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Paper derived biomorphic porous titanium carbide and titanium oxide ceramics produced by chemical vapor infiltration and reaction (CVI-R)

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Abstract

Chemical vapor infiltration (CVI) is used for producing biomorphic porous TiC ceramics derived from paper. The paper samples are first carbonized in inert atmosphere to yield biocarbon template structures (C_b-template). Subsequently, three routes for converting the C_b-templates into TiC ceramics are studied. The first route includes CVI with $TiCl_4$-H_2. The effect of methane as additional carbon source is investigated on the second route ($TiCl_4$-H_2-CH_4). Finally, a two step CVI process (Route 3), first $TiCl_4$-H_2 and subsequent $TiCl_4$-H_2-CH_4, is performed in order to improve both the grade of conversion of the C_b-template into TiC and the mechanical properties of the resulting porous TiC ceramics. Furthermore, porous TiO_2 ceramics are produced by high temperature oxidation of the TiC ceramics in air flow.

Keywords: Porous ceramics; Biomorphic ceramics; TiC; Chemical vapor infiltration

1. Introduction

Biomorphic cellular ceramics are a new class of ceramic materials with natural designed porous structure having recently attained particular interest. They are obtained by carbonization and consecutive conversion of biological preforms into ceramics. During the conversion their microstructure is neither destroyed nor altered, only a homogeneous shrinkage in all directions takes place during carbonization.[1,2] Various biotemplate processing technologies are developed for manufacturing of biomorphic SiC-based ceramics. Among these methods the most investigated are the Si liquid infiltration,[3–5] the Si gas infiltration,[5–7] the SiO vapor infiltration,[6,8] the polymer infiltration[9] and, the method used in this paper, the CVI-R method.[10–13] Compared to the other infiltration methods the chemical vapor infiltration (CVI) has the advantage of using relatively low processing temperatures, retaining the initial structure of the biotemplate on a micrometer level. Biomorphic SiC porous ceramics could be applied as high temperature filters or catalytic support structures due to their high thermal conductivity, good oxidation and corrosion resistance as well as high strength at elevated temperatures.

The properties of porous TiC ceramics are inferior to those of SiC, however, their improved corrosion resistance in phosphoric acid, the high electrical conductivity as well as the very good wet ability by metal melts made these materials interesting candidates for specific applications such as ceramic–metal composites[14] or catalyst supports for chemical and biochemical reactions.[15,16] TiO_2 ceramics are used as catalysts in photochemical and in biochemical reactions, for example in the purification of water.[17,18]

There exist only few reports about production of porous TiC and TiO_2 ceramics. The infiltration of dried wood or charcoal with titanium tetra-isopropoxide, followed by high temperature treatment yields highly porous TiO_2 ceramics.[19,20] A porous TiC ceramic is prepared by liquid vacuum infiltration of wood derived carbon structures with tetrabutyl-titanat.[21] First, the tetrabutyl-titanat decomposes to TiO_2, and then reacts with the carbon biotemplate at temperatures of about 1400 °C forming TiC.[21] In[22] our first results about the processing of TiC porous ceramic from wood by chemical vapor infiltration are reported.

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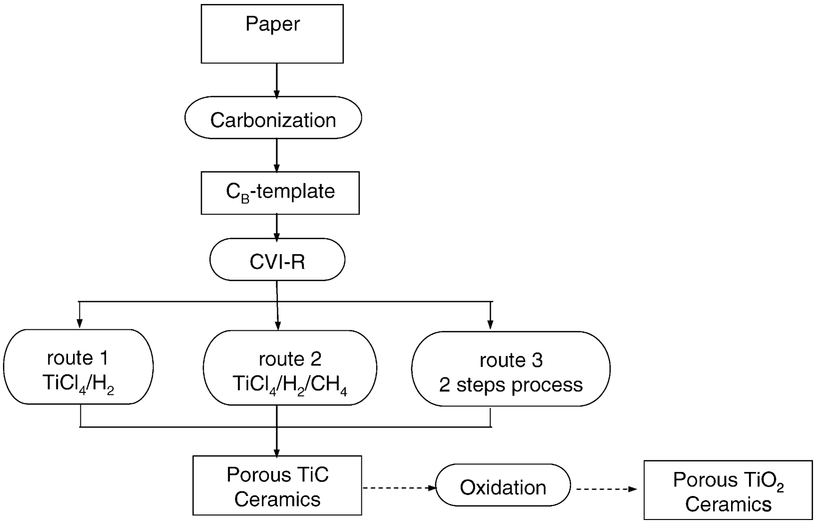

Fig. 1. Flow chart of the CVI-R ceramization process with three different routes.

