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Processing of biomorphic Si_3N_4 ceramics by CVI-R technique with $SiCl_4/H_2/N_2$ system

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Abstract

Biomorphic porous silicon nitride Si_3N_4 ceramics have been produced by chemical vapor infiltration (CVI) of carbonized paper preforms with silicon, followed by gas–solid chemical reaction (R) of nitrogen with the infiltrated silicon. The paper was first carbonized in inert atmosphere to obtain a biocarbon (C_b) template. In a second step, silicon tetrachloride in excess of hydrogen was used to infiltrate silicon into the pores of the C_b template and to deposit silicon onto the C_b fibers. Finally, a gas–solid chemical reaction between nitrogen and infiltrated silicon in a temperature range of 1300–1450 °C took place in N_2 or N_2/H_2 atmosphere to form reaction bonded silicon nitride (RBSN) ceramics. After nitridation, the samples consist mainly of α-Si_3N_4 phase for thermal treatment below the melting point of silicon (1410 °C) or of β-Si_3N_4 phase and β-Si_3N_4/SiC-mixed ceramics for treatment at temperatures above.

The crystalline phases α- and β-Si_3N_4 were identified by X-ray diffraction (XRD) analysis and the microstructure of these samples was investigated by scanning electron microscopy (SEM). Energy-dispersive X-ray analysis (EDX) was used to detect the presence of silicon, nitrogen, carbon and oxygen, whereas Raman spectroscopy was applied to identify the presence of Si and SiC. Using thermal gravimetric analysis (TGA), residual carbon was determined. It was found, that addition of 10% H_2 to the nitridation gas at temperatures near the melting point of silicon allows to increase the conversion of Si as well as to control the exothermic nitridation reaction obtaining the preferable needle-like microstructure.

Keywords: SiC; Si_3N_4; Fibers; Structural application; Chemical vapor infiltration (CVI)

1. Introduction

Manufacturing of biomorphic porous ceramics such as SiC, TiC and TiO_2, as a new class of structural materials, has attracted a lot of attention recently. This interest is due to the need for engineering ceramics that combine high strength with low density. These materials are prepared by biotemplating technique, where natural grown structures like wood, industrially manufactured cellulose fibers or corrugated cardboards are used as bulk templates for high-temperature conversion into technical ceramics by a ceramization process. This process includes generally several complex-processing steps as shown in Fig. 1. Firstly, a pyrolysis step in inert atmosphere is applied in order to convert the organic molecules of the paper fibers into a carbon lattice, called the biocarbon template (C_b template), followed by chemical vapor infiltration (CVI) with gaseous precursors, where a ceramic layer is deposited around the bio carbon fibers. Finally, a thermal treatment step, the chemical reaction in different atmospheres at different temperatures is applied, in order to convert the deposited ceramic precursor into the desired ceramic.

Beside SiC and TiC porous ceramics investigated earlier in[1–3] porous silicon nitride (Si_3N_4) ceramic is a promising candidate for high-temperature structural applications including metal-engineering components, biomaterials and catalyst supports because of its high-temperature strength, thermal shock resistance, chemical stability and excellent creep resistance[4]. Silicon nitride crystallizes in two hexagonal modifications α- and β-Si_3N_4[5–7] while cubic Si_3N_4 has recently been synthesized[8]. In the α and β form, the basic building unit is the Si–N tetrahedron, in which a silicon atom lies in the centre of a tetrahedron and a nitrogen atom at each corner. α-Si_3N_4 is known to convert into β-phase at high temperature via a solution-precipitation mechanism which is assisted in the presence of additives by liquid phase, while the reverse process is energetically unfavored[9–11].

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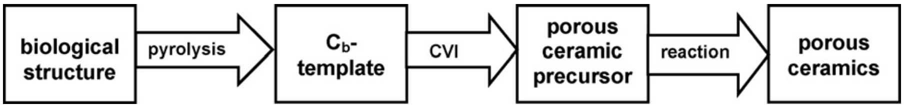


Fig. 1. Flow chart of processing of biomorphic porous ceramics from paper preforms.

