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Ceramics International 39 (2013) 6293–6298
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

The influence of different carbon sources in the carbothermal reduction and nitridation (CRN) synthesis of SiAlON from nanocomposite precursors based on Al–SBA-15

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Received 1 December 2012; received in revised form 15 January 2013; accepted 16 January 2013
Available online 30 January 2013

Abstract

Nanocomposites of Al–SBA-15 with the organic polymers poly-4-vinyl pyridine (P4VP) and polyacrylamide (PAM) were synthesized to produce SiAlON precursors containing various carbon contents. These CRN precursors, and their products after firing under N_2 at 1450 °C for 3 h were investigated by XRD, SEM/EDS and surface area analysis (BET) to compare the influence of the organic polymer carbon source. The results were also compared with those from precursors containing carbon black as the carbon source. XRD and SEM/EDS analysis of the Al–SBA-15 confirmed the formation of mesoporous structures, while BET and pore size distribution measurements indicated that the entry of P4VP into the Al–SBA-15 nanocomposite precursor is significantly more efficient than that of PAM. Firing these precursors in nitrogen produced β-SiAlON and β-cristobalite. At all carbon concentrations the P4VP nanocomposite precursors formed significantly more SiAlON than those of the PAM and carbon black precursors, due to the proximity of a greater amount of the organic carbon source to the silica template in the P4VP composite, and possibly also to the lack of oxygen in the P4VP monomer, in contrast with PAM. At least twice the stoichiometric amount of carbon was required in all cases, with optimal SiAlON formation occurring in the P4VP precursor containing 6 times the stoichiometric amount of carbon. Increasing the carbon content further suppresses SiAlON formation, possibly due to the build-up of back pressure of CO by-products in the pores of the nanocomposite.

Keywords: B. Nanocmposites; β-SiAlON; Carbothermal reduction and nitridation; Al–SBA-15; Poly-4-vinyl pyridine

1. Introduction

SiAlON ceramics are interesting candidte materials for various applications especially at high temperatures. β-SiAlON is generally prepared by sintering mixtures of Si_3N_4, Al_2O_3, AlN and SiO_2 at >1500 °C [1,2] or by carbothermal reduction and nitridation (CRN) of synthetic Al_2O_3/SiO_2 mixtures. Natural aluminosilicate minerals can be used as starting materials for the synthesis of SiAlON ceramics [3] but new methods are still of interest for the synthesis of high purity β-SiAlON [4].

SBA-15 is a mesoporous silica with a 4–6 nm pore size and a high surface area, and has been widely studied [5], especially since carbon and aluminium may readily be introduced into its nanosized channels [6]. Yan et al. [6] have shown that the particle morphology of the resultant product is very similar to that of the parent SBA-15, suggesting that the morphology of β-SiAlON formed from this CRN precursor might be controlled by controlling that of the template SBA-15 [7]. Possible applications of the resulting β-SiAlON powders are the preparation of high performance SiAlON ceramics or enhancing ceramic composites [7].

Yan et al. [6] recently reported the CRN synthesis of high-purity β-SiAlON powder from SBA-15 infiltrated with sucrose as the carbon source and we have demonstrated

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http://dx.doi.org/10.1016/j.ceramint.2013.01.051

the use of poly-4-vinyl pyridine (PV4P) as a carbon source for CRN synthesis of β-SiAlON from Al–SBA-15 [8]. In the present work we compare the results obtained from P4VP with those of another polymer carbon source, polyacrylamide (PAM), to produce nanocomposite β-SiAlON CRN precursors P4VP/Al–SBA-15 and PAM/Al–SBA-15 in which the Si/Al ratio = 1.66 corresponds to a β-SiAlON with $z=2.25$. The effect of the carbon concentration on the CRN formation from these precursors was also studied. These results were compared with those of a more conventional CRN synthesis using carbon black as the carbon source.