In this study, chemical vapor infiltration-and reaction (CVI-R) process with $TiCl_4$-H_2 and $TiCl_4$-H_2-CH_4 systems is investigated to produce biomorphic cellular TiC ceramics by converting carbon fibers from paper biotemplates into TiC. The processing scheme is presented in Fig. 1. Three routes for converting the carbon biotemplates (C_b) into TiC ceramics are investigated. The first route includes chemical vapor infiltration with $TiCl_4$-H_2. The effect of methane as additional carbon source is investigated on Route 2. Finally, on the third route, two step CVI process is performed with $TiCl_4$-H_2 and subsequently with the $TiCl_4$-H_2-CH_4 system. The grade of conversion of the C_b-template into TiC as well as the mechanical properties of the resulting porous TiC ceramics should be improved with the two step process. Furthermore, first results on the processing of porous TiO_2 ceramics by oxidation of the TiC ceramics in air flow are presented.

2. Experimental procedure

The substrates used in this study are flat paper preforms of 0.80 mm thickness with a geometrical density of 0.22 g/cm^3. The initial porosity of the papers is 82% with a mean pore size of 25 μm. The papers are cut to 40 mm × 40 mm squares and carbonized at the conditions described below.

The carbonization of the paper performs and the chemical vapor infiltration of the resulting carbon biotemplates is performed in a horizontal hot-wall tubular flow reactor operated at atmospheric pressure.

The paper is carbonized in inert atmosphere (He, 5 cm/s) at the following conditions: 1 K/min ramp up to 350 °C, 1 h dwell time, followed by 2 K/min ramp up to 850 °C and additional also 1 h dwell time.

$TiCl_4$ is used as a titanium source for converting C_b into TiC. It is vaporized in a bubbler and carried into the reactor by a carrier gas H_2 or He, dosed by mass flow controllers. The gaseous precursors diffuse into the pores of the carbon biotemplate, where reductive decomposition of $TiCl_4$ in excess of hydrogen and chemical reaction to TiC takes place simultaneously. The effect of the process parameters such as temperature (1000–1200 °C), gas flow velocity (5–18 cm/s), molar fraction of the precursor ($x_{TiCl_4} = 0.01 - 0.06$) and $H_2/TiCl_4$ molar ratio (7–55) on the mass gain and the porosity of the samples after infiltration is investigated. Three pieces of carbonized paper are infiltrated and converted into TiC ceramics in the isothermal zone of the reactor for each experiment.

Titanium oxide porous ceramics are produced by oxidation of TiC ceramics at 850 °C for 6 h in air flow (10 cm/s) in the same equipment.

The composition of the porous ceramics is determined by XRD and EDX. The X-ray diffraction spectroscopy (Phillips PW 3040) is performed with rotation of the samples and Cu Kα radiation in angle range $2\theta = 5$–$85°$. The morphology of the ceramics is investigated by Scanning Electron Microscopy coupled with an Energy Dispersive X-ray Analysis (SEM/EDX, JSM-6400) to determine the element distribution across the infiltrated layer. The porosity of the ceramics is determined by Hg-porosimetry (Carlo Erba Mercury Intrusion Porosimeter 2000).

According to German Standard Code DIN 52 292, coaxial double ring bending test (INSTRON Model 4204) is carried out to measure the bending strength of the ceramic specimen. A scheme of the experimental arrangement is presented in Fig. 2.

The bending strength σ_b of the specimen is related to the maximum load force F_{max} before crushing and the sample thickness s. For rectangular specimen, bending strength $\sigma_{b,max}$ is given by:

$$\sigma_{b,max} = 1.04\frac{F_{max}}{s^2}.$$

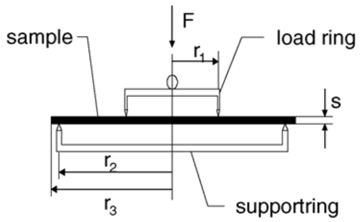

Fig. 2. Scheme of the double ring bending test arrangement.