Processing of porous Si_3N_4 based on the ceramization process shown in Fig. 2, has not been described in the literature up to now. So the main objective in this paper is to investigate the processing of these materials by CVI-R technique.

Our process starts from carbonized paper preforms, which are siliconized by CVI process to obtain green Si samples. This route which is illustrated in Fig. 2 uses $SiCl_4$ in an excess of hydrogen as investigated in a previous work[12]. This process is attractive because of the low price of the used raw materials (silicon and paper), the easy control of the shape and dimensions of the resulting ceramics and the relatively low production costs. The final step of the ceramization process for Si_3N_4 production is a thermal treatment of the siliconized samples in nitrogen or nitrogen-containing atmosphere in a temperature range of 1300–1450 °C, where gas–solid reaction takes place, according to the following equation:

$$Si_{(s)} + N_{2(g)} \xrightarrow{\Delta T} Si_3N_{4(s)} \tag{1}$$

Additionally, a solid–solid and/or liquid–solid reaction between the infiltrated silicon and the carbon template is possible during the thermal treatment step at temperatures in the region of the melting point of silicon (1410 °C) according to Eq. (2):

$$Si_{(l,s)} + C_{b(s)} \xrightarrow{\Delta T} SiC_{(s)} \tag{2}$$

Because of the exothermic nitridation reaction ($\Delta H = -723 + 0.315T$ kJ/mol), H_2 and/or He may be added to the nitridation gas as a diluent to lower the concentration of nitrogen for a better control of the nitridation rate and additionally by affecting the thermal properties and molecular diffusivity of the reactive gas. The properties of ceramics produced by this method can be affected by many process variables such as nitridation temperature,[13] composition of the nitridation gas,[14,15] impurities in the silicon as well as impurities in the nitridation atmosphere[16–18].

In the present study, paper preform has been used to fabricate biomorphic porous Si_3N_4 ceramics through a process of pyrolysis, silicon infiltration and thermal reaction using the $SiCl_4/H_2/N_2$ system. The properties of the resulting ceramics like composition and microstructure are investigated as a function of the operating conditions during the infiltration and the thermal treatment steps.

2. Experimental work

Ceramization process was applied in this work by a three-step approach to convert the biological raw materials (paper preform) into biomorphic porous Si_3N_4 ceramics.

2.1. Pyrolysis of the paper preforms

The paper sheets with dimensions 40 mm × 40 mm × 0.6 mm and a geometrical density of 0.27 g/cm^3 were put between two metallic sheets in the uniform temperature zone of a horizontal tubular reactor, an alumina tube of 32 mm inside diameter and 900 mm length, heated with external SiC heating elements. The paper sheet has been converted into carbonaceous preforms (C_b templates) by releasing all gases—H_2O, CO and CO_2 by heating the substrate carefully under helium flow (10 cm/s). The heating rate was maintained at 1 °C/min up to 350 °C and kept constant for 1 h, followed by 2 °C/min up to 850 °C and holding another hour. After that, the furnace was slowly cooled at a rate of 2 °C/min. By applying this schedule, the C_b template shows a maximum carbon yield with 80% mass loss and reflects the microstructure and morphology of the initial paper preform. After the pyrolysis step, the resulting dimension of the produced C_b template was ($30 \times 30 \times 0.37$ mm^3) with a geometrical density of 0.125 g/cm^3. The obtained C_b templates were then submitted to the infiltration step.

