Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 36 (2010) 2203–2207
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Thermal conductivity of porous SiC composite ceramics derived from paper precursor

Nadejda Popovska [a,*], Emad Alkhateeb [a], Andreas Paul Fröba [c], Alfred Leipertz [b,c]

[a] *Lehrstuhl für Chemische Reaktionstechnik, Universität Erlangen-Nürnberg, Egerlandstrasse 3, D-91058 Erlangen, Germany*
[b] *Lehrstuhl für Technische Thermodynamik, Universität Erlangen-Nürnberg, Germany*
[c] *Erlangen Graduate School in Advanced Optical Technologies (SAOT), Universität Erlangen-Nürnberg, Germany*

Received 25 March 2010; received in revised form 4 April 2010; accepted 12 May 2010
Available online 30 June 2010

Abstract

Biomorphic porous SiC composite ceramics were produced by chemical vapor infiltration and reaction (CVI-R) technique using paper precursor as template. The thermal conductivity of four samples with different composition and microstructure was investigated: (a) C-template, (b) C-SiC, (c) C-SiC–Si_3N_4 and (d) SiC coated with a thin layer of TiO_2. The SiC–Si_3N_4 composite ceramic showed enhanced oxidation resistance compared to single phase SiC. However, a key property for the application of these materials at high temperatures is their thermal conductivity. The later was determined experimentally at defined temperatures in the range 293–373 K with a laser flash apparatus. It was found that the thermal conductivity of the porous ceramic composites increases in the following order: C-template < C-SiC < C-SiC–Si_3N_4 < SiC–TiO_2. The results were interpreted in regard to the porosity and the microstructure of the ceramics.

Keywords: B. Porosity; C. Thermal conductivity; E. Thermal applications; Biomorphic SiC ceramics

1. Introduction

Porous silicon carbide based ceramics are attractive materials for high temperature applications such as heat exchangers, exhaust gas catalyst support or pore burner because of their light weight and very good oxidation resistance. Recently, we have published several articles describing the processing of biomorphic porous ceramics such as SiC, Si_3N_4 and SiC–Si_3N_4 by chemical vapor infiltration and reaction technique (CVI-R) using paper preforms as template [1–3]. SiC with different microstructure like amorphous and crystalline in addition to SiC–Si_3N_4 composites with different composition were obtained. SiC and SiC–Si_3N_4 possess the highest oxidation resistance among the non-oxide structural ceramics [4]. These materials oxidize to form an adherent SiO_2 protective film on the surface, which shows the lowest permeability to oxygen of all the common oxides [5].

In a previous study the effect of the microstructure and the composition of the SiC based ceramics on their oxidation behavior in airflow under isothermal conditions at 1450° for 50 h was investigated by TGA analysis [6]. Parabolic curves with a two-step oxidation behavior were observed. An initial high oxidation rate followed by a low oxidation rate, suggest formation of a protective layer, which prevents further oxidation of the SiC. Amorphous and crystalline SiC with coarse grains show increase in mass change with high oxidation rate while much lower mass change was observed with crystalline SiC with fine grains. Introducing a second phase of Si_3N_4 to SiC had a significant effect on the mass change after oxidation, microstructure and mechanical properties of the ceramics. In this composite, the oxidation rate decreased with increasing the Si_3N_4 content as well as with the degree of crystallization. Additionally, the presence of a Si_3N_4 phase reduces the thermal expansion mismatch between SiO_2 and SiC resulting in relatively small cracks and well-bonded layers. In conclusions, the oxidation protection of crystalline SiC with fine grain structure as well as SiC–Si_3N_4 ceramic composite is adequate for long service times under isothermal conditions in airflow at 1450 °C.

---

* Corresponding author. Tel.: +49 9131 8527428; fax: +49 9131 8527421.
E-mail address: n.popovska@rzmail.uni-erlangen.de (N. Popovska).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.05.028

Beside the oxidation resistance the thermal properties of these materials such as thermal conductivity are key factors for their application at high temperatures. The literature provides little data about the thermal conductivity of porous ceramics [9,10]. It depends strongly on many factors like porosity, microstructure, and chemical composition as well as on the manufacturing process [7].