The SiAlON precursors and the products formed after firing in flowing nitrogen at 1450 °C for 3 h were studied by a range of techniques including BET analysis, thermal analysis, SXRD and SEM/EDS analysis.

2. Experimental procedure

2.1. Synthesis of Al–SBA-15

In a typical synthesis, 2 g of the commercial structure-directing agent triblock copolymer pluronic P123 ($EO_{20}PO_{70}EO_{20}$;average MW 5800, Aldrich) was dissolved in 4.16 mL of 85% H_3PO_4 and 75 mL of deionized water. The solution was stirred at room temperature; then 1.58 g aluminium isopropoxide and 2.86 mL of tetraethyl orthosilicate (TEOS) were added, giving a Si/Al ratio of 1.66 corresponding to the β-SiAlON composition $z=2.25$. This solution was stirred at 35 °C for 24 h and heated at 95 °C for 24 h, before being filtered, washed with deionized water, oven dried at 95 °C for 12 h and then calcined at 250 °C for 3 h and 550 °C for 4 h.

2.2. Synthesis of the CRN precursors P4VP/Al–SBA-15 and PAM/Al–SBA-15

Three CRN precursor nanocomposites of P4VP/Al–SBA-15 were prepared, with carbon contents calculated as follows:

sample P4VP1, containing 32 mmol of carbon was prepared on the basis

0.5 ml P4VP ≡ 4.64 mmol P4VP ≡ 32 mmol carbon

This amount of carbon is in agreement with the experimental value determined from the mass of the sample before and after polymerization (28 mmol) and equals a C/Si ratio of 5.04. Since the stoichiometric C/Si ratio required for the CRN reaction represented by the following equation is 2.3, this nanocomposite contains approximately twice the stoichiometric amount of carbon:

$$3.75\ SiO_2 + 1.125\ Al_2O_3 + 8.625\ C + 2.875\ N_2\ (g) \rightarrow Si_{3.75}Al_{2.25}O_{2.25}N_{5.75} + 8.625\ CO\ (g) \qquad (1)$$

The amounts of P4VP needed to prepare samples P4VP2 and P4VP3, with carbon contents of 97 mmol and 162 mmol respectively, were calculated similarly.

Synthesis of P4VP/Al–SBA-15 with the same three different ratios of C/Si was carried out by mixing the calculated amounts of reagents as shown in Table 1 in a 50 mL round-bottom flask and refluxing for 6 h at 70 °C. The solution was filtered, washed with THF and dried in air, to obtain the P4VP/Al–SBA-15 nanocomposite powders.

In a similar way, three CRN precursor nanocomposites of PAM/Al–SBA-15 were prepared, with carbon contents identical to those of the P4VP compounds, calculated as follows:

sample PAM1, containing 32 mmol of carbon was prepared on the basis:

0.76 g PAM ≡ 10.8 mmol PAM ≡ 32 mmol carbon

The amounts of PAM needed to prepare samples PAM2 and PAM3 with carbon contents of 97 mmol and 162 mmol respectively, were calculated similarly.

Synthesis of PAM/Al–SBA-15 with different ratios of C/Si was carried out by mixing the reagents as shown in Table 2 in a 50 mL round-bottom flask and refluxing for 6 h at 65 °C. The solution was filtered, washed with THF and dried in air, to obtain the (PAM/Al–SBA-15) nanocomposite powder.

2.3. Preparation of the CRN precursors C/Al–SBA-15

For comparison with the CRN behavior of the above nanocomposites, three C/Al–SBA-15 mixtures with the same C/Si rations were prepared by hand mixing Al–SBA-15 with carbon black (mean particle size 5 μm, BDH) according to Table 3.

The nanocomposite powders containing the different polymer carbon sources and carbon black prepared as above with three carbon contents were fired in a tube furnace under flowing N_2 (20 mL/min) at 1450 °C at a heating rate of 10 °C/min and holding times of 3 h.

