, such as silicon tetrachloride, react with ammonia to produce fine pure amorphous phase Si_3N_4 powders in the range 1100 to 1300°C which crystallises after heat treatments for up to 15 h at 1500°C.

Carbothermal-reduction nitridation of SiO_2 [8–12] is becoming a strong candidate as a processing replacement for direct nitridation of silicon powder for commercial Si_3N_4 production. This is due to mainly to the availability and easy access of the raw materials source and unsophisticated production routes. Carbothermal reduction nitridation (CRN) involves reduction of oxides, such as silica (SiO_2) usually by mixing with a reducing agent in stoichiometric or excess amounts, in the temperature range 1300 to 1450°C for several hours under an inert atmosphere. This liberates Si or SiO in gaseous form, which further react with nitrogen to form silicon nitride following the general reaction.

$$3SiO_2 + 2N_2 + 6C \rightarrow Si_3N_4 + 6CO$$

Formation of final product may involve many intermediate stages. A high purity α-phase Si_3N_4 powders having high surface area may be produced by this method; high strength and fracture toughness of the densified products at room and elevated temperatures are reported [13, 14]. Factors such as the physical and chemical state of the starting materials, thermodynamics and reaction kinetics [15] strongly affect the formation and morphology of Si_3N_4 produced by a CRN process. Studies by Ekelund and Forslund [16] on the influence of starting material and synthesis parameters for producing silicon nitride by a CRN, using SiO_2 and a solid reducing agent, revealed that homogeneity of mixing in reactant precursors was important.

The rate of formation of Si_3N_4 in a CRN process was reported to be dependent on the initial specific surface area of the precursors such as that increase in Si_3N_4 yields was observed with an increase in the specific surface area of SiO_2 and carbon (starch, lamp lack and activated carbon) [9]. An increase in specific surface area of carbon black [17] or in the ratio C/SiO_2 [18]

Present Address: The Muğla University, Tek. Eğt. Fak., 48000/Muğla, Turkey.

affects the nucleation stage of Si_3N_4 synthesis and results in fine particles.

The main problem with synthesis of Si_3N_4 by a CRN is, in general, a high impurity content, mainly consisting of SiC, unreacted residual carbon and oxygen along with minor metallic impurities. However, it was demonstrated by van-Dijen *et al.* [19] that Si_3N_4 powders synthesised by CRN process can be sintered to high densities resulting in a good engineering product, provided that adequate precautions were taken during sintering.

1.2. Sepiolite as a Si source

Two previous attempts to synthesis Si_3N_4 using sepiolite (molecular formula for half a unit given as $(Mg_8)(Si_{12})O_{30}$ $(OH)_4$ $(OH_2)_4 \cdot 8H_2O)$ (20) as a Si source are reported by Sugahara [21] and Arik [22, 23]. Sugahara *et al.* [21] obtained Si_3N_4 by CRN of a mixture of Japanese sepiolite, with carbon black in various C/SiO_2 ratio; predominately β-phase Si_3N_4 with Mg_2SiO_4, Si_2N_2O and SiC secondary phases were reported although no evaluation of the Si_3N_4 was carried out. Arik *et al.* [22, 23] used Turkish origin sepiolite, received in purified form; the amount of CaO, Fe_2O_3 and Al_2O_3 was reported 1.73, 0.66 and 1.19 wt.% respectively and conditions that produced the best conversion, mainly β-phase with some α with different particle sizes and morphologies, was reported to be 16 hours CRN at 1400°C with a C/SiO_2 molar ratio of 4. A high Ca content (2.72 wt.%) along some Fe and Al was found.

In the current work as-received sepiolite (sieved to $-150 + 75$ μm size fraction) was subjected to various acid leaching pre-treatments before nitridation in order to eliminate the impurities, mainly dolomite, and also to modify the structure of the mineral for monomer absorption. Materials cost was a driving force behind the current investigation to produce a cheap Si_3N_4 powder while retaining good specific properties. In this respect, an attempt was made to obtain Si_3N_4 powders by thermal treatment of various mixtures of sepiolite with solid, discrete carbon particles or organic molecules. In the latter case acrylonitrile was used as an intercalating medium to mix with sepiolite at a molecular level.