In the present work the thermal conductivity of four biomorphic porous ceramics with different composition and microstructure was investigated: (a) C-template, (b) C-SiC, (c) C-SiC–Si_3N_4, and (d) SiC coated with a thin layer of TiO_2. The aim is to learn more about the factors influencing the thermal conductivity in porous ceramics.

2. Experimental

2.1. Processing of biomorphic porous SiC ceramic composites by chemical vapor infiltration and reaction (CVI-R) technique

Biomorphic SiC composite ceramics were produced by the CVI-R technique using carbonized paper preform as template. Paper consisting mainly of cellulose fibres was converted first into carbon by pyrolysis in inert atmosphere at 800 °C [1], followed by chemical vapor infiltration step under reduced pressure of 300 mbar with an appropriate precursor system such as methyltrichlorosilane (MTS)/H_2 or $TiCl_4$/CH_4/H_2 depositing a ceramic or preceramic layer onto carbon fibres. In some cases high temperature treatment was performed as an additional step after CVI, where solid–solid and/or solid–gas chemical reactions took place. The microstructure and the composition of the resulting biomorphic ceramics could be controlled in a wide range varying the precursor system and the conditions during the CVI-R process. Fig. 1 presents the flow chart of processing of biomorphic SiC ceramics with different composition.

2.1.1. C-SiC composite

MTS/hydrogen mixture was used as a precursor for the CVI to coat the carbon fibres of the template with stoichiometric SiC. The infiltration of the carbon template with MTS/H_2 at 1050 °C and $\alpha(H_2/MTS) = 3$ according to CVI 1 route (Fig. 1) results in deposition of crystalline SiC with fine grain structure [6] (Eq. (1)).

$$C + CH_3SiCl_3 \rightarrow C\text{-}SiC + 3HCl \tag{1}$$

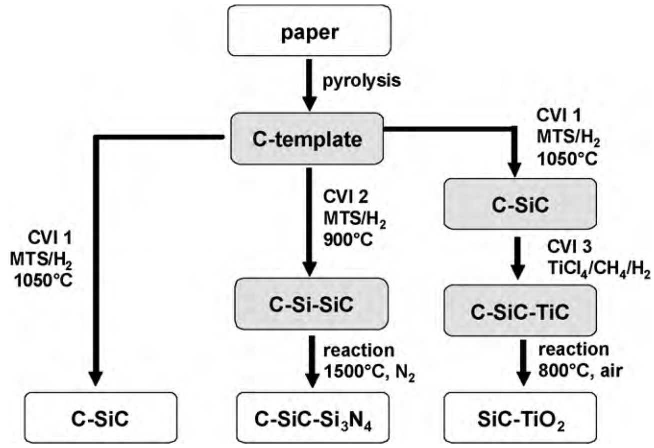

Fig. 1. Processing schema of biomorphic porous SiC ceramic composites derived from paper preforms by CVI-R technique.

2.1.2. C-SiC–Si_3N_4 composite

The CVI 2 route uses MTS in excess of hydrogen ($\alpha = H_2/MTS = 11$) at temperature as low as 900 °C to deposit Si rich SiC layer (C-Si–SiC) onto the carbon fibres according to Eq. (2) [1], followed by submitting the coated C-Si–SiC template to N_2 atmosphere at 1500 °C for 5 h. SiC–Si_3N_4 composite ceramic was obtained as a result of solid–liquid (C-Si) and liquid–gas (Si–N_2) chemical reactions (Eq. (3)). High temperature above the melting point of silicon (1410 °C) and long reaction time is required because of the low diffusion coefficient of the compounds in the solid phase.

$$C + CH_3SiCl_3 \rightarrow C\text{-}Si-SiC + HCl \tag{2}$$

$$C\text{-}Si-SiC \rightarrow C\text{-}Si_3N_4-SiC \tag{3}$$

2.1.3. SiC–TiO_2 composite

As a first step C-SiC ceramic was obtained according to the CVI 1 route (Eq. (1)), followed by infiltration with a precursor system consisting of $TiCl_4$/CH_4/H_2, route CVI 3. At 1100 °C a thin TiC layer was deposited (Eq. (4)). After oxidation of the C-SiC–TiC composite in airflow at 800 °C for 8 h SiC–TiO_2 composite with hollow fibres was obtained (Eq. (5)).

$$C\text{-}SiC + TiCl_4 + CH_4 \rightarrow C\text{-}SiC-TiC + 4HCl \tag{4}$$

$$C\text{-}SiC-TiC \rightarrow SiC-TiO_2 \tag{5}$$

The cross-section of the fibres in the biomorphic SiC composite ceramics is presented schematically in Fig. 2.

