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Sepiolite-PAN intercalation used as Si_3N_4 forming precursor

ALI O. KURT*, TOM J. DAVIES
Manchester Materials Science Centre, Grosvenor St., M1 7HS, Manchester, UK

Silicon nitride (Si_3N_4) formation was investigated using sepiolite and polyacrylonitrile as silicon and carbon source, respectively. It was found that purified sepiolite could readily adsorb a sufficient amount of acrylonitrile (AN) reagent without pre-treatment. Polymerisation of sepiolite-AN mixtures and subsequent cyclization of the polymerised complex yielded a precursor, which was found ideal as a starting material in carbothermal reduction-nitridation (CRN) for the formation of silicon nitride powders. The quantity of silicon nitride, grain size and morphology were found to be dependent on the reaction conditions and starting reagent. Fine grain size, high surface area (up to approx. 12.4 m^2/g) powders of mainly β-Si_3N_4 were obtained via pyrolysis of sepiolite-PAN complex after 4 h heating at 1400°C in 1000 ml/min nitrogen flow with a heating rate of 300°C/h. Mg retained in the molecular structure of the mineral must have promoted the formation of β-grains in CRN process. © *2001 Kluwer Academic Publishers*

1. Introduction

1.1. Ceramics from cheap raw materials

The development of ‘advanced’ ceramics, such as nitrides and oxides, has made considerable progress in the area of high temperature/high strength industrial applications due to their ability to withstand high stresses and corrosion at elevated temperatures. As the properties demanded by design engineers increase, the more these engineering ceramics are replacing metal alloys. Applications in the area of structural components, however, are limited by their low impact resistance, i.e., low fracture toughness, compared to metal alloys. Traditionally ceramics have long been produced from earth clay minerals with a little modification of their chemical constitution for applications in the electrical industry and kitchenware goods. Unlike conventional ceramics, advanced ceramics often require high temperature and pressure synthesis and processing stages such as chemical vapour deposition (CVD), reaction bonding, sol-gel technology, polymer pyrolysis, HIP (hot isostatic pressing), etc. Interest is growing for the utilization of silicon nitride (Si_3N_4) ceramics with an increase in demand in advanced engineering applications.

Work carried out by Cho and Charles [1] is typical of a procedure which gave high quality single-phase β-SiAlON by a carbothermal reduction-nitridation (CRN) route from cheap raw materials, in this case from kaolin clay mineral and carbon black mixture. Particular attention has been given to those clay minerals of the alumina silicate type [2–5], such as kaolins [1, 6–8] and montmorillonite [9], as a source for Si and Al. Many attempts were successfully used (on laboratory scale) to synthesise Si_3N_4 ceramics from an unusual source of silicon on the presence of a reducing agent. For instance, Rahman [10] and Kumar and Godkhindi [11] reported the formation of α-Si_3N_4 from rice husk, digested with NHO_3 and pyrolysed before heat-treating at 1430°C in flowing nitrogen; the authors pointed out the advantages of having a homogeneous mix of silica and carbon in the starting material.

The resulting silicon nitride powders from CRN reactions are however, not free from impurities [12] and the particulates are usually coarser compared to other production methods; fine powders with a homogenous size distribution may be obtained by seeding [13] the reactants with α-Si_3N_4 particles.

1.2. Ceramics via intercalation

Using clay minerals as an alternative to silica gives rise to problems with impurity content. To minimise the effects of impurities in the reagents, i.e., carbon and silicon source, a treatment may be needed so that any impurity, which might have an adverse effect on the synthesis and later processing stage, could be minimised. In this respect, intercalation of clay minerals is an alternative way to reduce any impurity contribution that comes from a carbon source. In this process, a carefully selected organic molecule is hosted by a layered clay structure where there is an intimate mixing with silicon and carbon. It is known that the reactivity in the carbothermic reactions could be improved when the total surface area of reducing agent, i.e. carbon, is increased [14]. Coincidentally, the surface area might be optimised by introducing elemental carbon into the

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* *Present address*: The Muğla University, Teknik Eğitim Fakültesi, 48000/Muğla, Turkey.

intermolecular spacing of a reactant, such as the interlamellar spacing in a clay mineral.