2. Experimental procedure

2.1. Materials

Brown sepiolite from Eskişehir-Turkey was received in the form of coarse particles which were sieved to different size fractions. The powder remaining on a sieve $+150\,\mu$m was ball milled with Si_3N_4 milling balls and then sieved to $-150\,\mu\text{m} + 75\,\mu$m size fraction. Ball milling time was limited to 6 h because it had been reported previously that excessive grinding could cause severe distortion of the structure of sepiolite [24]. Chemical and mineral composition of the as-received sepiolite sample is given in Table I. Chemical analysis of the sepiolite powders (Table I) was carried out quantitatively using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The mineral analysis was determined semi-quantitatively using the results obtained from thermogravimetry (TG), energy dispersive analysis (EDX) and ICP-AES. Acrylonitrile (AN) was used as a clean carbon source (Hopkin & Willams Ltd) and azo-iso-butyronitrile (*GPR*) was used as an initiator (0.5 wt.%) in the polymerisation of the AN monomer.

Charcoal, carbon black and petroleum coke were primarily used as reducing agents; specifications and supplier's names are given in Table II. Carbon black supplied by Cabot Carbon was used as-received without

TABLE I Chemical and mineral composition (wt.%) of sepiolite, as-received material $-150 + 75$ μm size fraction after sieving

Chemical composition (wt.%)									
SiO_2	MgO	CaO	Al_2O_3	Fe_2O_3	K_2O	TiO_2	Na_2O	P_2O_5	IL[a]
47.11	20.48	5.62	0.94	0.44	0.08	0.05	0.02	0.01	25.25
Mineral composition (wt.%)									
Sepiolite					Dolomite				
81.52 ± 1.00					18.48 ± 1.00				

[a] Ignition loss at 1000°C.

TABLE II Reducing agents used in processing

Materials	Supplied by	Purity (%)	Pour density (kg/m^3)	Tap density (kg/m^3)	Mean particle size (μm)	Surface area (m^2/g)
Carbon Black (Vulcan-10H)	Cabot	99.7	345	390	5	110
Charcoal (Granular) (C/4120/53)	Fisher Scientific	92.8	–	–	1500	–
Charcoal, Ball Milled (4h)	As above (C/4120/53) processed	92.8	333	488	30	777
Petroleum Coke D44 GAO 43B	James & Durans Ltd.	99.0	761	904	70	60

any further processing. Charcoal, however, was supplied in the form of big granular shaped particles; this was ball-milled to a fine powder with a high surface area. The specifications for the charcoal after ball milling are also given in Table II.

2.2. Purification and preparation of precursors

To reduce impurities the sepiolite was leached in hydrochloric acid (HCl) the sepiolite was added to the leaching solution by one of two methods:

(a) Without any pre-mixing with the reducing agent before the leaching process. (Designation code used for the precursor is A-SX.) The letter "A" means that the reducing agent was added to the sepiolite after leaching. "S" stands for sepiolite and "X" means carbon black (Car) charcoal (Char) or petroleum coke (Petc).

(b) Mixed with a reducing agent before commencing the leaching. (Designation code used for the precursor is B-SX.) The letter "B" means that the reducing agent was added to the sepiolite before leaching. "S" and "X" have the same meaning as above.

In the former case, the reducing agent was added to the sepiolite after leaching but before the CRN stage. Powders obtained in this method were also used for the intercalation with acrylonitrile. In the second method, carbon black and sepiolite were hand-mixed in a mortar, whereas charcoal and petroleum-coke were added to sepiolite (+150 μm size) after milling. The intention of mixing sepiolite with a reducing agent *before* leaching was to obtain (a) intimate homogeneous mixtures of constituents and (b) to reduce the number of subsequent processing steps.

HCl leaching was varied by changing the testing conditions using a dilute solution of 0.06 to 0.27 M (prepared in advance). Magnesium perchlorate ($Mg(ClO_4)_2$) of analytical grade was used in some experiments to suppress the dissolution of Mg cations in sepiolite. After leaching, samples were washed several times with distilled water at the same temperature until the solution was neutralised. After washing, the sample slurry was filtered, dried and lightly ground before taking powdered samples for elemental analysis by scanning electron microscope (SEM) & transmission electron microscope (TEM) (EDX attached) and infrared spectroscopy IR. A schematic representation of the experimental stages is given in Fig. 1.