The XRD powder patterns of the precursors and fired products were collected using a Philips PW 1700 computer-controlled goniometer using Cu Kα radiation and a graphite monochromator, and small-angle XRD (SXRD)

Table 1
Reagent mixtures for the synthesis of nanocomposite P4VP/Al–SBA-15.

Sample	C/Si	Al–SBA-15 (g)	P4VP (mL)	BPO[a] (g)	THF[b](ml)
P4VP1	5.04	0.5	0.5	0.03	5
P4VP2	15.85	0.5	1.5	0.09	11
P4VP3	25.16	0.5	2.5	0.15	20

[a] Benzoylperoxide.
[b] Tetrahydrofuran.

Table 2
Reagent mixtures for the synthesis of nanocomposite PAM/Al–SBA-15.

Sample	C/Si	Al–SBA-15 (g)	PAM (mL)	BPO (g)	THF (mL)
PAM1	5.04	0.5	0.76	0.07	14
PAM2	15.85	0.5	2.30	0.18	25
PAM3	25.16	0.5	3.84	0.34	35

was carried out on a Bruker D8 Avance diffractometer using Cu Kα radiation and a Ni filter.

The microstructures of the powdered samples were observed by SEM (JEOL JEM6500) at an accelerating voltage of 20 kV, fitted with an EDS system.

The specific surface areas, pore size distributions and pore volumes were determined from the adsorption–desorption of nitrogen at 77 K by the BET method, using a Gemini model 2365 apparatus.

3. Results and discussion

3.1. Structures of the meoporous precursors

The small-angle XRD pattern (SXRD) of the hexagonally ordered mesoporous precursor SBA-15 (Fig. 1a) shows three reflections at 2θ values in the range 0.5–3° consisting of the strong (100) peak and weak (110) and (200) reflections, confirming the presence of a highly ordered hexagonal mesoporous silica framework [5] and the 2D hexagonal mesostructure of the space group p6mm. The introduction of aluminium in the precursor Al–SBA-15 decreases the degree of ordering of the SBA-15 structure, as evidenced by the disappearance of the (110) and (200) reflections from the XRD pattern (Fig. 1b), although the persistence of the (100) reflection confirms the retention of the mesoporous structure of this compound. These results are consistent with a previously reported study [9]. Previously reported TEM micrographs of SBA-15 and Al–SBA-15 [8] confirm the presence of porous mesostructures in these compounds; the TEM micrographs of the latter taken perpendicular and parallel to the pore axis confirm the SXRD observation that incorporation of Al into the SBA-15 results in a decrease in the hexagonal structural ordering [8].

Table 3
Reagent mixtures for the preparation of nanocomposite C/Al–SBA-15.

Sample	C/Si	Al–SBA-15 (g)	Carbon black (g)
C1	5.04	0.3	0.233
C2	15.85	0.1	0.233
C3	25.16	0.3	1.168

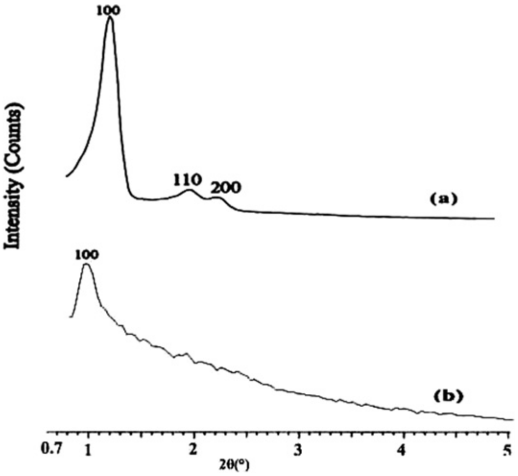

Fig. 1. Small-angle XRD patterns of (a) mesoporous silica SBA-15 and (b) Al–SBA-15.

