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Paper derived SiC–Si_3N_4 ceramics for high temperature applications

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Abstract

Biomorphic Si_3N_4–SiC ceramics have been produced by chemical vapour infiltration and reaction technique (CVI-R) using paper preforms as template. The paper consisting mainly of cellulose fibres was first carbonized by pyrolysis in inert atmosphere to obtain carbon bio-template, which was infiltrated with methyltrichlorosilane (MTS) in excess of hydrogen depositing a silicon rich silicon carbide (Si/SiC) layer onto the carbon fibres. Finally, after thermal treatment of this Si/SiC precursor ceramic in nitrogen-containing atmosphere (N_2 or N_2/H_2), in the temperature range of 1300–1450 °C SiC–Si_3N_4 ceramics were obtained by reaction bonding silicon nitride (RBSN) process. They were mainly composed of SiC containing α-Si_3N_4 and/or β-Si_3N_4 phases depending on the nitridation conditions. The SiC–Si_3N_4 ceramics have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and Raman spectroscopy. Thermal gravimetric analysis (TGA) was applied for the determination of the residual carbon as well as for the evaluation of the oxidation behaviour of the ceramics under cyclic conditions. The bending strength of the biomorphic ceramics was related to their different microstructures depending on the nitridation conditions.
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1. Introduction

Silicon carbide and silicon nitride based ceramics have been extensively studied in high temperature applications, such as turbine, automobile engine components and heat exchangers, due to their excellent strength to density relationship and outstanding thermo-mechanical performances [1]. Although Si_3N_4 and SiC ceramics exhibit very attractive properties, the design of composite SiC–Si_3N_4 ceramic composites is of particular interest recently due to their improved high temperature strength and resistance to oxidation and chemical attack [2]. Several methods have been described in the literature to produce SiC–Si_3N_4 composite ceramics such as conventional powder processing by mixing of monolithic powders [3], carbothermal reduction of silica in silicon nitride matrix [4], gel casting followed by two-step sintering using commercial resin as carbon source [5]. Recently, porous SiC–Si_3N_4 composite was obtained using SiC (and Si_3N_4) powder by extrusion process [6].

The present work introduces a novel method for the production of biomorphic SiC–Si_3N_4 ceramics by chemical vapor infiltration and reaction technique (CVI-R) using carbon bio-template originating form paper preforms. This approach was applied successfully in our laboratory to produce a variety of porous ceramic materials like SiC [7], Si_3N_4 [8], TiC [9] and TiO_2 [10]. Paper molding technology allows forming complex and variable structures. After carbonization at moderate temperatures they provide lightweight pre-ceramic structures. Use of CVI technique leads thus to lower production costs for a wide variety of ceramic materials.

In this work biomorphic SiC–Si_3N_4 ceramics were produced in a three-step process. First, the paper perform was carbonized by pyrolysis to obtain carbon bio-template, which was infiltrated by CVI with methyltrichlorosilane (MTS) in excess of hydrogen, depositing Si rich SiC layer onto the carbon fibres. After a thermal treatment in the range of 1300–1450 °C in nitrogen-containing atmosphere (N_2 or N_2/H_2) where reaction bonding silicon nitride (RBSN) was formed, Si_3N_4–SiC ceramics were obtained. This approach has the advantages of near-net shape dimension fabrication and low

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cost of production for SiC–Si_3N_4 composite ceramics compared to the other methods described in the literature. Moreover, the relatively low melting point of silicon (1410 °C) and its high reactivity with carbon and N_2 as well to form porous SiC–Si_3N_4 ceramic composites make this method attractive in comparison with direct addition of reinforcement phases. In the last case the cost of fine powder with high purity for the two monolithic phases is prohibitive. Furthermore, the starting powders are usually highly agglomerated, and thus achieving a uniform dispersion of the phases is difficult. The present study focuses on the investigation of the processing of biomorphic SiC–Si_3N_4 ceramics as well as studying the effect of the nitridation conditions on their mechanical performance and oxidation behavior.