2.3. Nitridation

Sepiolite powders pre-mixed with a reducing agent were taken directly to the carbothermic reduction process after purification and chemical analyses. Samples purified without the presence of carbon were wet-mixed with carbon black, petroleum coke or ball-milled charcoal using distilled water. This final slurry was dried and powdered before nitridation. All solid reducing agents were added in a predetermined C/SiO_2 mole ratio of 4, which were determined from preliminary results on similar experiments in sepiolite-solid reducing agents systems [21, 22].

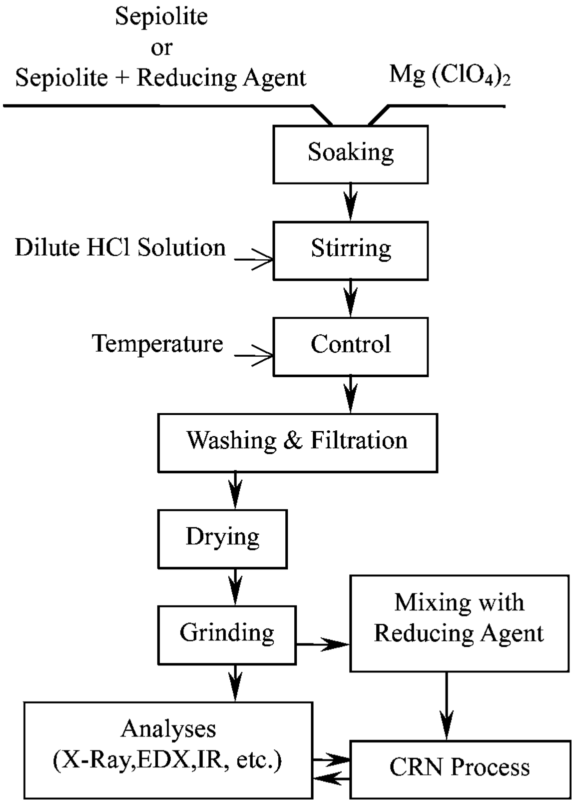


Figure 1 The flowchart showing experimental stages of the leaching process.

Purified sepiolite after dehydration (140°C, 2 h) was used for intercalation with acrylonitrile (AN) monomer and this mixture was polymerised at 60°C for 12 h in a closed system in the presence of an initiator. Subsequent cyclization of the polymerised complex in an oxidising atmosphere yielded a sepiolite-PAN intercalation compound that was found suitable for CRN process. Detailed information regarding to intercalation of sepiolite with acrylonitrile and synthesis of Si_3N_4 from cyclized sepiolite-PAN complex has been reported elsewhere [25].

Thermal processing of the precursors was carried out using an alumina tubular furnace; (Ø 80 × 750 mm). Samples, in the form of fine powder (2–5 g), were heated from ambient temperature to the predetermined temperature in nitrogen flowing at 200–2000 ml/min. The time at the reaction temperatures (1300–1475°C) was varied from 0.1 to 16 h. Each sample was weighed before and after reaction to calculate weight loss and conversion.

3. Results and discussion

3.1. Effects of purification on sepiolite

The effectiveness of each leaching event was checked by measuring the calcium content semi-quantitatively using EDX (for simplicity, the Ca content is given as element weight percent and all Ca present in as-received sepiolite mineral is attributed to the dolomite impurity). Any excess Ca is balanced with the other elements present in sepiolite, i.e., Si and Mg. The concentration of Fe and Al are not given because the reduction in content after chemical leaching was not significant.