Some oxides, having layered structures and microvoids can accommodate certain organic molecules and form intercalation compounds [15]. Such a mixture of high purity clay mineral (as a silicon source) and intercalated organic molecule (for carbon source) could be an ideal precursor for synthesising ceramic powders provided that the following basic steps are followed.

i. Infiltration of host material by a monomer,
ii. Polymerisation of the mixture,
iii. Stabilisation of the polymerised complex in an oxidising atmosphere,
iv. Carbothermic reduction and nitridation of precursor after step iii.

A suitable monomer having a free radical initiator (for subsequent polymerisation) is impregnated into the channels or layers of a suitable oxide host. In some instances, a host material may be subjected to hydrometallurgical treatments to eliminate impurities and/or modify the molecular structure. To increase the absorption ability of swellable clay minerals (in other words to ensure adequate monomer absorption at a later stage), a pre-treatment may be required [16] using a chemical such as hexylammonium hydrochloride before soaking. In the second step of intercalation, the monomer impregnated inside the crystalline inorganic host material is polymerised using conventional polymerisation mechanisms [17] in vacuum or in an inert atmosphere in a low temperature heating cycle [18]. Subsequent heating of the system in air stabilises (by oxidation) the polymerised intercalated complex. In the final step, a high temperature treatment in an inert atmosphere, i.e., usually nitrogen, yields a nitrogen based structural ceramic in the presence of carbon formed by pyrolysis of the stabilised intercalated polymer.

Significantly, there is little emphasis given to the purification of precursor of any material in the literature. Consequently, in this investigation sepiolite [$Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4nH_2O$] [19], a hydrated magnesium silicate clay mineral, with open porosity lying along the long fibre axis, was leached with HCl solution to eliminate impurities and also to allow intercalation of guest molecules into the framework before the carbothermal reduction and nitridation processes.

2. Experimental procedure

2.1. Materials

Sepiolite from Eskiçehir-Turkey was received in the form of coarse particles, which were ball-milled using Si_3N_4 milling balls and then sieved to $-150+75$ μm size fractions, which is used throughout the investigation. The chemical composition of $-150+75$ μm size fraction sepiolite was as follows (in wt %): SiO_2 47.11, MgO 20.48, CaO 5.62, Al_2O_3 0.94, Fe_2O_3 0.44 and K_2O 0.08. An ignition of loss at 1000°C was 25.25 wt %, remaining 0.08 wt % was due to the trace amounts of TiO_2, Na_2O and P_2O_5. Chemical analysis of the sepiolite powders was determined quantitatively using inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-ray diffraction pattern of the above sample showed dolomite [$MgCa(CO_3)_2$], (present approx. 18.00 ± 1.00 wt.%), as a crystalline impurity compound. (The figure for dolomite composition was determined semi-quantitatively using the results obtained from thermogravimetry (TG), energy dispersive analysis (EDX) and an inductively coupled plasma atomic emission spectroscopy (ICP-AES).) To eliminate dolomite from other possible undetected impurities in the mineral, a hydrochloric acid (HCl) leaching process was used. Leaching was carried in a 0.21 M HCl solution of 60°C for 2 h with a 10/150 solid to liquid ratio, i.e. 10 g sepiolite powders were added in 150 ml 0.21 M HCl solution. After washing, the sample slurry was filtered, dried and lightly ground before taking the powdered samples for elemental analysis by SEM and transmission electron microscopy (TEM-EDX attached). Purified sepiolite powders were dehydrated at 140°C for 2 h in order to eliminate free water molecules before mixing with the monomer. Acrylonitrile (AN), used as a clean carbon source, was supplied by Hopkin & Willams Ltd. Azo-iso-butyronitrile (*GPR*) was used as an initiator (0.5 wt.%) in polymerisation of the AN monomer.