2. Experimental work

2.1. Processing of biomorphic SiC–Si_3N_4 ceramics

Biomorphic SiC–Si_3N_4 ceramics derived from paper preforms were produced by chemical vapor infiltration and reaction (CVI-R) technique in a three-step process as shown in Fig. 1.

2.1.1. Carbonization of the paper perform

Flat paper sheets 30 mm × 30 mm were converted into carbon templates by pyrolysis at 800 °C in helium flow. The procedure is described in details elsewhere [7].

2.1.2. Chemical vapor infiltration (CVI) of the carbon templates

In a second step the carbon templates were infiltrated with a precursor system consisting of methyltrichlorosilane (MTS) in excess of hydrogen and helium as a carrier gas for 1 h under following reaction conditions: reactor temperature 950 °C, molar fraction of MTS in the reaction gas 0.08, gas flow velocity 30 cm/s and H_2/MTS ratio of 11. It was found, that under these conditions – relatively low temperatures and excess of hydrogen – the carbon fibers of the template were coated with a silicon rich silicon carbide layer (Si/SiC) [7].

2.1.3. Reaction bonding silicon nitride (RBSN)

The Si/SiC infiltrated carbon templates were thermally treated in nitrogen atmosphere for 5 h at temperatures ranged from 1300 to 1450 °C. At this conditions silicon nitride phase is formed as a result of the solid–gas reaction between silicon and nitrogen but also a solid–solid reaction between silicon and carbon template is possible.

2.1.4. Removal of the residual carbon by oxidation

The residual carbon from the template was removed by burning it out of the SiC–Si_3N_4 ceramics in synthetic air flow (125 Nl/h) at 750 °C for 5 h.

2.2. Characterization methods

2.2.1. XRD

The SiC–Si_3N_4 ceramics were analyzed by X-ray diffraction (XRD) with Cu Kα radiations to identify the crystalline phases as α-Si_3N_4, β-Si_3N_4, Si and SiC (Philips PW 3040 diffractometer). The amount of ß-Si_3N_4 ($R_ß$) was estimated after nitridation at different temperatures according to the following equation proposed by Gazzara and Messier [11] considering the most intensive peaks I (1 0 1) and I (2 1 0) for α-Si_3N_4 and β-Si_3N_4, respectively,

$$R_\beta = \frac{I_{\beta(101)} + I_{\beta(210)}}{I_{\beta(101)} + I_{\beta(210)} + I_{\alpha(201)} + I_{\alpha(210)}} \quad (1)$$

2.2.2. Raman spectroscopy

Raman Spectroscopy was used to analyze the composition (C, Si, SiC) of samples after every processing step (He/Ne laser, Labram HR, Dilor ISA).

2.2.3. SEM/EDX

Scanning electron microscopy equipped with energy dispersive X-ray spectroscopy analysis (SEM-EDX Philips XL 30) was used for investigation of the microstructure and elemental analysis of the samples obtained at different nitridation conditions.

2.2.4. TGA

Thermo Gravimetric Analysis (STA 409, Fa. Netzsch-Gerätebau GmbH) was applied to evaluate the residual carbon in the ceramic composites. Additionally, the composites were tested by mass change after 10 oxidation cycles between 550 and 1100 °C in air flow (80 ml/min).

2.2.5. Bending strength and oxidation resistance

The oxidation resistance of the SiC–Si_3N_4 composites was evaluated by measuring the mass change and the bending strength after 10 cycles of oxidation in air flow (125 Nl/h). Each cycle consisted of heating up the sample from 550 to 1100 °C followed by cooling to 550 °C. The whole oxidation cycles took around 42 h where the sample was exposed to the air.

Fig. 1. Flow chart of processing of SiC–Si_3N_4 ceramics by CVI-R technique.