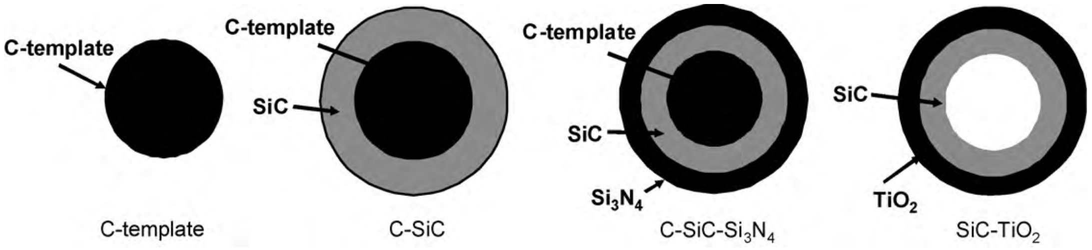

Fig. 2. Cross-section of the fibres in SiC based biomorphic composite ceramics (schematically).

2.2. Determination of the thermal conductivity of the biomorphic porous ceramics

The thermal conductivity of the samples was measured by the Laser Flash Method by Fa. NETZSCH, Germany. The front surface of a plan-parallel sample was heated by a laser pulse. The temperature rise on the rear surface was measured versus time using an IR detector, which allows determining the thermal diffusivity (a) and the heat capacity (c_p) of the ceramics. The thermal conductivity was calculated according to Eq. (6). The density of the porous ceramics (ρ) was measured experimentally by Mercury porosimetry as described below:

$$\lambda = a \,.\, c_p \,.\, \rho \tag{6}$$

The uncertainties for the determination of the thermal conductivity by the Laser Flash Method could be estimated to be in the range 3–5%.

The porosity of the ceramics (P) was determined according to Eq. (7), with ρ: density of the porous ceramics and ρ_0: density of the bulk ceramic material. Both densities were determined by Mercury porosimetry (PASCAL 140, Fa. POROTEC) measuring the volume of the sample without and with applying of pressure. First the volume of the porous sample (V) including the free spaces between the fibres was determined at near atmospheric pressure. In a second step a pressure of 400 kPa was applied in order to determine the volume of the bulk ceramic material (V_0) when mercury penetrates in the free spaces between the fibres as well as in pores down to 2 μm in diameter. Concerning the weight of the sample (m) the density of the ceramics with free spaces ($\rho = m/V$) and without free spaces ($\rho_0 = m/V_0$) was calculated.

$$P = 1 - \frac{\rho}{\rho_0} \tag{7}$$

The porosity P conforms to the free space between the fibres in the fibre network.

The specific surface area of the ceramics was measured by low temperature (77 K) nitrogen adsorption and calculated using the Brunauer–Emmett–Teller (BET) analysis.

3. Results and discussion

The biomorphic ceramics investigated in this study can be considered as fibre network with free spaces between the fibres expressed as porosity (P). Porous ceramics generally consist of a solid frame work, which is filled with a fluid. The fluid may flow through the solid frame in the case of open porosity. The thermal conductivity in a porous solid is not a homogenous material property. It is a combination of several different mechanisms taking place in a pore size level [7]. The foremost mechanism is the effective conductive path through the solid phase. It conforms to the bridge density between the fibres in a fibre network, which decreases with increasing the porosity. Also convective and radiation transfer may occur mostly via the pore phase [8]. However, radiation plays a significant role exclusively at high temperatures. The convection contribution at pore size smaller than 3–4 mm, as in our case, is considered to be negligible.