2.2. Chemical vapor infiltration (CVI)

In the second ceramization step, the obtained C_b templates are infiltrated at atmospheric pressure with silicon tetrachloride

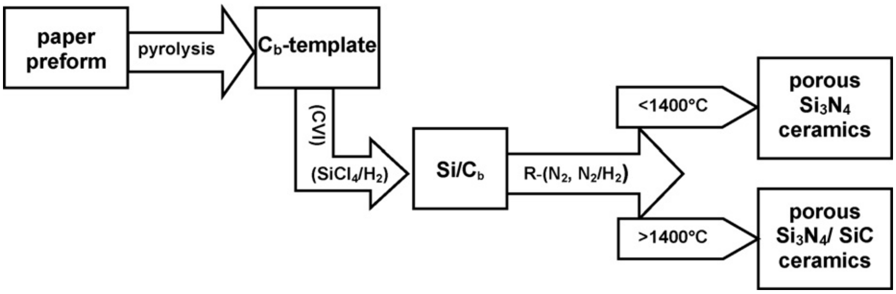


Fig. 2. Flow chart of the ceramization steps for the production of biomorphic Si_3N_4 ceramics.

in excess of hydrogen. A solid Si layer is deposited around each fiber in the template according to the following equation:

$$SiCl_{4(g)} + 2H_{2(g)} \rightarrow Si_{(g)} + 4HCl_{(g)} \quad (3)$$

The liquid silicon tetrachloride ($SiCl_4$) precursor is transferred into the gas phase by bubbling a carrier gas through evaporator to introduce it into the reactor. The evaporator temperature was kept constant at 10 °C based on the vapor pressure curve to get the desired concentration of $SiCl_4$ in the gas phase.

Prior the CVI experiments, parameter screening for surface reaction controlled deposition of Si from $SiCl_4/H_2$ was performed using non-porous graphite plates as substrate. Based on these results, the following infiltration parameters were found to be optimal to achieve homogeneous infiltration of the C_b template: 900 °C, 3 h, molar fraction of $SiCl_4$ in the gas phase of 0.065 with $H_2/SiCl_4 = 17$, residence time of the reactants in the reactor of 3.5 s, corresponding to a gas velocity of 25 cm/s. Under these conditions the mass gain of the C_b samples after infiltration was 400% to ensure Si/C ratio more than 1.

2.3. *Reaction bonded silicon nitride (RBSN)*

The silicon infiltrated substrates were heated at a rate of 5 °C/min in a helium flow to the reaction temperature in the range of 1300–1450 °C. Once the system had reached the temperature, the nitridation was initiated by supplying a nitrogen or atmosphere containing nitrogen (N_2/H_2, N_2/He, N_2/Ar) for 5 h at atmospheric pressure. The flow rate of the reactive gas was between 150 and 180 Nl/h. After nitridation reaction, the nitrogen supply was stopped and the produced ceramics were cooled in helium flow at 5 °C/min to room temperature.

2.4. *Characterization methods*

X-ray diffraction (XRD) is used for phase identification, structure determination and chemical analysis of components of the different crystalline phases in the solid materials. In this study the main constituents of the ceramics are unreacted silicon, α-Si_3N_4, β-Si_3N_4, SiC and residual carbon from the C_b template. The ratio between α- and β- Si_3N_4 can be determined according to the Gazzara and Messier method which uses the peak intensities of the (2 1 0) plane[19,20]:

$$\beta\text{-}Si_3N_4 = \frac{I_\beta(2\,1\,0)/L_\beta(2\,1\,0)}{I_\beta(2\,1\,0)/L_\beta(2\,1\,0) + I_\alpha(2\,1\,0)/L_\alpha(2\,1\,0)} \quad (4)$$

where L is a structure-related parameter, L_α (2 1 0) = 6.97, and L_β (2 1 0) = 11.21.

The XRD measurements were carried out on a Philips PW 3040 diffractometer by using Cu Kα radiation in the range 2θ, 10–70°.

Energy-dispersive X-ray spectroscopy analysis (EDX/SEM Philips XL 30) was used to get qualitative and quantitative analysis of elements like carbon, nitrogen, silicon and oxygen in the obtained ceramic layer, whereas scanning electron microscopy (SEM) was used to characterize the surface morphology after each processing step as a function of the operating conditions.