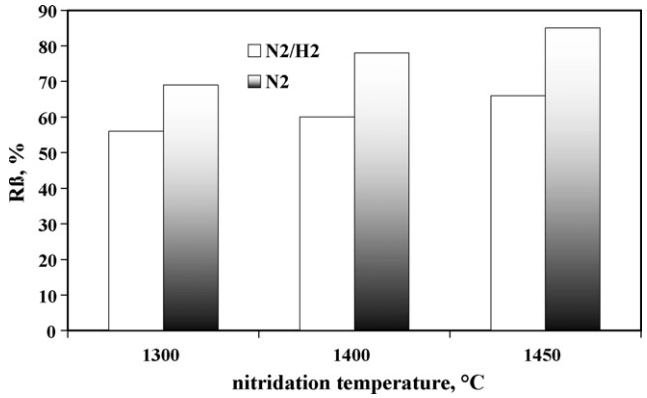

Fig. 2. Fraction of ß-Si_3N_4 in the SiC–Si_3N_4 ceramics.

The bending strength of the ceramic composites at ambient temperature before and after cyclic oxidation was measured by coaxial double ring bending test (INSTRON Model 4204).

3. Results and discussion

3.1. Composition and phase structure of the SiC–Si_3N_4 ceramics

The XRD patterns of the Si/SiC substrates nitrided at three temperatures around the melting point of Si: 1300, 1400 and 1450 °C in N_2 atmosphere show the formation of a mixture consisting of α-Si_3N_4, β-Si_3N_4 and β-SiC phases. According to these results, the composition of the ceramics seems to be strongly dependent on the treatment temperature.

The melting point of Si (1410 °C) appears to be a critical temperature, just above when fast nitridation occurred leading to less residual silicon. The fraction of the β-Si_3N_4 phase in the composites obtained at different temperatures and nitridation atmosphere are calculated by Eq. (1) using XRD and plotted as a function of temperature in Fig. 2. It can be seen clearly that β-Si_3N_4 content increases gradually as the temperature increases, independent of the nitridation atmosphere used. Furthermore, the use of pure N_2 as nitriding atmosphere increases the content of β-Si_3N_4 compared to N_2/H_2 mixture. This can be explained by the effect of hydrogen as discussed in details in a previous work [8].

Raman spectroscopy was used also to investigate the composition of the C_b/Si/SiC precursor ceramics after treatment at 1300, 1400 and 1450 °C in N_2 and He atmosphere as shown in Fig. 3a and b, respectively. Two broad Raman peaks are observed for ß-SiC, (TO) band at 797 cm^{-1} and (LO) band at 980 cm^{-1} at 1300 °C in both cases, whereas crystalline SiC at 797 cm^{-1} is observed in N_2 and He at 1450 °C. On the other hand, the intensity of the Si peak is decreasing as treating temperature increases. So, depending on the thermal treatment atmosphere, two reactions of the C_b/Si/SiC precursor ceramic can be carried out to form either SiC–Si_3N_4 [Eq. (2)] or SiC [Eq. (3)] in N_2 and He, respectively, according to:

$$C_b/Si/SiC + N_2 \rightarrow C_b/SiC/Si_3N_4 \quad (2)$$

$$C_b/Si/SiC \xrightarrow{He} SiC/SiC_b \quad (3)$$

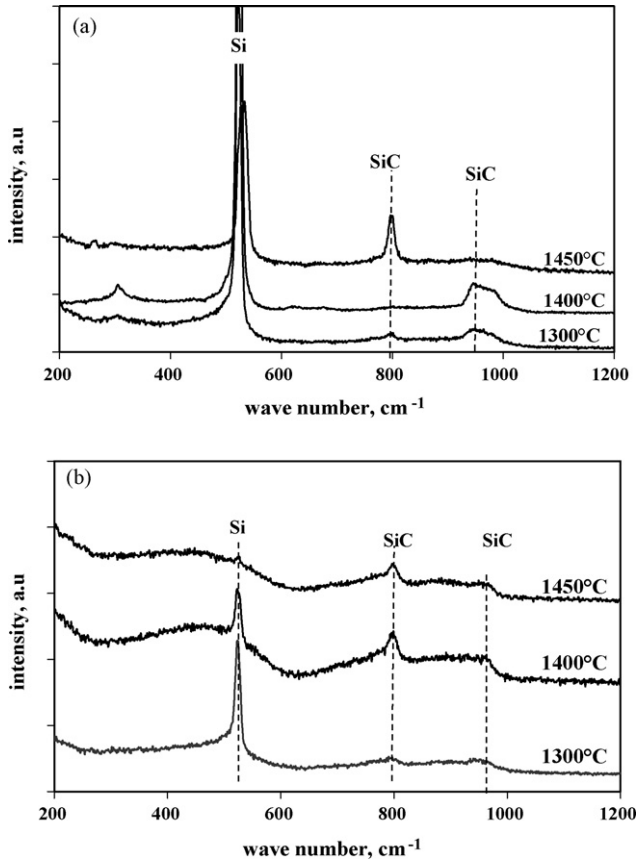

Fig. 3. Raman spectra for C_b/Si/SiC treated at different temperatures in (a) N_2 and (b) He.

In nitrogen atmosphere the nitridation reaction of silicon-to-silicon nitride (Eq. (2)) is more favoured, so that silicon can react with the carbon bio-template to SiC simultaneously at temperatures above its melting point.

3.2. Morphology of the SiC–Si_3N_4 ceramics

The evolution of different microstructure of β-SiC, α-Si_3N_4 and β-Si_3N_4 phases in the composite ceramics after thermal treatment of the C_b/Si/SiC precursor ceramic at 1300, 1400 and 1450 °C in N_2 and N_2/H_2 atmosphere was monitored by SEM as shown in Figs. 4–6, respectively. After thermal treatment at 1300 °C in nitrogen atmosphere, the ceramics consist mainly of SiC with uniform distributed grains of Si_3N_4, the size of which depends on the reactive gas used. Addition of hydrogen leads to formation of much smaller grains as can be seen in Fig. 4a.

A completely different microstructure was obtained at 1400 °C using N_2/H_2 and N_2 atmosphere as shown in Fig. 5a and b, respectively. A large amount of α-Si_3N_4 whiskers with approximately 20 μm length was dispersed in the SiC ceramic matrix by addition of hydrogen to the nitriding atmosphere, whereas hexagonal prisms with cross-section of 2 μm, identified as β-Si_3N_4, were observed in N_2 atmosphere at the same temperature. Prisms with well-faceted planes grow towards each other meet themselves and agglomerate. So the addition of hydrogen to the nitridation gas enhances the whisker formation at temperature below the melting point of silicon due

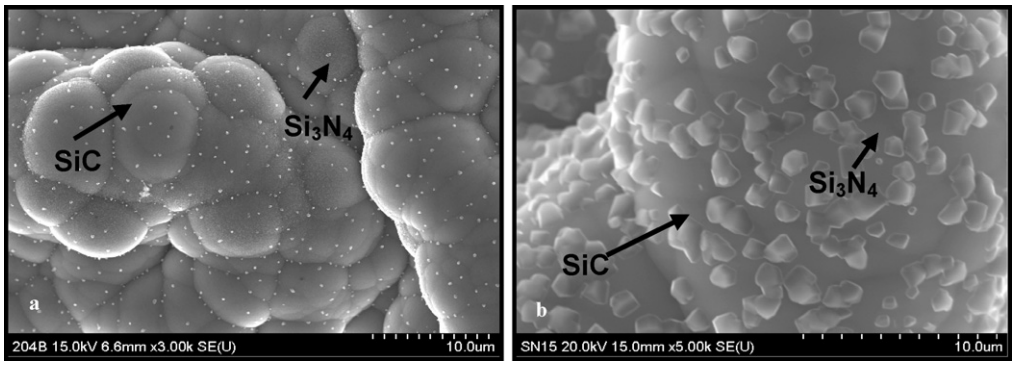

Fig. 4. Morphology of SiC–Si_3N_4 obtained at 1300 °C in (a) N_2/H_2 (b) N_2.