TABLE III The effect of acid strength and leaching time on the dolomite content and the recovery value of as-received sepiolite. Leaching carried out in a closed flux. Temperature of the slurry was constant, 60°C. Solid to liquid ratio was 2/30 (g/ml)

Sample run	XM HCl (X)	Time (h)	Recovery (%)	Ca (wt.%)
1	0.06	0.5	95.38	8.21
2	0.06	1	93.76	5.90
3	0.09	1	92.43	5.50
4	0.15	1	89.92	2.64
5	0.18	1	85.22	0.88
6	0.21	1	79.91	0.32
7[a]	0.21	1.5	84.02	0.10
8[a]	0.21	2	83.25	nd[b]
9	0.24	1	76.68	0.14

[a] Open flux was used.
[b] Not detected.

The results of material are given in Table III. A progressive reduction in the Ca content was observed by increasing acid strengths of the solution from 0.06 to 0.24 M, for samples 1 to 9, inclusive. Excess of acid concentration (above 0.21 M) did not affect dolomite dissolution. Sepiolite powders (Sample 7 in Table III) had high recovery value after 1.5 h leaching in 0.21 M HCl solution at 60°C in an open flux and it was possible to eliminate Ca completely as seen on Sample 8 (Table III) by increasing reaction time to 2 h; this led to a slight reduction in the recovery value. Microscopic surface analysis in the calcium free samples showed that sepiolite retained its fibrous morphology (Fig. 2) although there was a slight distortion of the molecular frame as evidenced by the reduction of (110) diffraction (Fig. 3). A second X-ray pattern (II in Fig. 3) obtained from the sample (used as a reference) leached in a solution with controlled pH (6.5–6.7) at 45°C for 1 h with solid to liquid ratio of 3/100 (g/ml) showed that the acid strength resulted in distortion of the Si–O bonds at the edge of the sepiolite fibres. The IR data (450–6500 cm^{-1}) of the purified sample (Sample 8 in Table III) had a very good match with that of as-received materials, with an increase in the intensity of sepiolite absorption peaks [25]. This shows that sepiolite retained its molecular and structure framework at an atomic level after acid leaching.

Leaching was affected by the kinetics of initial rapid dissolution of dolomite. At constant acid concentration, (0.15 M) leaching for various reaction times led to decreased rate of dissolution of dolomite, from a rapid rate in first-half hour of reaction time, in which 2/3 of the dolomite dissolved to 1/3 dissolved in the following half-hour. Increasing the reaction time up to 3 hours did not substantially reduce the Ca content further.

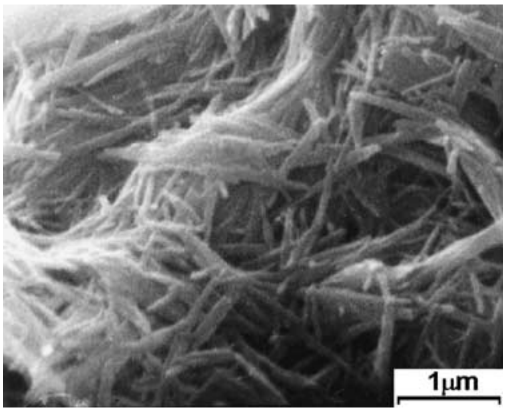


Figure 2 SEM micrograph of purified sepiolite after polymerisation and cyclization with polyacrylonitrile.

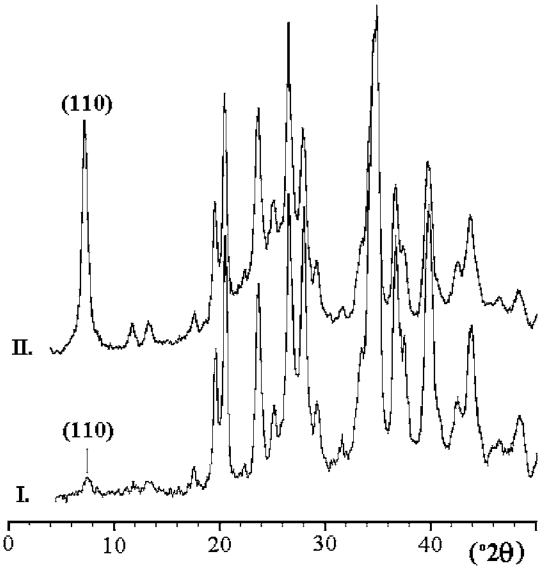


Figure 3 X-ray diffractographs of purified sepiolite samples: (I.) the sample leached with 0.21 M HCl for 2 h in an open flux, (II.) the sample leached in a solution with controlled pH (6.5–6.7) at 45°C for 1 h, solid to liquid ratio of 3/100 (g/ml). All peaks are attributed to sepiolite.