SEM micrographs of Al–SBA-15, as well as nanocomposites P4VP/Al–SBA-15 and PAM/Al–SBA-15 are shown in Fig. 2. The SEM micrographs of Al–SBA-15 and the nanocomposites P4VP/Al–SBA-15 and PAM/Al–SBA-15 show that all these materials consist of similar cluster microstructures. The corresponding EDS analyses confirm the presence of aluminium in Al–SBA-15, and both aluminium and carbon in the mesostructure of the nanocomposites P4VP/Al–SBA-15 and PAM/Al–SBA-15. SEM/EDS images with X-ray mapping (not shown here) indicate that the aluminium and carbon are distributed throughout the nanocomposite precursors, suggesting that both these compounds could be efficiently converted to SiAlON in the CRN reaction, provided the polymer enters the mesoporous structure of Al–SBA-15.

Information about this latter point is available from the BET measurements (Fig. 3A, Table 4) which indicate that the porous properties (BET surface area, pore volume and pore size distributions determined from BET isotherms and the BJH method, Fig. 3B) of the original Al–SBA-15 template are very similar to those of the PAM nanocomposite, whereas all of these parameters are significantly decreased in P4VP/Al–SBA-15. The pore volumes Vp were determined from the BET isotherms, whereas the pore diameters Dp were determined by the pore size distributions (Fig. 3B).These data suggest that the pores in the P4VP nanocomposite are largely occupied by the P4VP polymer, whereas very little PAM has entered the Al–SBA-15 pore structure, and is therefore most likely to be located on the exterior surfaces of the silica template. The conclusion that P4VP enters the nanopores of the composite is supported by previously-reported ^{29}Si-MAS-NMR data [8]. The pore size distributions of Al–SBA-15, P4VP/Al–SBA-15 and PAM/Al–SBA-15 (Fig. 3B) show that the pores in all the samples are in the lower end of the mesoporous range (2–50 nm), and that the pore size distribution of Al–SBA-15 is broader than in P4VP/Al–SBA-15 and PAM/Al–SBA-15.

In summary, the present syntheses have been shown to produce nanocomposites with the mesoporous structure of SBA-15, containing aluminium and the polymers P4VP and PAM, the former more likely to reside in the mesoporous structure. The incorporation of Al decreases the hexagonal ordering of the SBA-15 structure, but no further structural disruption is caused by the formation of nanocomposites with P4VP and PAM. The aluminium and carbon are homogeneously distributed in these nanocomposites.

3.2. CRN products from these precursors

Fig. 4 shows the XRD patterns of the nanocomposites of P4VP/Al–SBA-15, PAM/Al–SBA-15 and C/Al–SBA-15