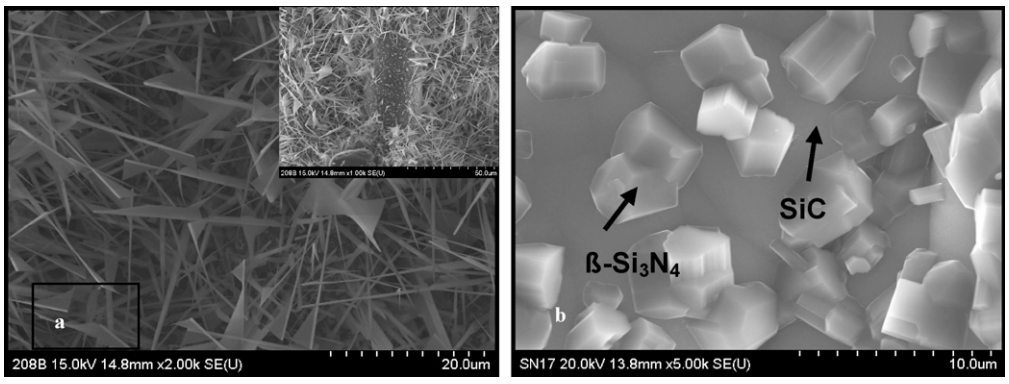

Fig. 5. Morphology of SiC–Si_3N_4 obtained at 1400 °C in (a) N_2/H_2 (b) N_2.

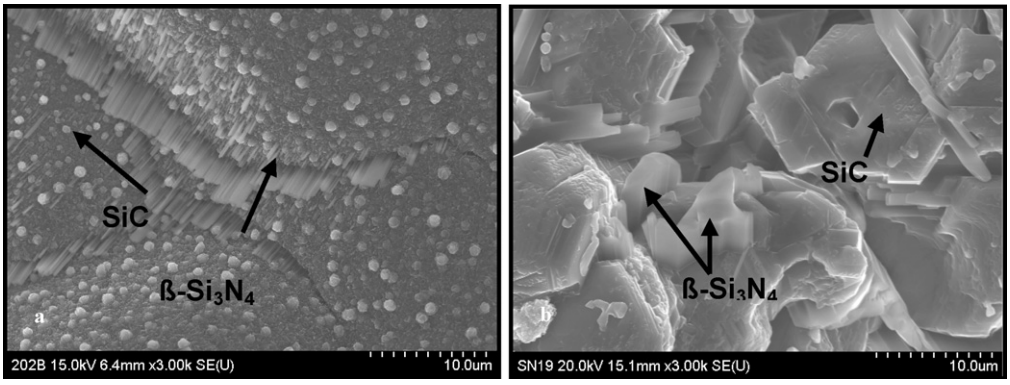

Fig. 6. Morphology of SiC–Si_3N_4 obtained at 1450 °C in (a) N_2/H_2 (b) N_2.

to the homogenous supply of SiO intermediate for α-Si_3N_4 phase as discussed in previous work [8].

At nitridation temperature above the melting point of silicon, e.g., 1450 °C different morphology is observed for both Si_3N_4 and SiC phases. The elongated grains are the typical appearance of β-Si_3N_4 with around 5 μm length for both N_2 and N_2/H_2 atmospheres in addition to small particles of SiC crystals with approximately 500 nm diameter in the case of N_2/H_2 atmosphere (Fig. 6a). The SiC nanoparticles suppressed the grain growth of β-Si_3N_4 in this case, resulting in fine grain microstructure. Large amount of Si_3N_4 is located at the SiC boundaries, whereas at lower temperature, Si_3N_4 grains are formed on the surface as well as on the initial SiC boundaries.

3.3. Bending strength of the SiC–Si_3N_4 ceramics

The strength of SiC and SiC–Si_3N_4 is strongly affected by temperature and thermal treatment atmosphere as shown in Fig. 7. Increasing the nitridation temperature causes an increase in the bending strength in the case of composite ceramics quite contrary to SiC obtained by thermal treatment of C_b/Si/SiC precursor ceramic at the same temperature but in He atmosphere. The presence of SiC increased the strength via reduction in grain size of ß-Si_3N_4 as shown in Fig. 6. This figure shows also the absence of any molten silicon which could cause bigger grain size as well as bigger pores that deteriorate the strength as observed in the previous work where $SiCl_4/H_2/N_2$