3. Results and discussion

The ceramization of paper performs includes two processing steps—carbonization and chemical vapor infiltration.

Polyaromatic hydrocarbon polymers like cellulose, hemicelluloses and lignin are completely decomposed to a carbon lattice releasing H_2O, CO, CO_2 and other volatile components. This leads to significant weight loss of about 80 wt.%, associated with volume shrinkage in the range of 30–40 vol.%. The geometrical density of the carbonized paper is reduced from 0.22 to 0.125 g/cm^3 and the porosity increases slightly from 82 to 90%, due to the high mass loss. The specific surface area of the C_b-templates lays around 1 m^2/g. Despite the high weight loss and volume shrinkage, the microstructure and the morphology of the original organic fibers are retained and transformed into the carbon preform.

The chemical vapor infiltration process involves many steps. The most important are diffusion of the reactant gases into the pores of the carbon template followed by reductive decomposition of $TiCl_4$ with H_2 to titanium bearing intermediate species and chemical reaction with the carbon to form TiC. A homogeneous infiltration of the pores of the carbon biotemplates can only be achieved if the diffusion rate of the reactants in the pores is higher than the rate of the chemical reaction. This precondition is fulfilled at the investigated range of deposition parameters because of the large pores of the carbon biotemplate allowing a high rate of diffusion. However, limiting factor for the grade of conversion of the biomorphic carbon into TiC is the diffusion of the both reactants carbon and titanium through the steadily growing TiC layer. The thicker is the layer, the slower is the diffusion. Therefore, in order to optimize the infiltration and reaction process (CVI-R) three routes with different precursor systems are studied (Fig. 1).

3.1. CVI-R of TiC from $TiCl_4$-H_2 in C_b-templates (Route 1)

Biomorphic cellular TiC ceramic are produced by CVI-R process within a biocarbon template according to the following equation:

$$TiCl_4 + 2H_2 + C_b \rightarrow TiC_b + 4HCl \quad (1)$$

To determine the optimum CVI conditions, the $TiCl_4$ molar fraction and $H_2/TiCl_4$ molar ratio are varied systematically in order to investigate their influence on the infiltration rate expressed as a mass gain of the samples after infiltration.

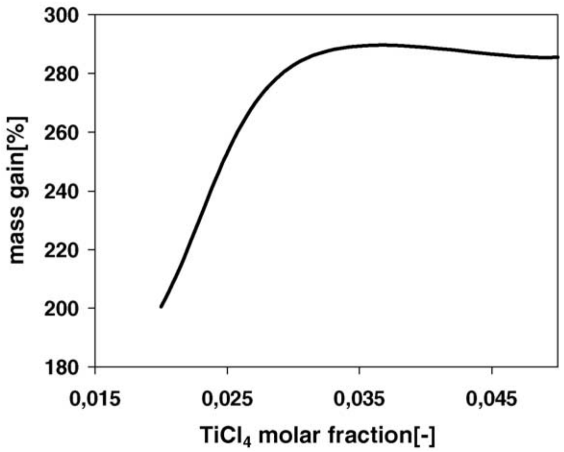

Fig. 3. Effect of the $TiCl_4$ molar fraction on the mass gain of the resulting ceramics with the $TiCl_4$-H_2 system.

3.1.1. Molar fraction of $TiCl_4$

Fig. 3 shows the mean mass gain of the C_b-templates infiltrated at three different $TiCl_4$ molar fractions. The mass gain increases significantly up to about 280% when the $TiCl_4$ molar fraction increases from 0.02 to 0.03 and remains constant for higher values. This behaviour confirms the assumption that the titanium diffusion into and the C_b diffusion out of the C_b-core through the formed TiC layer are the limiting steps for the deposition of TiC. During the infiltration process C_b is converted into TiC, which covers the carbon fibres and the formed TiC layer prevents further chemical reaction.