3.2. Si_3N_4 formation

The positive effect of temperature increase on the Si_3N_4 formation was observed for all reducing agent mixtures. A typical example of this is given in Fig. 4, where a purified sepiolite and charcoal mixture (A-SChar) was nitrided at different temperatures. When other

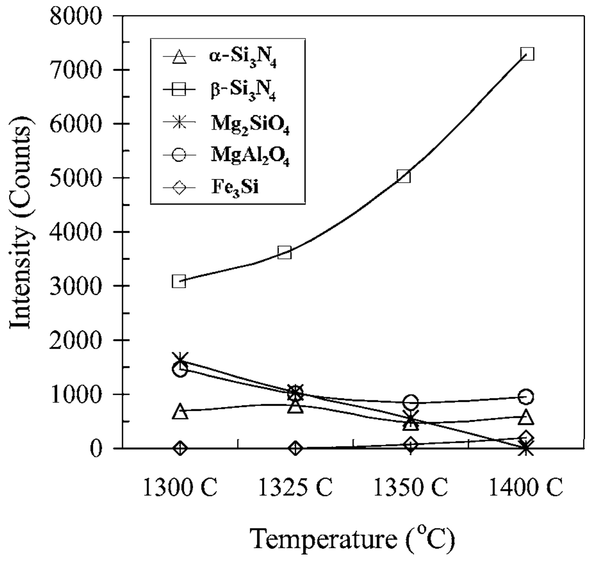


Figure 4 Intensities of main XRD peaks from the phases after nitridation of sepiolite charcoal mixture (A-SChar) at different temperatures. Heating-rate, holding-time and N_2-flow rate were 300°C/h, 4 h and 1000 ml/min, respectively. (Sepiolite was wet-mixed with fine charcoal powders after HCl leaching in 0.21 M HCl solution.)

parameters were kept constant the Si_3N_4 yield increased with an increase in temperature. A sample nitrided at 1300°C showed a forsterite (Mg_2SiO_4) content whereas increasing the temperature to 1400°C resulted in increased Si_3N_4 content and a reduction of forsterite peaks (Fig. 4), possibly following reaction;

$$3Mg_2SiO_4 + 2N_2 + 12C \rightarrow Si_3N_4 + 6Mg_{(g)} + 12CO_{(g)} \tag{1}$$

Forsterite had totally disappeared at 1400°C where the crystallinity of the product (Si_3N_4) was improved as indicated by X-ray diffraction pattern; this high crystallinity allowed iron silicide (Fe_3Si) an impurity phase, to be resolved in what was previously background noise. A small reduction on the intensity value of $MgAl_2O_4$ peak was also found with an increased temperature (Fig. 4). (Miller indices and d-values of the X-ray diffraction (XRD) peaks used for the representation of the phase concentration are given in Table IV.)

Chemical analysis of the powders deposited inside the alumina reaction tube after nitridation of A-SChar mixtures showed considerable quantities of Mg (31.1 wt.%), Si (39.9 wt.%) along with K (10.7 wt.%), Al (8.2 wt.%), Ca (3.4 wt.%) confirming that loss of Mg was high as predicted by Equation 1. The presence of Si also suggest that some Si was lost during nitridation, possibly due to the formation and liberation of some SiO(g), and elements such as Al and Ca are possibly associated with charcoal ash. Thermo-gravimetric analysis carried out on the granular charcoal (0.5 g) after 4 h heating at 1000°C yielded 7.2 wt.% ash content of the total charged amount and subsequent chemical analysis of the residue (by EDX) revealed impurity elements such as Ca (20%), Al (22%) and Fe (17%) along with Si (32%); minor amounts of Mg, Ti, K and Na were also detected. Similar tests on carbon black, petroleum coke and cyclized PAN yielded only a small ash content, insufficient for quantitative chemical analysis.