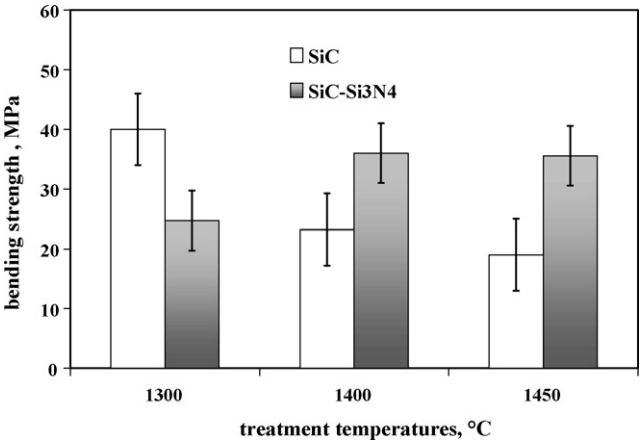

Fig. 7. Maximum bending strength of SiC and SiC–Si_3N_4.

system was used [8]. In the case of SiC ceramics the grain size will be increased at higher treatment temperature which could reduce the strength of the obtained ceramics.

3.4. Oxidation behavior of the SiC–Si_3N_4 ceramics

In this work, isothermal and cyclic oxidation test methods were developed for evaluation of the oxidation behavior of the SiC–Si_3N_4 composite ceramics in comparison to SiC ceramic. The isothermal oxidation was performed at 750 °C for 5 h in air flow in order to determine the residual carbon in the ceramics. The mass change related to original carbon

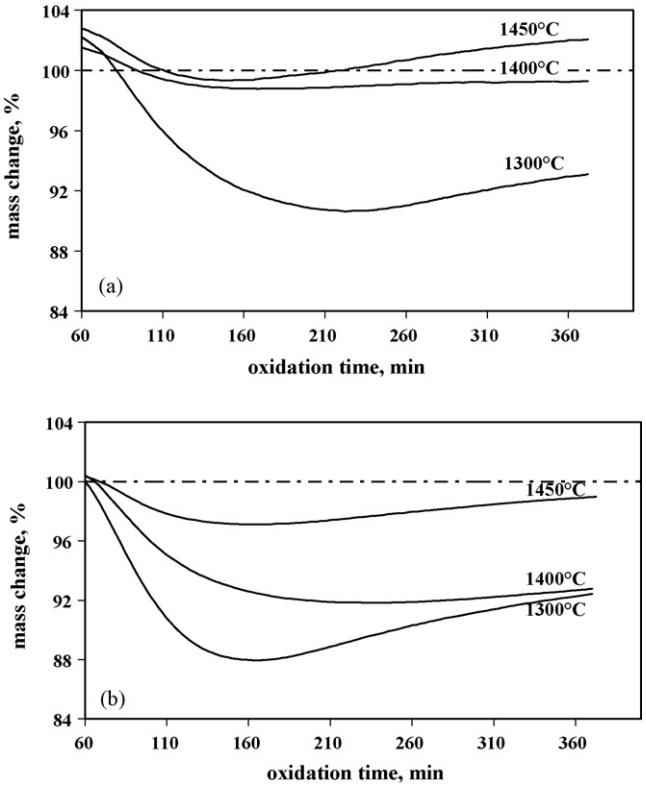

Fig. 8. Determination of residual carbon by TGA at 750 °C 5 h for (a) SiC–Si_3N_4, (b) SiC.

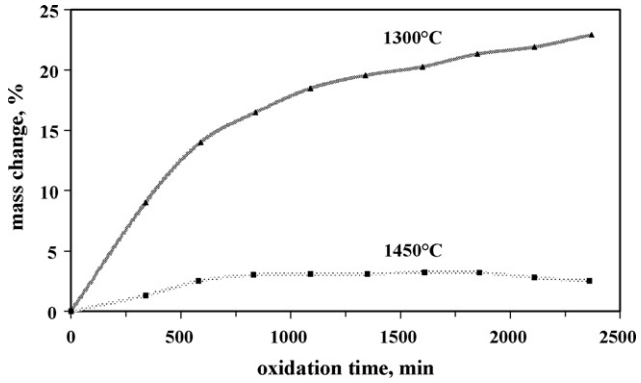

Fig. 9. Cyclic oxidation of SiC–Si_3N_4 obtained at 1300 and 1450 °C in nitrogen.

content of the C_b-template was plotted as a function of oxidation time for SiC–Si_3N_4 and SiC as shown in Fig. 8a and b, respectively. The curves show that after thermal treatment at 1300 °C both SiC–Si_3N_4 and SiC show mass loss in approximately the same extent due to the oxidation of the residual carbon. However, at higher treatment temperatures almost no mass loss was observed in the case of SiC–Si_3N_4, indicating that the Si_3N_4–SiC composite ceramic provides better oxidation protection than SiC alone.