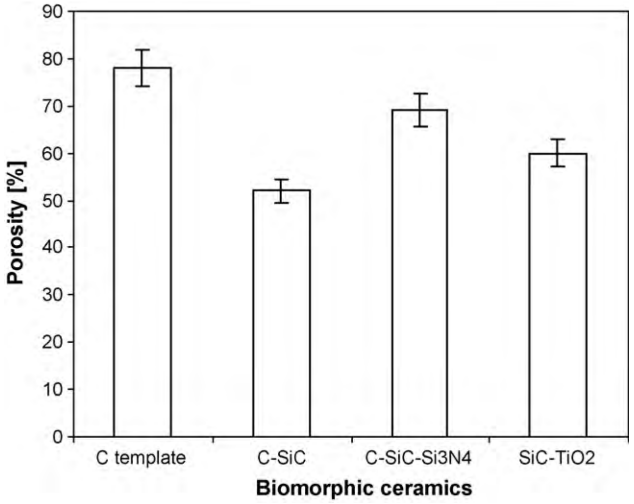

Fig. 3. Porosity of biomorphic porous ceramics.

Based on this knowledge the thermal conductivity of the SiC based ceramics in the present study is expected to decrease with increasing the porosity. At low temperature the solid contribution dominates the total thermal conductivity. Other factor to be considered is the issue whether there are regions of lower conductivity other than the pores in the solid conductive path e.g. due to grain boundary or other interfacial phases.

The thermal conductivity of biomorphic SiC based ceramic composites at 298 K and the corresponding porosity are presented in Figs. 3 and 4.

Concerning the thermal conductivity of the bulk ceramic materials, there are many different values published depending on their microstructure and processing method. However, there are general trend, so that the following order can be expected.

$$\lambda_{TiO_2} < \lambda_C < \lambda_{Si_3N_4} < \lambda_{SiC}$$

However, the ceramics differ not only in chemical composition but also in porosity and microstructure, which influence their

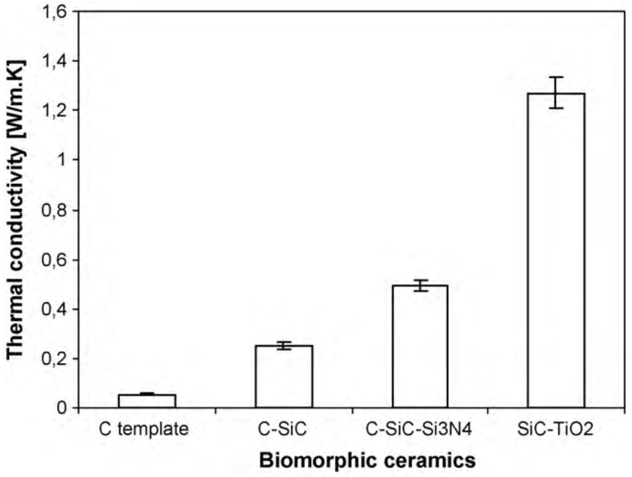

Fig. 4. Thermal conductivity of biomorphic porous ceramics at 298 K.

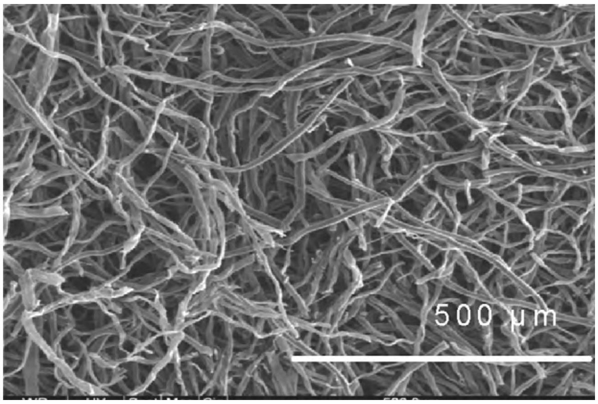

Fig. 5. Morphology of C-template.

thermal conductivity in a complex way and have also to be considered.

3.1. C-template

Carbon template was derived from paper preforms by pyrolysis at 800 °C. Because of the relatively thin carbon fibres ($<10\ \mu m$) it shows large free spaces between the fibres ($P = 78\%$) with low bridge density (Fig. 5), but no pores ($SSA = 0.1\ m^2\ g^{-1}$). C-template possesses amorphous structure with low grade of order because of the low carbonization temperature. All these result in low thermal conductivity of the carbon material.