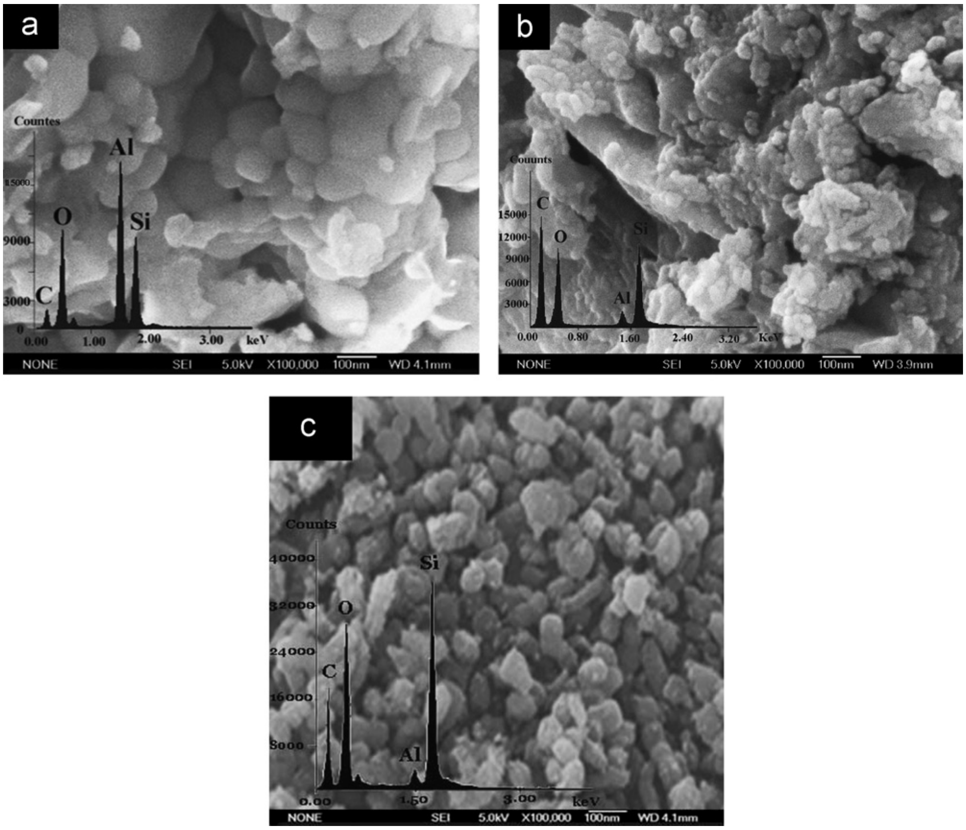

Fig. 2. SEM/EDS images of (a) Al–SBA-15, (b) nanocomposite P4VP/Al–SBA-15 and (c) nanocomposite PAM/Al–SBA-15.

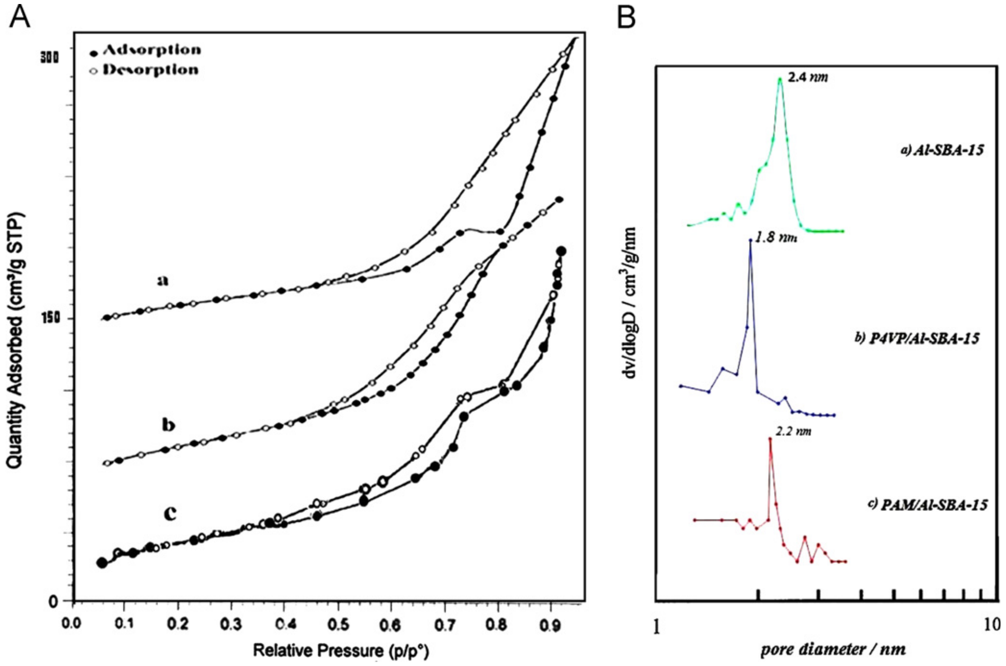

Fig. 3. (A) N_2 adsorption–desorption isotherms of (a) Al–SBA-15, (b) the nanocomposite P4VP/Al–SBA-15 and (c) the nanocomposite PAM/Al–SBA-15. (B) Pore size distributions of (a) Al–SBA-15, (b) nanocomposite P4VP/Al–SBA-15 and (c) nanocomposite PAM/Al–SBA-15.

containing different ratios of C/Si, heated in flowing nitrogen at 1450 °C. All the samples contain SiAlONs, principally β-SiAlON, and β-cristobalite, and the C/Al–SBA-15 samples also formed traces of mullite. The presence of mullite in the latter reflects the poorer reactivity of the system in which the carbon source is merely mechanically mixed; the least amount of mullite is formed in sample C3, where the available carbon is 10 times the stoichiometric requirement.