Extensive investigations regarding the diffusion of titanium in TiC, carbon in TiC and carbon in titanium have been performed by Sarian.[23–25] The results from these and following investigations[26,27] have shown that the diffusion

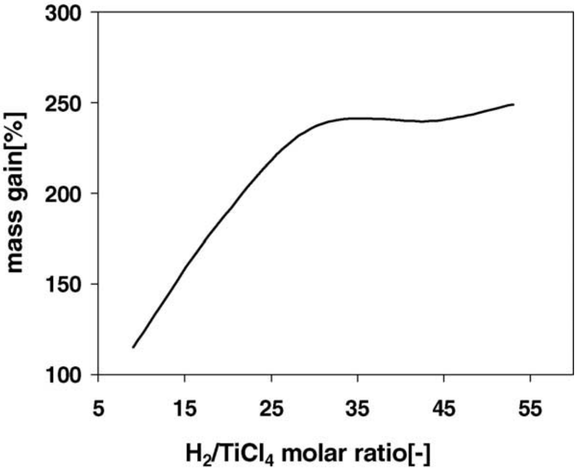

Fig. 4. Effect of the $H_2/TiCl_4$ molar ratio on the mass gain of the resulting ceramics with the $TiCl_4$-H_2 system.

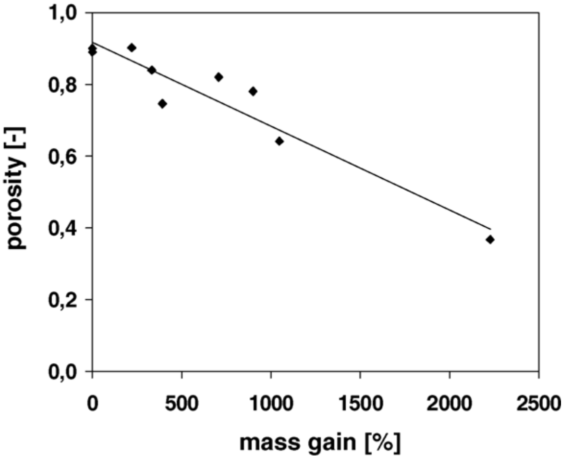

Fig. 5. Dependence of the porosity of the final ceramics on the mass gain after infiltration.

rate of carbon in TiC is by a factor 10^4 higher than that of titanium in TiC. The diffusion of carbon in titanium is also very fast, followed by a solid state reaction to TiC. The diffusivity of titanium through the formed TiC layer is negligible, while carbon can still diffuse slowly. The same behaviour is observed by the CVI-R technique investigated here. The C_b-template reacts first with the titanium bearing species originated from the reductive decomposition of $TiCl_4$ to TiC. As soon as the layers are up to a few micrometers the carbon has to diffuse through the TiC layer to react with titanium. But after the layer has reached a thickness of around 3–4 μm, even the carbon diffusion is too slow, so that it cannot reach the deposited titanium to form TiC. On the other hand, the deposition rate of pure titanium in absence of carbon is much slower than that of TiC. Therefore, stagnation in the mass gain is observed as shown in Fig. 3.

3.1.2. $H_2/TiCl_4$ ratio

Fig. 4 shows the mass gain dependence on the $H_2/TiCl_4$ molar ratio α, varied between 9 and 49. The mass gain of the C_b-templates increases linearly up to about 240% while increasing α from 9 to 30, and then keeps almost constant at this level. Hydrogen is both reactant as well as carrier gas for $TiCl_4$. To obtain a certain flow rate and to decompose $TiCl_4$ reductive completely, maximum H_2 amount should be applied in the reaction gas.

3.1.2.1. Characterization of the TiC ceramics. The infiltrated carbonized papers are characterized by XRD. For all the samples sharp peaks corresponding to TiC are identified.

The porosity of the final ceramics is measured by Hg-porosimetry. An inverse proportional dependence of the porosity of the obtained ceramics on their mass gain after infiltration is observed. The porosity varies between high porous ceramics with 70 to 90% porosity at mass gains of up to 500% to dense ceramics with porosity below 40% at mass gain of more than 2000% (Fig. 5). With the $TiCl_4$-H_2 system a maximum mass gain of 375% is obtained, corresponding to a porosity of 84% (Fig. 6c and d).