2.2. Sepiolite polyacrylonitrile intercalation

A sepiolite to acrylonitrile ratio of 1 : 2 i.e. 1g of leached sepiolite powder was intercalated in 2 ml of acrylonitrile monomer having azo-iso-butyronitrile (0.5 wt.%) as an initiator. Soaking and polymerisation were carried out in 10 ml glass bottles. Sepiolite in the form of fine powders was poured in the bottles simultaneously with the monomer, which was slowly sprayed out of the syringe on top of the sepiolite powders. The bottle lids (made of black PVDC plastic) were sealed by high vacuum grease to prevent evaporation of AN during the soaking and polymerisation stages. After soaking for 24 h, the mixture was subsequently heat-treated to permit polymerisation at 60°C for 12 h periods in the sealed bottles. Polymerisation of the sepiolite-AN mixture produced a sepiolite-polyacrylonitrile (sepiolite-PAN) complex. The sepiolite-PAN complex was further heated at 225°C for 6 h to 48 h intervals in air to affect the stabilisation process by cyclization. Weight changes in the samples were recorded, after each step was completed, in order to work out (approximately) the yield of carbon before the nitridation stage.

2.3. Nitridation of sepiolite-PAN precursor

In order to produce Si_3N_4 powders, cyclized sepiolite-PAN complexes were subjected to high temperature pyrolysis using nitrogen gas at various temperatures, times and N_2 gas-flow rates. Thermal processing was carried out in a horizontal tubular furnace with an alumina tube of ∅80 mm inner diameter, 750 mm long. Approximately 2 to 5 g of powdered samples were placed on a semi-cylindrical recrystallized alumina boat and nitrogen (oxygen free) gas (*BOC GASES*) (99.998% min pure) passed over them, with various flow rates set by a manual-control valve gas flow meter sensitive to 100 ml/min. The gas flow was maintained constant throughout the reaction in the range of 200 to 2000 ml/min. Heating and cooling rates were the same for all experiments, at 300°C/h. The carbothermic reduction process in a controlled nitrogen atmosphere was carried out in the temperature range of 1300°C to 1475°C for 0.1 h to 16 h duration at the plateau temperature. After cooling down to 350°C, the N_2-flow was stopped and the sample was allowed to cool room temperature. This test was repeated a number of times under different conditions of holding time, temperature, charged mass, etc. Synthesised powders were oxidised at 700°C for 4 h to remove any residual carbon. Ultimately, the reaction products were examined at room temperature.

Scanning electron microscopy (SEM), *Philips SEM 525 and SEM 505-EDX 9100*, was used to observe changes in surface morphology. To identify the crystalline phases, a X-ray diffractometer, type *Philips X'pert APD monochromator*, was operated at 40 kV and 50 mA with Cu-K_α radiation. Surface area measurements were performed on a *Quantasorb* BET (*Steptech Instrument Services Ltd*).

3. Results and discussion

3.1. Purification of sepiolite

Sepiolite powders subjected to acid leaching (0.21 M HCl for 2 h) have retained their fibrous morphology (Fig. 1) with the main molecular framework, as evident by the results obtained from SEM, X-ray diffraction and IR spectroscopy. A recovery value of the mineral after leaching was approximately 83.25 ± 0.10 (wt %) of the total sepiolite used for the process. Calcium, attributed totally to the dolomite impurity, was not detected (within a limit of the measurement in SEM-EDX Philips 505) for the sample after purification. Some slight distortion of the molecular structure of sepiolite in the high acid concentration has occurred, possibly by interacting with oxygen atoms sitting on the edges of the fibres. This could result in a distortion of reflection from (110) layers. This was evident by the observation of the (110) diffraction peak, which did not retain its maximum intensity value, obtained from X-ray diffraction pattern of purified sample (data is not given here). X-ray pattern and IR spectrum prove that the molecular and crystal structure of sepiolite at an atomic level was preserved, as seen in Fig. 2 from IR. The major absorption bands for sepiolite as-received material have been preserved and with an increase in the peak intensities, as expected following purification. The peaks at 716, 881 and 1457 cm^{-1} (Fig. 2), corresponding to dolomite absorption bands have been eliminated by leaching.