3.2. C-SiC composite

The composite consists of amorphous carbon core with low thermal conductivity surrounded by a SiC layer of about 3–4 μm thickness with high thermal conductivity (Fig. 6). The C-SiC composite has low fraction of free spaces between the fibres ($P = 52\%$), which corresponds to high bridge density within the framework. As can be seen in Fig. 6, SiC has fine crystallite structure with large grain boundary, which is a factor reducing the thermal conductivity.

3.3. C-SiC–Si_3N_4 composite

This composite ceramic contains compared to the previous one additionally a very thin Si_3N_4 cover layer of about 100 nm (Fig. 7), which was formed as a result of high temperature chemical reaction at 1500 °C (Fig. 1), leading to increased crystallinity of the ceramic with large crystallite size and small grain boundary. On the other hand, the high temperature treatment causes a better ordered carbon microstructure, which improves its thermal conductivity. As a result much higher value for the thermal conductivity of the C-SiC–Si_3N_4 composite was measured in spite of the higher porosity of 69% compared with C-SiC (52%) (Fig. 3).

3.4. SiC–TiO_2 composite

This composite consists of hollow SiC fibres with fine crystalline microstructure similar to C-SiC (Fig. 6), surrounded with a thin about 500 nm microporous TiO_2 layer (Fig. 8).

It is the only composite ceramic with developed specific surface area of $5.2\ m^2\ g^{-1}$ caused by the TiO_2 layer. The evaluation of many SEM micrographs shows that the fibre diameter does not increase as a result of the TiO_2 coating and is comparable with those of the C-SiC composite ceramic. Therefore, the absence of carbon core seems to be a key factor leading to increasing the thermal conductivity (Fig. 4) despite of the higher porosity compared with C-SiC.

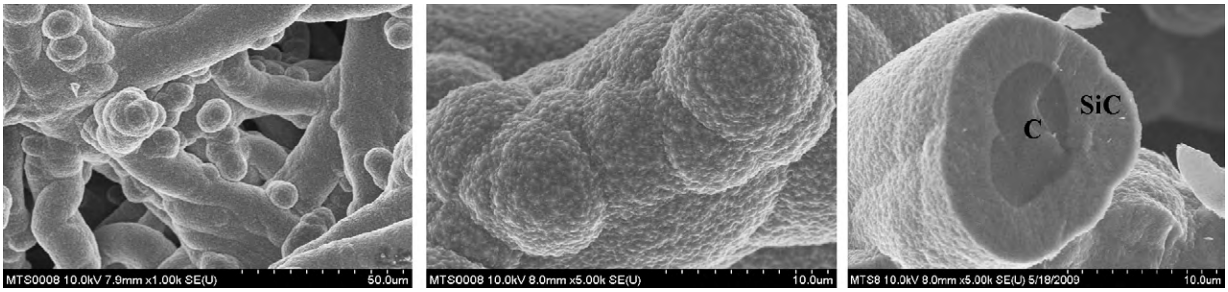

Fig. 6. Morphology of C-SiC composite ceramic.

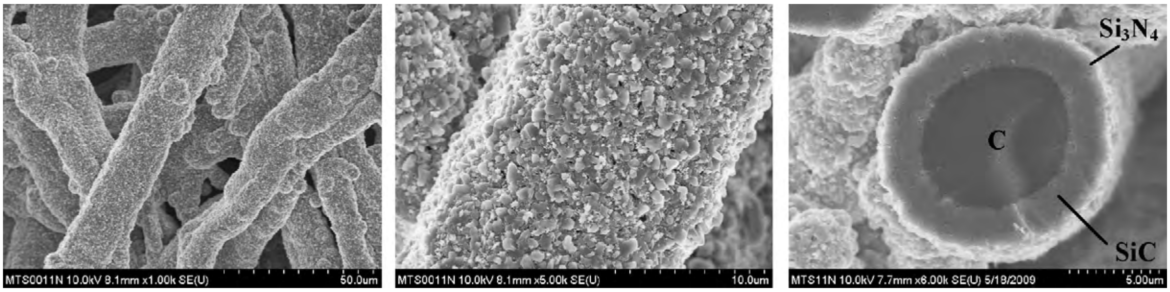

Fig. 7. Morphology of C-SiC–Si_3N_4 composite ceramic.