Thermal gravimetric analysis (TGA, Simultan-Thermo-Analysen-Gereat STA 409 Firma Netzsch-Gerätebau GmbH) of the ceramized samples allows continuous weight measurement, whilst the sample was oxidized in flowing air at 750 °C for 6 h. Thus the amount of residual carbon can be determined from the mass loss of the sample.

3. Results and discussions

The grade of conversion of Si infiltrated C_b template into ceramics as well as their composition (Si_3N_4 or Si_3N_4/SiC) and microstructure (α- or β-Si_3N_4) are strongly affected by the temperature and the reactive gas atmosphere during the last thermal treatment step of the ceramization procedure.

3.1. *Grade of conversion of Si into Si_3N_4*

The conversion of Si into Si_3N_4 is strongly affected by the temperature of the thermal treatment. This can be observed by estimating the nitridation grade (NG) by the following

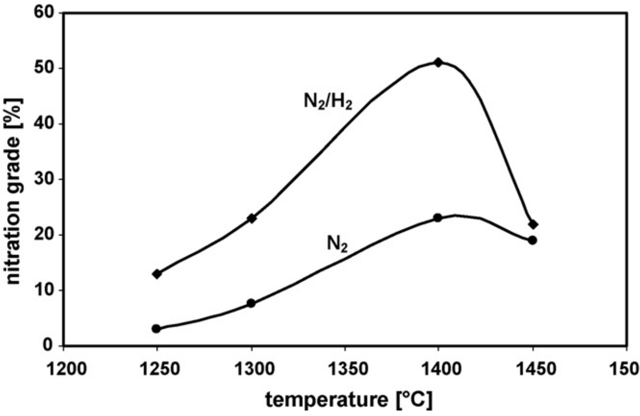


Fig. 3. Effect of nitridation temperature and gas composition on the nitridation grade.

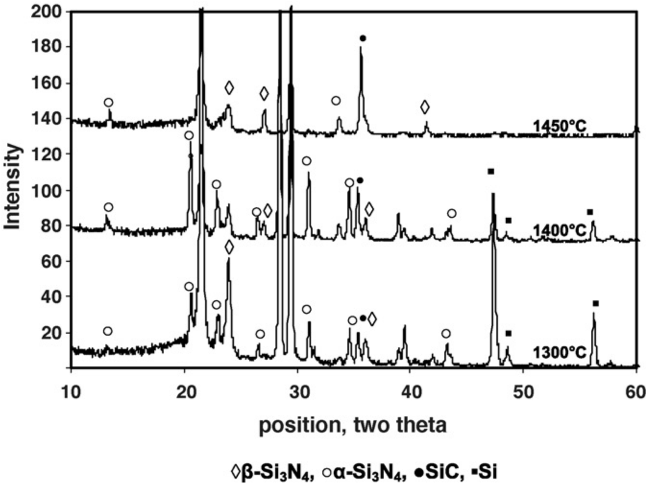


Fig. 4. XRD of ceramics treated at different temperatures and gas atmosphere.

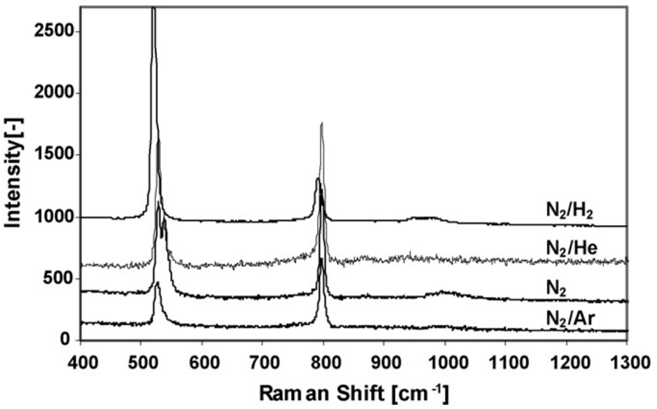


Fig. 5. Raman spectra for samples nitrided in different atmospheres at 1450 °C.