A semi-quantitative estimate of the relative amounts of these phases was made by scaling the traces to the same intensity and measuring the peak areas of the (101) β-SiAlON reflection at $d=2.71$ Å, the (101) β-cristobalite reflection at $d=4.02$ Å and the (110) mullite reflection at $d=5.38$ Å. The results of these analyses (Table 5) indicate that the greatest amount of β-SiAlON was formed in the nanocomposite P4VP/Al–SBA-15, whereas the performance of the nanocomposite PAM/Al–SBA-15 as a CRN β-SiAlON precursor was no better than that of the conventional CRN precursor containing mechanically mixed carbon black. There are two possible reasons for this result: differences in the chemical composition of the polymeric carbon sources, or differences in their stereochemistry. In the first instance, the monomer of P4VP (C_7H_7N) contains nitrogen but no oxygen, whereas the additional presence of oxygen in the monomer of PAM (C_3H_5NO) may require further reduction of this nanocomposite to form SiAlON. However, of greater importance in determining the relative reactivity of these precursor compounds appears to be the ability of the polymer to enter the porous silica structure; the BET results suggest that P4VP is much superior in this respect. The difficulty experienced by PAM to enter the porous template renders it no more efficient a CRN precursor than carbon black, notwithstanding the uniform distribution of Al, Si and C within the matrix of both organic nanocomposite precursors and the presence of nitrogen in both monomers which should also assist the reaction.

Table 4
BET data for Al–SBA-15 and the polymer composite precursors with C/Si = 15.85.

Sample	BET surface area ($m^2\ g^{-1}$)	Vp[a] ($cm^3\ g^{-1}$)	Dp[b] (nm)
Al–SBA-15	173	0.06	2.4
P4VP/Al–SBA-15	62	0.02	1.8
PAM/Al–SBA-15	121	0.05	2.2

[a] Total pore volume from BET measurements.
[b] Pore diameter from BJH analysis of pore size distributions (Fig. 3 B).