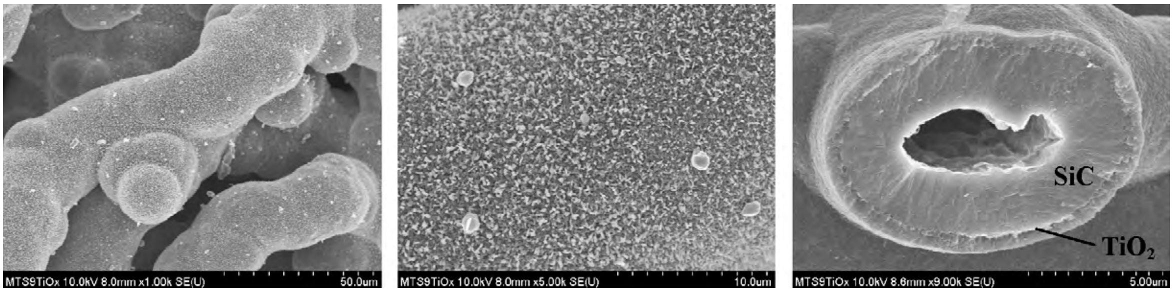

Fig. 8. Morphology of SiC–TiO_2 composite ceramic.

4. Conclusions

The thermal conductivity in biomorphic SiC based composite ceramics considered as a fibre network is not a homogeneous material property. It is a combination of many different influence factors, which can be summarized as follows:

- High bridge density in the fibre network favours the thermal conductivity. It decreases with increasing the porosity, which describes the free spaces between the fibres.
- High grade of crystallinity and big crystallite size corresponding to small grain boundaries favour the thermal conductivity.

Compared to the factors discussed above the thermal conductivity of the bulk material plays in the case of porous ceramics an inferior role.

Acknowledgements

The authors thank Fa. NETZSCH, Germany, for the measurements of the thermal conductivity. The authors A.P. Fröba and A. Leipertz gratefully acknowledge funding of the SAOT in the frame of the German Excellence Initiative by the German National Science Foundation (DFG).

References

[1] D.A. Streitwieser, N. Popovska, H. Gehard, G. Emig, Application of the chemical vapor infiltration and reaction (CVI-R) technique for the preparation of highly porous biomorphic SiC ceramics derived from paper, J. Eur. Ceram. Soc. 6 (2005) 817–828.
[2] H. Ghanem, N. Popovska, H. Gerhard, Processing of biomorphic Si_3N_4 ceramics by CVI-R technique with $SiCl_4/H_2/N_2$ system, J. Eur. Ceram. Soc. 27 (2007) 2119–2125.
[3] H. Ghanem, H. Gerhard, N. Popovska, Paper derived SiC–Si_3N_4 ceramics for high temperature applications, Ceram. Int. 35 (2009) 1021–1026.
[4] H. Du, R.E. Tressler, K.E. Spear, G. Pantano, Oxidation studies of crystalline CVD silicon nitride, J. Electrochem. Soc. 5 (1989) 1527–1536.
[5] N.S. Jacobson, Corrosion of silicon-based ceramics in combustion environment, J. Am. Ceram. Soc. 76 (1993) 3–28.
[6] H. Ghanem, E. Alkhateeb, H. Gerhard, N. Popovska, Oxidation behavior of silicon-based biomorphic ceramics prepared by chemical vapor infiltration and reaction technique, Ceram. Int. 35 (2009) 2767–2774.
[7] M. Scheffler, P. Colombo (Eds.), Cellular Ceramics-Structure, Manufacturing, Properties and Applications, Wiley-VCH Verlag, 2005.
[8] L. Gibson, M. Ashby, Cellular Solids, Cambridge University Press, 2001.
[9] K.E. Pappacena, K.T. Faber, H. Wang, W.D. Porter, Thermal conductivity of porous silicon carbide derived from wood precursors, J. Am. Ceram. Soc. 90 (9) (2007) 2855–2862.
[10] K.E. Pappacena, M.T. Jonson, H. Wang, W.D. Porter, K.T. Faber, Thermal properties of wood-derived copper–silicon carbide composites fabricated via electrodeposition, Compos. Sci. Technol. 70 (2010) 478–484.