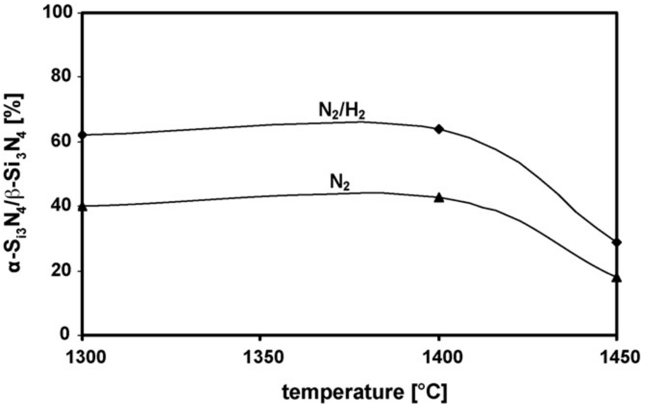


Fig. 6. Effect of the thermal treatment conditions on the ratio between α- and β-Si_3N_4.

equation[21]:

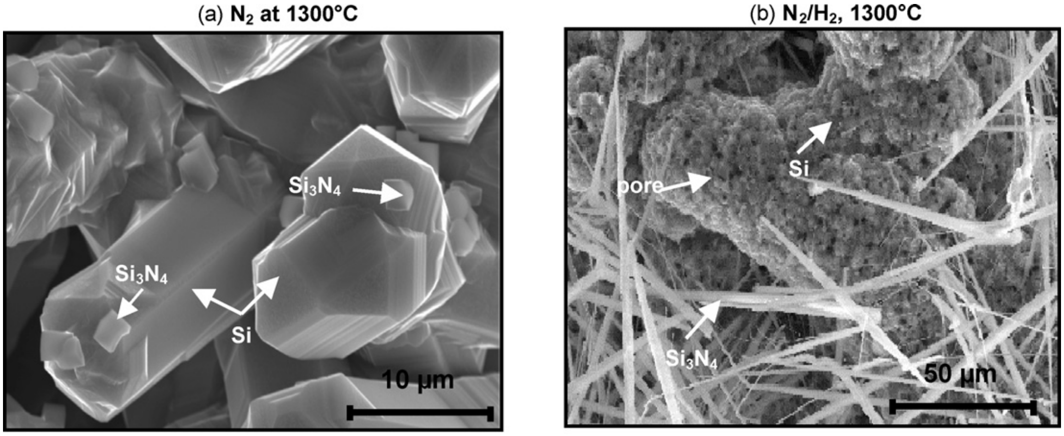
$$NG = \frac{W_{NS} - W_{IS}}{1.6 \times W_{IS}} \times 100 \qquad (5)$$

where W_{NS} and W_{IS} are the weight of nitrited and Si infiltrated sample, respectively.

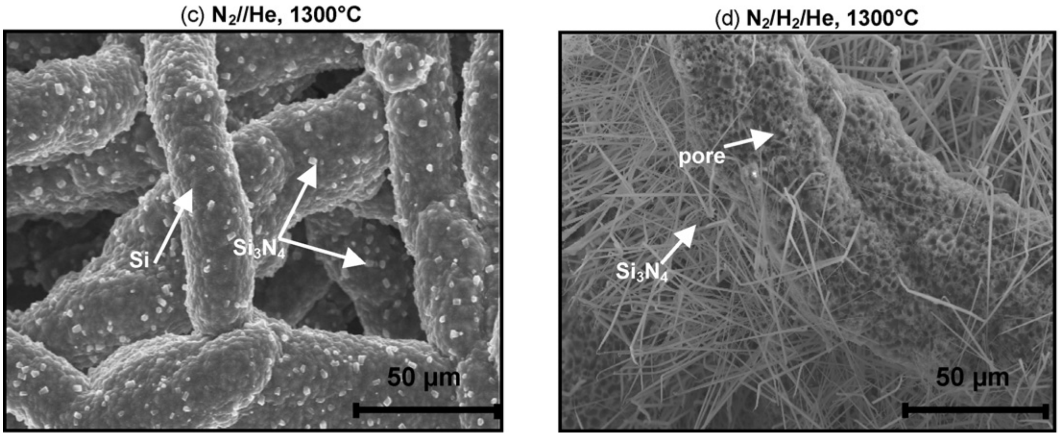
Based on Eq. (5), the nitridation grade in N_2 and N_2/H_2 atmosphere was calculated and plotted in Fig. 3 as a function of the reaction temperature. It can be seen, that both treatment atmospheres show the same trend with maximum nitridation grade of 50% (N_2/H_2) and 25% (N_2) at 1400 °C.