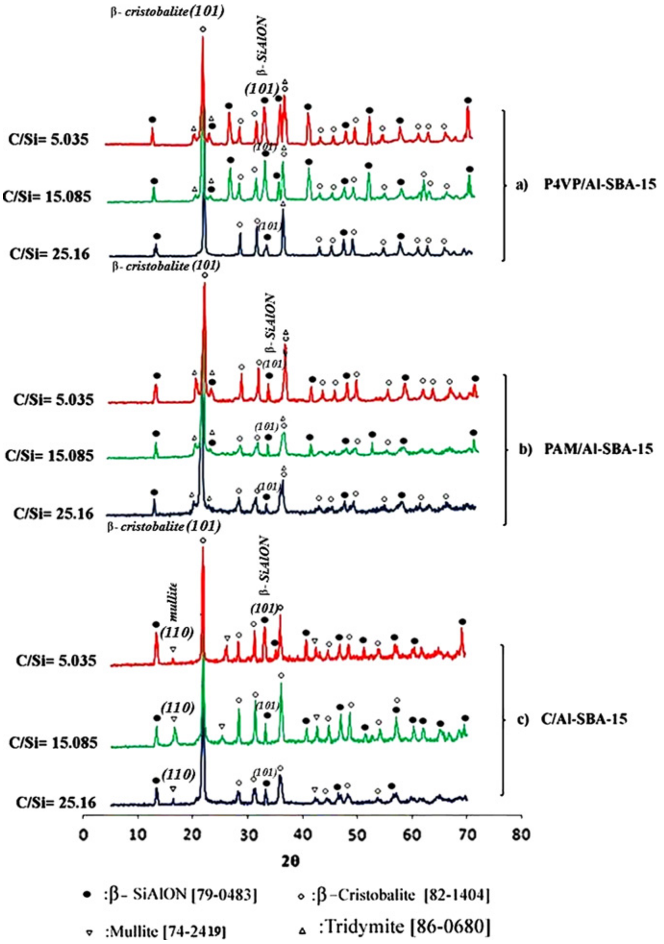

Fig. 4. XRD patterns of (a) P4VP/Al–SBA-15, (b) PAM/Al–SBA-15 and (c) C/Al–SBA-15 nanocomposite heated in nitrogen at 1450 °C (C/Si = 5.04, C/Si = 15.85, C/Si = 25.16). The indexed reflections are those used to semiquantitatively estimate β-SiALON, β-cristobalite and mullite.

The formation of β-cristobalite arises from the unreacted silica in the precursor nanocomposite matrix; this is greatest in the carbon black precursors at all carbon concentrations (Table 5) and is consistent with the relatively low yield of SiAlON from these precursors. However, the low yield of β-cristobalite in the PAM nanocomposites, in which SiAlON formation is also low, suggests a different mechanism in this and in the P4VP precursor, in which the presence of carbon in the macropores drives the carbothermal formation of SiO(g):

$$SiO_2 + C \rightarrow SiO_{(g)} + CO_{(g)} \tag{2}$$

The effect of the carbon content on the formation of β-SiAlON (Fig. 5) shows similar behavior in the PAM/Al–SBA-15 and C/Al–SBA-15 precursors, in which the optimum SiAlON formation is obtained with C/Si = 5.04 (twice the stoichiometric amount of carbon). Increasing the carbon content above this level suppresses SiAlON formation, possibly due to the formation of additional CO and the build-up of CO back-pressure in the mesopores of the precursor, with a consequent need for this to be overcome with a greater partial pressure of nitrogen to remove the gaseous reaction products. By contrast, the optimum carbothermal reaction occurs in the P4VP nanocomposite at 6 times the stoichiometric amount of carbon, but when the carbon content is increased to 10 times the stoichiometric

Table 5
Relative peak areas of the principal phases in the samples fired under nitrogen at 1450 °C for 3 h.

Sample	C content (mmole)	(101) peak area β-SiAlON	(101) peak area β-cristobalite	(110) peak area mullite
P4VP1	32	142	834	–
P4VP2	97	182	1522	–
P4VP3	162	84	1193	–
PAM1	32	67	758	–
PAM2	97	33	766	–
PAM3	162	32	784	–
C1	32	63	2184	28
C2	97	48	2191	44
C3	162	41	2199	14

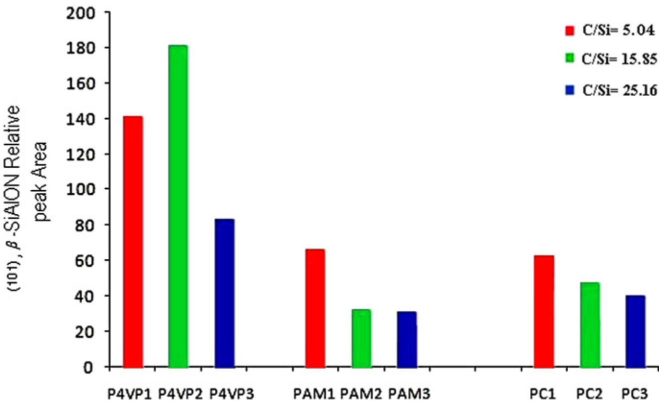

Fig. 5. Graph bar SiAlON phase of the samples P4VP/Al–SBA-15, PAM/Al–SBA-15 and C/Al–SBA-15 nanocomposite heated in a nitrogen atmosphere at 1450 °C (C/Si=5.04, C/Si=15.85, C/Si=25.16).

amount, the degree of SiAlON formation decreases (Fig. 5), possibly due to the mechanism outlined above.