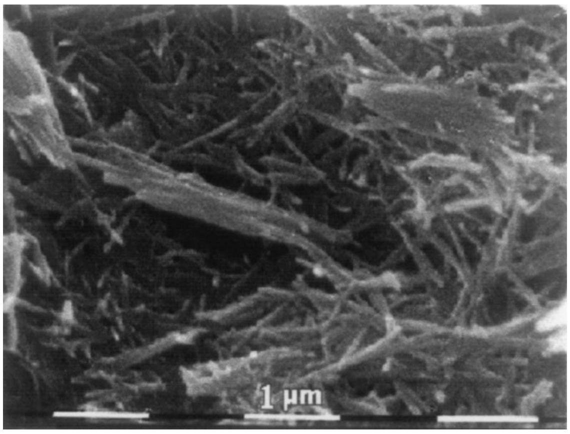


Figure 1 SEM micrograph of the sepiolite fibres after polymerisation.

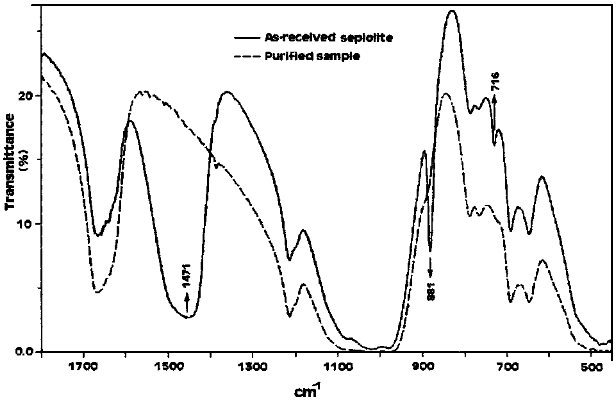


Figure 2 IR-spectroscopy of as-received brown sepiolite and a purified sample in 0.21 M HCl solution.

The surface area measurements carried out on the samples before and after leaching revealed that the specific surface area of sepiolite is doubled after purification, from 87 m^2/g for sepiolite as-received material to 161 m^2/g for the sample after leaching. This increase in specific surface area suggests that although a high acid concentration may affect the crystallographic structure of sepiolite fibres slightly at an atomic level as explained above, it had not significantly changed the colloidal properties.

3.2. Sepiolite-PAN intercalation

Acrylonitrile absorption of sepiolite and subsequent polymerisation were followed by X-ray. An increase in basal spacing (*d-value*) along the *y-axis* in the *b*-direction was observed using 010 diffraction as the base from 26.72 Å to 28.80 Å for the purified sepiolite and the sample after polymerisation, respectively. There was also a small contraction on the *x-axis* as indicated by a reduction of *d-value* (d_{100}) along the *a*-direction from 11.89 Å to 11.59 Å for the purified sample and the polymerised sample, respectively. An increase in basal spacing along the *b*-direction is a clear indication of intercalation and polymerisation within the channels of the sepiolite fibres. The records of changes on the Si-O absorption spectrum using IR may also relate to the internal polymerisation shown in Fig. 3. The broad band at approx. 1023 cm^{-1} is attributed to the Si-O absorption band (Fig. 3) for the purified sepiolite before intercalation. After polymerisation of the sepiolite-AN, the Si-O stretching band sharpens with an increase in the transmittance (approx. 5%) indicating that the polymerisation within the sepiolite channels causes stretching at an atomic level. In addition, a similar distortion of the Si-O bending mode at 460 cm^{-1} was also observed.