The effect of the Ca content of sepiolite on Si_3N_4 formation was explored using two precursors, where selective samples (B-SCar) with and without Ca impurity were nitrided under identical conditions, i.e., at 1400°C for 8 h with a 1000 ml/min N_2-flow rate. A residual large amount of Ca (3.70 wt.%) was deliberately retained after leaching to explore the effect of dolomite impurity on nitridation; in this case nitridation was not complete and considerable secondary phases, especially Mg_2SiO_4 and $MgSiN_2$ remained in the final product. In the absence of Ca impurity, the nitrided product showed higher yields of Si_3N_4 and in some cases, elimination of secondary phases.

TABLE IV Miller indices and d-values of the peaks used to determine the phase composition after nitridation

Phase	Miller indices	d-value (Å)	2θ (°)[a]
α-Si_3N_4	(210)	2.547	35.2
β-Si_3N_4	(210)	2.489	36.1
$MgSiN_2$	(121)	2.415	37.2
Mg_2SiO_4	(211)	2.457	36.5
$MgAl_2O_4$	(311)	2.437	36.9
Fe_3Si	(110)	2.005	45.2
α-SiC	(102)	2.511	35.7

[a] The values were calculated using $\lambda = 1.5406$ (Cu K_α).

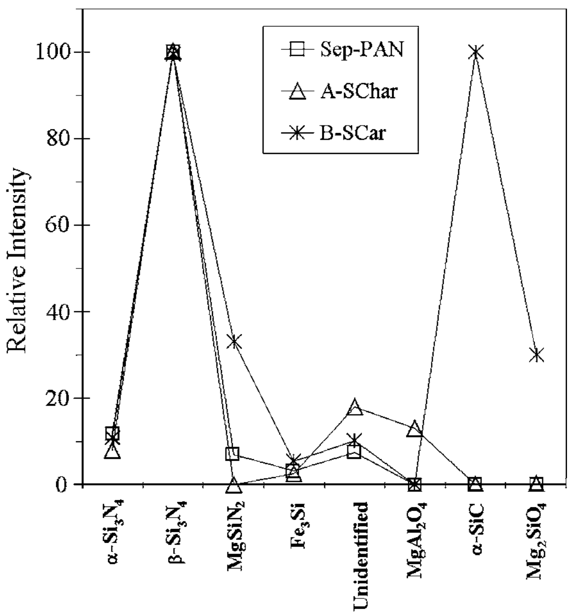


Figure 5 Relative-intensities of main XRD peaks of the phases after nitridation of sepiolite-PAN (SepPAN), sepiolite-charcoal (A-SChar) and sepiolite-carbon black (B-SCar) mixtures. Reaction temperature (1400°C), holding time (4 h), heating rate (300°C/h) and N_2-flow rate (1000 ml/min) were kept constant.

Fig. 5 compares phase formation after nitridation of sepiolite mixed with a different reducing agent. Testing conditions were identical i.e., the same purified sepiolite sample used and nitrided identically at 1400°C for 4 h with 300°C/h heating rate and 1000 ml/min N_2-flow rate. The SepPAN mixture gave the best results in terms of high Si_3N_4 yield and minimal secondary phases (Fig. 5) followed by the (A-SChar), carbon black and petroleum coke. A sepiolite carbon black mixture (B-SCar), on the other hand, yielded varying amounts of secondary phases (such as silicon carbide, magnesium silicon nitride and forsterite) in addition to the main constituent, β-Si_3N_4 (Fig. 5). SiC was identified as the α-form using ASTM powder diffraction database (card number 29-1128).

The α/β ratio was very low in general for all samples (Figs 4 and 5). It was possible to increase the α-Si_3N_4 yield by carefully altering the reaction conditions. For instance, lowering the heating rate by a half from 300°C/h to 150°C/h and increasing the reaction time by a factor of two, from 4h to 8h, resulted in a considerable increase in α/β ratio for sepiolite-carbon black (B-SCar) mixture (Fig. 6); these changes also contributed to a reduction in the $MgSiN_2$ and $MgAl_2O_4$ content and the complete disappearance of SiC (Fig. 6). It is presumed that a lower heating rate means an increased the reaction time for the free Si, by reduction of the metastable oxide phases such as Mg_2SiO_4 as well as intermediate nitrides such as $MgSiN_2$, to react with molecular nitrogen to form α-Si_3N_4. A similar effect was noted with sepiolite-charcoal mixture after prolonging reaction time to 16 h and lowing the temperature to 1300°C (Fig. 6).