3.2. Composition of the Si_3N_4 ceramics

The composition of the obtained Si_3N_4 ceramics depends mainly on the temperature during the thermal treatment step regardless of the atmosphere. As already shown in Fig. 3, the grade of nitridation decreases at temperatures above the melting


(a) N_2 at 1300°C

(b) N_2/H_2, 1300°C


(c) $N_2//He$, 1300°C

(d) $N_2/H_2/He$, 1300°C

Fig. 7. SEM of Si_3N_4 obtained at different nitridation atmospheres for 5 h at 1300 °C.

point of silicon due to fact that silicon melts before its reaction with nitrogen could take place. This situation enhances the formation of SiC according to Eq. (2) prior to Eq. (1) because liquid silicon and nitrogen cannot react until Si_3N_4 nuclei have been introduced into the system[22]. According to Niihara and coworkers[23,24] SiC formed in this way can provide nucleation sites for β-Si_3N_4. As a result mixed ceramics was obtained.

The presence of SiC in the ceramics was confirmed by XRD (Fig. 4) and Raman spectroscopy (Fig. 5). The Raman spectra show sharp peak for crystalline SiC at 790 cm^{-1} in addition to Si peak at 520 cm^{-1} for samples nitrated at 1450 °C in different atmospheres. Actually, the conversion of carbon from the C_b template into SiC was estimated by exposing the porous ceramics to synthetic air at 750 °C for 6 h. The amount of reacted carbon is calculated based on the difference between the mass of the initial C_b template and the mass loss of the ceramized samples due to oxidation of the residual carbon. The conversion of carbon into SiC increases from 15% to 31.6% and to 85.5% for the Si infiltrated samples treated at 1300, 1400 and 1450 °C, respectively. This can also be observed from the increase in intensity of the SiC peaks in the XRD diagram with increasing temperature (Fig. 4).

Based on the results presented above, it can be concluded, that at temperatures below the melting point of silicon predominantly Si_3N_4 was formed, whereas at higher temperatures mixed Si_3N_4/SiC ceramics were obtained.

The crystalline phases of the silicon nitride depend also on the thermal treatment conditions. The identification of α- and β-Si_3N_4 phases as well as the determination of the α/β ratio as a function of the temperature has been done by XRD as shown in Figs. 4 and 6, respectively. The transformation of α- into β-phase with 80% β-Si_3N_4 took place above the melting point of Si.

3.3. Morphology of the Si_3N_4 ceramics

Typical morphologies of samples nitridated at 1300, 1400 and 1450 °C are shown in Figs. 7–9, respectively. A needle-like microstructure of α-Si_3N_4 is obtained predominantly from silicon impregnated samples treated at temperature of 1300 and 1400 °C in an atmosphere consisting of 10% H_2 and 90% N_2 as shown in Fig. 7b and Fig. 8b, respectively, whereas thermal treatment in pure N_2 or N_2/He leads to formation of α-Si_3N_4 hexagonal prism microstructure, Fig. 7(a and c) and Fig. 8(a and c). Furthermore, the samples treated at 1450 °C (Fig. 9) show β-Si_3N_4 phase with elongated grains connected randomly in three-dimensional morphology independent from the nitridation atmosphere used. As the reaction proceeds, the spikes become larger and fill up more and more of the original silicon grain. Finally, the spikes merge together and appear to be one large