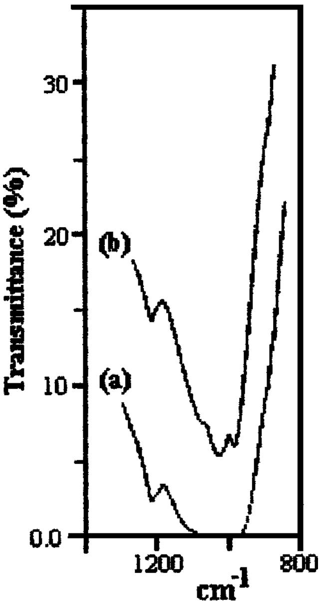


Figure 3 IR spectra of a pure sepiolite, (a) and sepiolite-PAN intercalation, (b).

The specific surface area of the polymerised sample was reduced from 171 m^2/g for as-purified sepiolite (after dehydration of zeolitic water) to 1.90 m^2/g for the polymerised sepiolite-AN intercalated sample. Sepiolite-PAN complex showed no obvious external bulk polymer coating of the fibres as evident from the surface morphology of the SEM micrograph in Fig. 1. Such a dramatic decrease in specific surface area suggests that although there is no optically visible external polymer coating on the fibres, a thin coating of polymer must exist over the bundle of fibres. Also, the channels and pores of the fibres, which were previously open, must have been filled by the monomer and the subsequent polymerisation would then block and cover the sepiolite fibres with a thin coating of polymer.

Cyclization treatment of sepiolite-PAN complex had no obvious external effects on the fibrous morphology of sepiolite and the surface morphology of sepiolite fibres after oxidation treatment looked similar to the one given in Fig. 1. There was, however, an increase in the specific surface area of the sample after cyclization (6.30 m^2/g). It was possible to detect the reaction of nitride groups to form a closed ring structure during the cyclization stages carried out 10–40 h by IR (data is not given here). Reduction in the intensity of C≡N stretching band and corresponding formation and increase in the double bonds C=C and C=N indicate a successful stabilisation process. It was noted that the substantial changes in the behaviour of the absorption bands, especially those recorded in C≡N stretching band and C=C double bonds, occur in the first 20 h period of treatment and that further change occurs with increase in cyclization time. It was proven at a later stage (in nitridation) that cyclization at 225°C for 20 h was sufficient for stabilisation of PAN within the sepiolite host structure to produce an adequate amount of carbon during the pyrolysis. This may be because the fine structure of the sepiolite host provides a suitable high surface area precursor and hence oxidative stabilisation of PAN occurs in a short time.

The amount of PAN in a final product of the sepiolite-PAN complex after cyclization was estimated (by the weight measurements) to be 51 ± 3.00 wt.% when a sepiolite to monomer ratio of $1:2$ (g/ml) was used. An approximate yield of carbon from the cyclized bulk PAN is about 50 wt.%, so the resulting products are consistent with a C/SiO_2 ratio in the range 4.2 to 4.7; this is suitable for the subsequent carbothermal-reduction reaction.

3.3. Si_3N_4 synthesis from cyclized sepiolite-PAN complex

In order to synthesise Si_3N_4, cyclized sepiolite-PAN precursor was heat-treated at temperatures 1300–1400°C for several hours in a nitrogen atmosphere. Forsterite (Mg_2SiO_4) was found to be a dominant phase after 4 h nitridation at 1300°C although β-Si_3N_4 appeared along with a trace amount of α-Si_3N_4. As the reaction temperature was increased to 1350°C, the intensity of the Mg_2SiO_4 peaks was reduced considerably resulting in an increase in the intensities of β-Si_3N_4 peaks. A further increase in temperature to 1400°C resulted in the disappearance of the forsterite peaks and the formation of a new phase, $MgSiN_2$. This increase in temperature (1400°C) further accelerated the formation of Si_3N_4 in general by reducing the intermediate phases via the reaction:

$$\begin{aligned} &Mg_2SiO_4 + 2MgSiN_2 + 4C \\ &\quad \rightarrow Si_3N_4 + 4Mg_{(g)} + 4CO_{(g)} \end{aligned}$$

Reaction time had a similar effect on the formation of silicon nitride during nitridation. An increase in holding time at the plateau temperature (1400°C) resulted in an increase in the formation of Si_3N_4 (Fig. 4) and silicon nitride of fine particle size was obtained after 4 h nitridation at 1400°C, with a small amount of $MgSiN_2$ phase (Fig. 4).