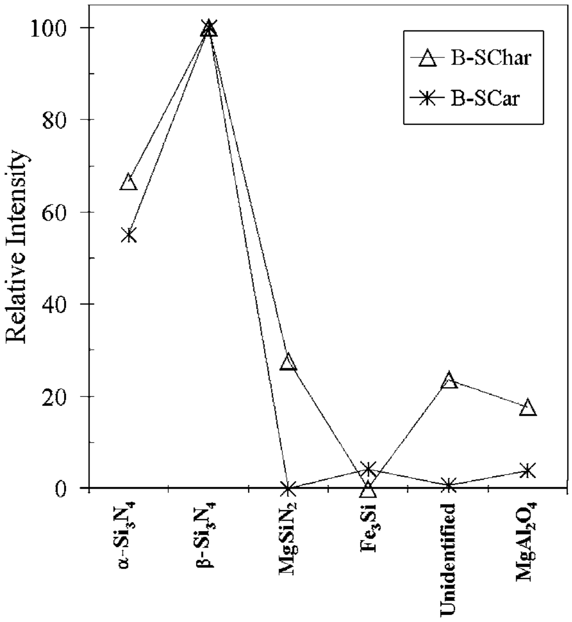
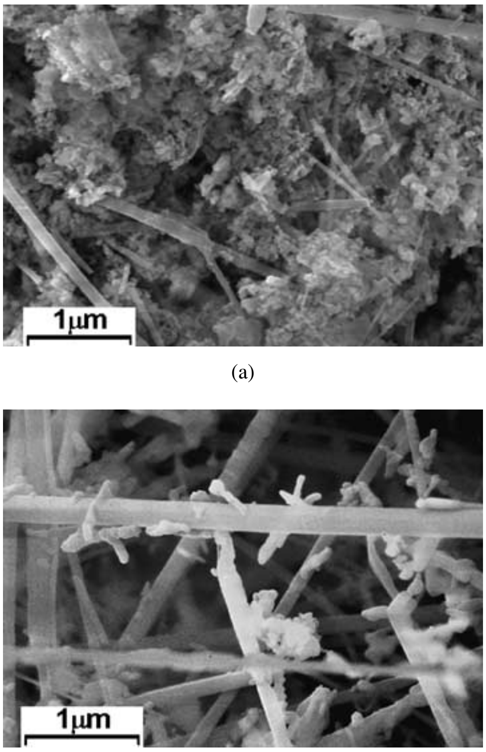


Figure 6 Relative-intensities of main peaks (from XRD) of the phases after nitridation of sepiolite-carbon black, B-SCar, (1400°C, 8 h, 150°C/h) and sepiolite-charcoal, B-SChar, (1300°C, 16 h, 300°C/h) mixtures. N_2-flow rate was 1000 ml/min for both samples.

Silicon nitride was not obtained with sepiolite-petroleum coke precursor (B-SPetc), under similar experimental conditions. Forsterite (Mg_2SiO_4) and proto-enstatite ($MgSiO_3$) were the dominant crystalline phases along with sinoite (Si_2N_2O) and a small amount of β-Si_3N_4, after 4 h nitridation at 1450°C. The reason was attributed to the low specific surface area of the sepiolite-petroleum coke precursor, a value (74 m^2/g) compared to sepiolite charcoal mixture (A-SChar) 176 m^2/g and sepiolite carbon black (A-SCar) 134 m^2/g. It was surprising that one of the higher yields of Si_3N_4, identical testing conditions, was obtained using SepPAN precursor (Fig. 5), which had the lowest specific surface area (6 m^2/g) before nitridation. An important issue here could be the intimacy of mixing sepiolite and molecular carbon at an "atomic" level. Although initially having a low specific surface area, at a late stage in the pyrolysis (during nitridation), the surface area is expected to increase. Reducing agents with a high specific surface area increase the reactivity of the carbothermic treatment by increasing the number of nucleation sites and result in fine grain size Si_3N_4. Microscopic examination of particle morphologies from various sources confirmed this, particularly the silicon nitride yield from sepiolite-PAN. The Si_3N_4 powders obtained from pyrolysis of cyclized sepiolite-PAN had the highest specific surface area (~12.4 m^2/g) and finest grain size (Fig. 7a) followed by charcoal (5.67 m^2/g) carbon black and petroleum coke; however, the impurity level in the Si_3N_4 was high. Thermo-gravimetric analysis carried out on the granular charcoal (0.5 g) after 4 h heating at 1000°C yielded 7.2 wt.% ash content of the total charged amount. Subsequent chemical analysis carried out on the residue by EDX revealed large amounts of impurity elements such as Ca, Al and Fe along with Si; minor amounts of Mg, Ti, K and Na were also detected. Similar tests on carbon black, petroleum coke and cyclized PAN showed only a small ash content, insufficient for quantitative chemical analysis.