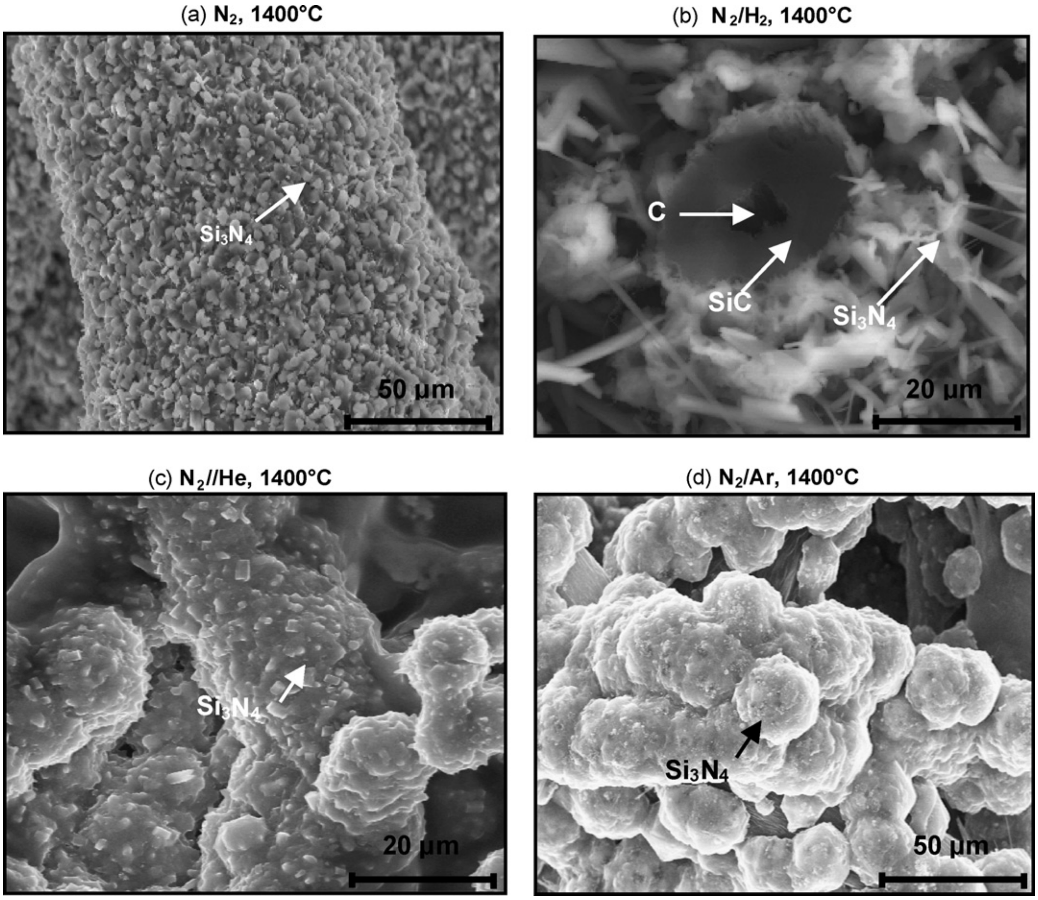


Fig. 8. SEM of Si_3N_4 obtained at different nitridation atmospheres for 5 h at 1400 °C.