Chemical analysis by EDX on the 4 h sample (Fig. 4) identified small amounts of iron and aluminium. These elements might have formed as crystalline compounds

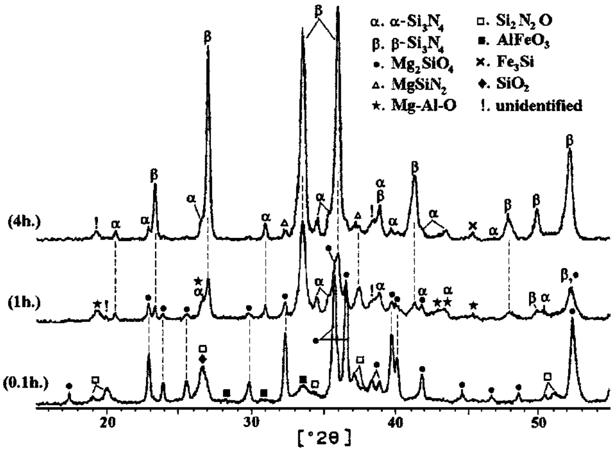


Figure 4 X-ray diffraction patterns of the products after nitridation of cyclized sepiolite-PAN intercalation compound. Heating rate, N_2 flow rate and temperature were constant, 300°C/h, 1000 ml/min and 1400°C, respectively.

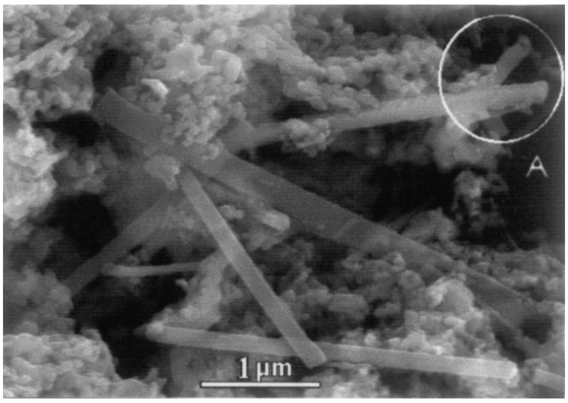
during nitridation and remained in the final product; unidentified peaks in the figure for the corresponding sample line, marked as (4 h.), could possibly due to these phases containing iron and aluminium. In fact, a peak at 45.34° (2θ) was cautiously attributed to an iron-silicide phase, suessite, (Fe_3Si). Aluminium formed $AlFeO_3$ at an initial stage (labelled as 0.1 h. in Fig. 4) and appeared as Mg-Al-O after 1 h holding time; this however, disappeared as the reaction time increased to 4 h. This shows that $AlFeO_3$ and Mg-Al-O phases were reduced as the temperature increased. Iron subsequently forms Fe_3Si after 4 hours duration, aluminium on the other hand was not detected in a crystalline form but it must have changed either into the amorphous phase or incorporated within the β-Si_3N_4 structure. The amount of Al was insufficiently low to allow a qualitative identification of any likely SiAlONs-type phases. The sample run for 4 hours at 1400°C (Fig. 4) gave reasonably good result in terms of the crystallinity and yield of Si_3N_4 and the small amount of impurity phases in the final product.