These results indicate that the amount of carbon and its location in the CRN precursor are important factors in the SiAlON-forming reaction, and in all cases more carbon than the stoichiometric amount is required for optimum SiAlON formation.

4. Conclusions

CRN precursors were synthesized from the mesoporous silica SBA-15 into which aluminium was incorporated. Nanocomposites of this Al–SBA-15 with the organic polymers P4VP and PAM were prepared, containing aluminium and carbon distributed throughout the mesoporous SBA-15 structure, which is not compromised by the formation of the nanocomposites. BET measurements indicate that the entry of P4VP into the precursor is significantly more efficient than that of PAM. A series of samples containing various carbon contents were prepared, and analogous Al–SBA-15 samples containing carbon black were also prepared for comparison.

Firing these precursors at 1450 °C for 3 h in nitrogen produced β-SiAlON and β-cristobalite. At all carbon concentrations the P4VP nanocomposite precursors formed significantly more SiAlON than the PAM and carbon black precursors, due to the greater proximity of the organic carbon source to the silica template in the P4VP composite. At least twice the stoichiometric amount of carbon was required, with optimal SiAlON formation occurring in the P4VP precursor containing 6 times the stoichiometric amount of carbon. Increasing the carbon content further suppresses SiAlON formation, possibly due to the build-up of back pressure of CO by-products in the pores of the nanocomposite.

References

[1] K.H. Jack, Review; Sialon and related nitrogen ceramics, Journal of Materials Science 11 (1978) 1135–1158.

[2] H. Yoshimatsu, T. Yabuki, H. Mihashi, Preparation of Sialon from mixture of SiO_2 and $Al_2O_3 \cdot 2H_2O$ by thermal carbon-reduction, Journal of the Ceramic Society of Japan 95 (1987) 590–594.

[3] M. Sopicka-Lizer, R.A. Terpstra, R. Metselaar, Carbothermal production of β-Sialon from alumina, silica and carbon mixture, Journal of Materials Science 30 (1995) 6363–6369.

[4] A.D. Mazzoni, E.F. Aglietti, Mechanism of the carbonitriding reaction of SiO_2–Al_2O_3 minerals in Si–Al–O–N system, Applied Clay Science 12 (1998) 447–449.

[5] D. Zhao, J. Feng, Q. Hou, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, Science 279 (1998) 548–552.

[6] Q. Yan, Q. Liu, Q.F. Liu, Synthesise of rod-like high-purity β-Sialon powder by a novel carbothermal reduction–nitridation method with a nanocasting procedure, Journal of the American Ceramic Society 93 (2010) 2471–2473.

[7] D.Y. Zhao, J.Y. Sun, Q.Z. Li, G.D. Stucky, Morphological control of highly ordered large pore mesoporous silica SBA-15, Chemistry of Materials 12 (2000) 275–279.

[8] S. Abbaspour, A.A. Nourbakhsh, R.J. Kalbasi, F. Golestani-Fard, K.J.D. MacKenzie, CRN synthesis of β-SiAlON from a nanocomposite precursor of mesoporous silica–alumina (Al–SBA-15) with poly-4-vinyl pyridine, Journal of Porous Materials 19 (2012) 775–780.

[9] M. Go mez-Cazalillaa, J.M. Merida-Roblesa, A. Gurbanib, E. Rodrıguez-Castellona, A. Jimenez-Lopeza, Characterization and acidic properties of Al–SBA-15 materials prepared by post-synthesis alumination of a low-cost ordered mesoporous silica, Journal of Solid State Chemistry 180 (2007) 1130–1140.