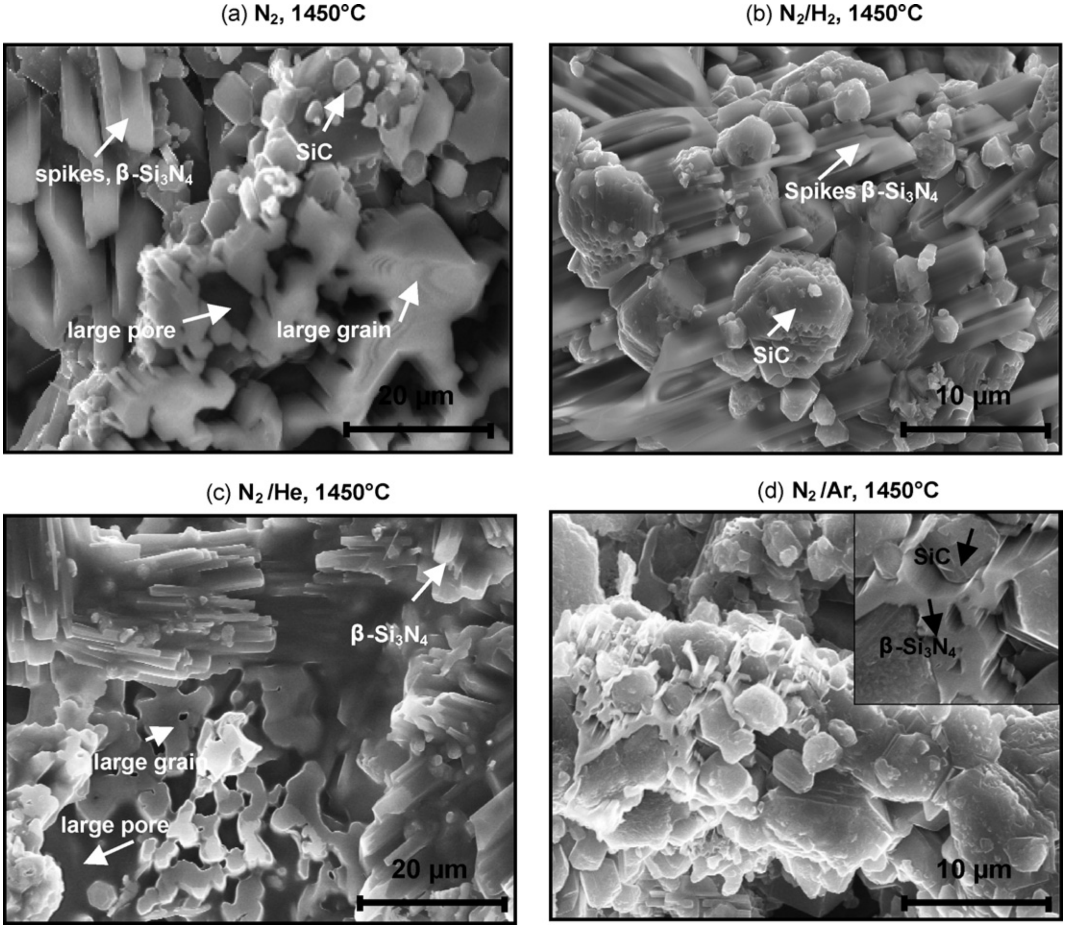


Fig. 9. SEM of Si_3N_4 obtained at different nitridation atmospheres for 5 h at 1450 °C.

grain with large pores (poor microstructure) in addition to unreacted silicon. In this case no needle-like morphology is present.

4. Conclusions

Chemical vapor infiltration technique was used successfully to convert paper preforms into biomorphic porous Si_3N_4 ceramics. This has been carried out by the infiltration of C_b template with $SiCl_4/H_2$ to deposit silicon feasible for further nitridation reaction at temperature between 1300 and 1450 °C. It was found that the conversion of silicon to Si_3N_4, the ratio between α- and β-Si_3N_4 and the morphology of the resulting ceramics are affected strongly by the nitridation conditions like temperature and composition of the reactive gas.

The optimum conditions for the Si_3N_4 production were determined experimentally. Addition of 10% of H_2 to the nitridation gas at temperatures near the melting point of silicon allows to increase the conversion of Si as well as to control the exothermic nitridation reaction, obtaining the preferable needle-like microstructure.

By applying these conditions at temperature above the melting point of silicon, additional SiC can be formed by solid–solid and solid–liquid reaction parallel to Si_3N_4 to produce SiC/Si_3N_4-mixed ceramics, which can enhance the thermal properties of the resulting materials at higher temperatures.

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