Additionally, SiC–Si_3N_4 composite ceramics obtained after thermal treatment of C_b/Si/SiC precursor ceramics in nitrogen atmosphere at 1300 and 1450 °C were exposed to cyclic oxidation between 550 and 1100 °C and the mass change is shown in Fig. 9. (Each point represents mass change after one cycle.) In both cases mass gain due to the oxide formation was estimated during the 42 h test period. The formation of silicon oxide with approximately 22% mass increase is relatively high at nitridation temperature of 1300 °C because of the higher amount of free silicon which under these conditions was not able to react completely with nitrogen and/or carbon. The mass gain decreases to a very low value of 2% with increasing the reaction temperature to 1450 °C. The bending strengths of the SiC and SiC–Si_3N_4 ceramics after cyclic oxidation are plotted as function of the treatment temperature in Fig. 10. Improved strength compared to the strength before cyclic oxidation

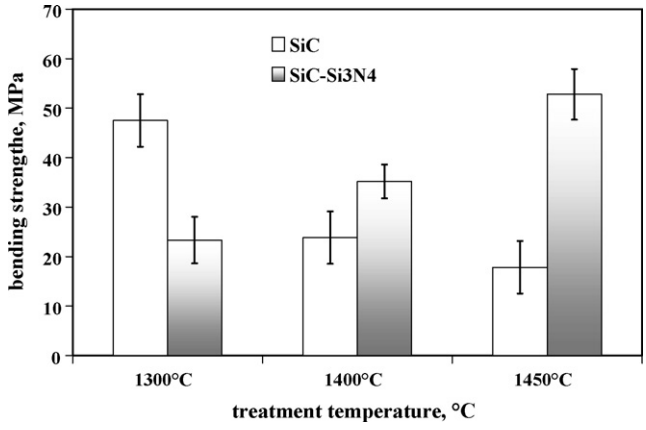

Fig. 10. Maximum bending strength of SiC and SiC–Si_3N_4 after cyclic oxidation.

(Fig. 7) was observed for SiC and SiC–Si_3N_4. In the case of the composite ceramic this can be explained by the formation of silicon oxynitride phase after cyclic oxidation which was detected by EDX which reduces microstructures degradation of composite materials and could have an influence on improved mechanical properties [12]. Additionally, the mass loss up to 77% of carbon related to the initial mass of the carbon template with the composite ceramics was in agreement with the mass balance of carbon. This amount of carbon loss is related to non-reacted carbon in the ceramics which could affect negatively the behavior of the composite ceramics at higher temperature applications. On the other hand, the loss in strength of SiC was up to 50% when temperature increases up to 1450 °C due to formation of large grain size at higher temperature.

4. Conclusions

Chemical vapor infiltration and reaction technique was used to produce SiC–Si_3N_4 composite ceramics derived from biological template. The paper preform could be successfully converted into composite ceramics consisting either of SiC, SiC-α-Si_3N_4 or SiC-β-Si_3N_4 by heat treatment of the infiltrated C_b/Si/SiC precursor ceramic in He and nitrogen-containing atmosphere up to 1450 °C. α-Si_3N_4 whiskers were formed in the SiC matrix at 1400 °C in N_2/H_2 atmosphere, whereas β-Si_3N_4 was formed on the surface of SiC at temperature below the melting point of Si and at the grain boundaries of SiC at higher temperature. The results show the feasibility of using such approach to obtain ceramics with different compositions and properties to be used effectively in high temperature applications due to the improved bending strength as well as oxidation resistance.

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