(a)

(b)

Figure 7 SEM micrographs of powder samples, (a): SepPAN produced after 4 h reaction at 1350°C, and (b): B-SChar obtained after 16 h nitridation at 1300°C.

The α/β Si_3N_4 ratio is dependant on the reducing agent. In the sepiolite-PAN tests, β-Si_3N_4 formation was favoured and a high α-phase silicon nitride content was only achieved by seding the reactant with fine α-Si_3N_4 particles. The α-Si_3N_4 content increased when PAN was replaced by discrete carbon particles as charcoal or carbon black.

SEM examination revealed three main morphological types in the final product obtained from the CRN; single crystal laths of α-Si_3N_4 (Fig. 7b) (identified by electron micrographs of sharp bend contours), agglomerates of fine particles mainly β-Si_3N_4 (Fig. 7a) and irregular-shaped growths. The average size of agglomerates was small; they were weakly bonded as evident when ultrasonic shaking is applied they were broken up easily at very low frequency. Powders synthesised from the purified sepiolite-charcoal mixture possessed a fibrous form mainly with some needle-like crystals and whiskers (Fig. 7b) indicating that a substantial part of the reaction occurred in the gas phase, i.e. the concentration of $SiO_{(g)}$ must have been high in the presence of the highly reactive reducing agent, charcoal, before the nitridation started. The sepiolite-PAN precursor, however, produced mostly fine particles of agglomerates (mainly β-Si_3N_4), shown in Fig. 7a indicating that a solid → liquid → solid reaction was occurring; these fine particles coexisted with a long lath-shaped fibres. The preponderance of fine particles in the product after nitridation of the sepiolite-PAN precursor corresponded with high specific surface areas, two to three times higher than specific surface areas of sepiolite-carbon mixture products.

An EDX analysis on the individual fibres shown in Fig. 7b and a revealed only silicon and these fibres were assumed to be entirely Si_3N_4, possibly the α-from. On the other hand, particulate material contained silicon, magnesium, iron and aluminium. It is likely that these particulates were a mixture of Si_3N_4 and secondary phases, such as magnesium-silicon-nitride ($MgSiN_2$); this is supported by the XRD results on the same sample (sample B-SChar in Fig. 6). When the carbon black was the reducing agent, the product contained slightly coarser particles and smaller size fibres compared to the charcoal mixtures, this led to a relatively low specific surface area ($\sim$4.1 m^2/g) product.

4. Conclusions

Silicon nitride of fine particle size with high surface areas was obtained starting from liquid acrylonitrile (AN) intercalated in sepiolite, polymerised *in situ*, and reduced by carbon under a nitrogen flow.

Changes in process parameters, such as temperature and heating rate affected the particle morphology and size of the powders formed.

It was found that carbothermal reduction was sensitive to the physical state of carbon incorporated in sepiolite.

The state of precursor and reducing agent affected the quality and α/β ratio of the product.

An inexpensive synthesis method using cheap and readily available raw materials were used to produce Si_3N_4 powders. The product may have applications where high purity is not a essential requirement such as thermocouple protection sheaths, riser and delivery tubes in low-pressure diecasting operations and cutting edges for scissors.

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