3.4. Microscopic observations

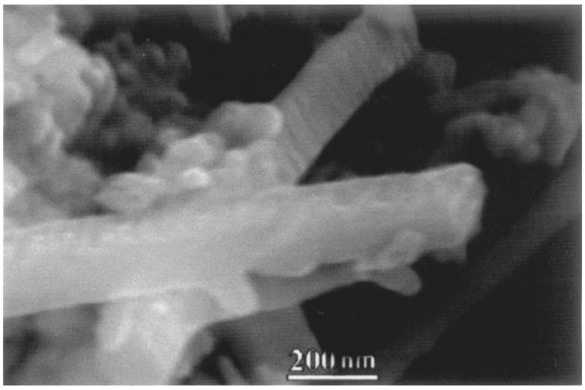
The 'white fur' consisted of fibres and needles of α-Si_3N_4, formed on the surfaces of the nitrogen-treated powders as well as on the alumina crucible, near the gas exit. This is probably due to the reaction of gaseous products, $SiO_{(g)}$ and $CO_{(g)}$ in the flowing N_2-gas. The amount of this fur product was small compared to the total weight of the product.

An initial dark brownish colour of the precursor changed to a light greenish tone after carbon burning of the nitrided sample. The greenish colour was dominant and uniform as the Si_3N_4 content of the powder increased in the final product. SEM examination revealed two main morphological types in the final product after residual carbon burning; single crystal laths of α-Si_3N_4 (identified by the electron micrographs of sharp bend contours) and agglomerates of fine particles mainly of β-Si_3N_4 (Fig. 5). The fraction of fibres was low compared to the total weight of particles estimated from X-ray diffraction pattern.

The preponderance of fine particles in the product after nitridation of the sepiolite-PAN precursor corresponded with the high specific surface areas measured, 12.4 m^2/g, which is an approximate value of high yield Si_3N_4 products. A point analysis carried out by EDX (attached to the TEM) on the individual fibres shown in Fig. 5 showed only silicon. These pillar-shaped fibres with square cross sections are assumed to be entirely Si_3N_4, possibly the α-from. On the other hand, particulates analysed for silicon along with some Mg with small concentrations of Fe and Al as impurities. 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 (Fig. 4). Intimate contact of silicon with carbon in sepiolite-PAN inclusion at molecular level could have promoted the formation of fine particles of β-Si_3N_4 in the CRN process by possibly increasing nucleation sites. High β-phase content in the final product could also have been due to the retained metallic elements. Impurity elements, Fe and Al, might have resulted in the formation of low melting point eutectics such as Fe_3Si (Fig. 4) with SiO_2 and MgO, which are the main constituent of sepiolite. These liquid phases could act as nucleation sites for the formation of β-phase Si_3N_4 powders during nitridation of sepiolite-PAN complex. It is likely the β-silicon nitride formed by precipitation from local liquid pools at an early stage of nitridation. In fact, it was evident from Fig. 4 that high concentration of β-phase Si_3N_4 formed with a small amount of α-phase at a holding time of 1 h at the reaction temperature. An increase in holding time to 4 h had virtually no effect on the α-phase content but resulted in an increased β-Si_3N_4 yield. It was therefore deduced that the formation of β-Si_3N_4 occurred by a solid → liquid → solid (SLS) mechanism, which resulted in fine equiaxed particles, as shown in Fig. 5a.



(a)



(b)

Figure 5 SEM micrographs of Si_3N_4 powders synthesised from sepiolite-PAN precursor, showing (a): a mixture of uniaxial β-phase particles with lath-like shaped α-phase fibres. (b): enlargement of area A.

4. Conclusions

Sepiolite leached with a dilute HCl solution showed an increase in specific surface area with a total elimination of dolomite impurity. The purification process had no obvious adverse effect on the molecular structure of the mineral used for intercalation. A sufficient amount of acrylonitrile was intercalated in purified sepiolite and polymerised *in-situ* without any additional pre-treatments of the host.

Fine crystalline silicon nitride with a high specific surface area of mainly β-particles has been synthesised by pyrolysis of purified sepiolite and polyacrylonitrile intercalation complex. In the current work, using sepiolite as a host material and a Si source, it was shown that the duration times for polymerisation and cyclization could be less than half of that reported earlier in similar intercalation systems in the literature; this yielded a stabilised sepiolite-PAN complex that gave silicon nitride on subsequent pyrolysis in nitrogen.

There was no evidence of stable SiC formation due possibly to the comparatively low temperatures and short time periods used in nitridation.

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