Further the samples are characterized by SEM/EDX. Fig. 6 show SEM micrographs of the sample with 278%

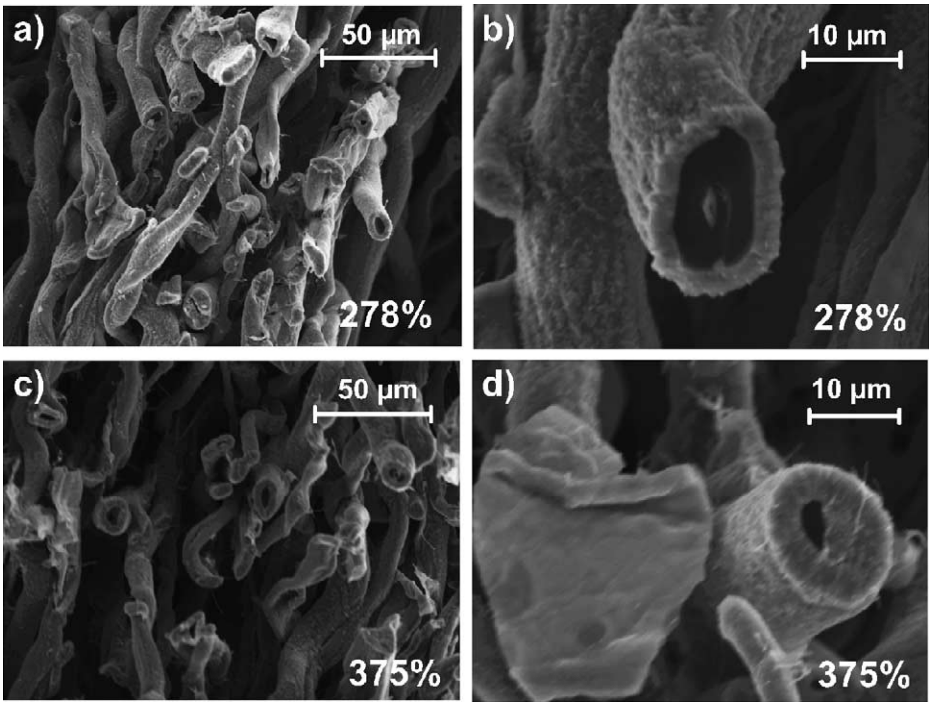

Fig. 6. SEM micrograph of a sample infiltrated with $TiCl_4$-H_2 system with 278% mass gain: (a) 500× and (b) 2000× magnification and 375% mass gain: (c) 500× and (d) 2000× magnification.

mass gain, corresponding to a porosity of 86%, prepared after 4 h infiltration with the $TiCl_4$-H_2 (a and b). It can be seen that the carbon fibres of the carbonized paper have not been converted into TiC completely due to the slow solid–solid diffusion. The carbon fibres are covered with TiC with a thickness of about 2 μm, acting as a diffusion barrier for the reaction between the deposited titanium and the carbon. This explains the limited mass gain of maximal 375% of the TiC ceramics obtained from $TiCl_4$-H_2 system under optimum infiltration conditions for 6 h infiltration time.

3.1.3. Bending strength of the TiC ceramics

The bending strength of the porous TiC ceramics is measured by coaxial double-ring bending tests. Generally, C_b-templates with higher mass gain after infiltration, and therefore, lower porosity tend to higher values of the bending strength. However, the maximum mass gain achieved in this case is 375%, leading to a bending strength of only 4–5 MPa (Fig. 7), which is too low to ensure stability, so that the samples break easily even during handling.

Summarizing the results presented above, it can be concluded that C_b-templates derived from paper could not be converted into TiC completely by CVI-R with $TiCl_4/H_2$ due to the slow solid-solid diffusion of carbon as well as titanium through the grown TiC layer. The infiltration of the preform is homogeneous, but only the surface region of the carbon fibres from the template is converted into TiC, which results in poor mechanical properties of the ceramics.

3.2. CVI-R of TiC from $TiCl_4/H_2$ with additional methane (Route 2)

In order to improve the strength of the porous TiC ceramics, methane (CH_4) is added to the precursor and supplied as carbon source additional to that from the C_b-template (Eq. (2)).

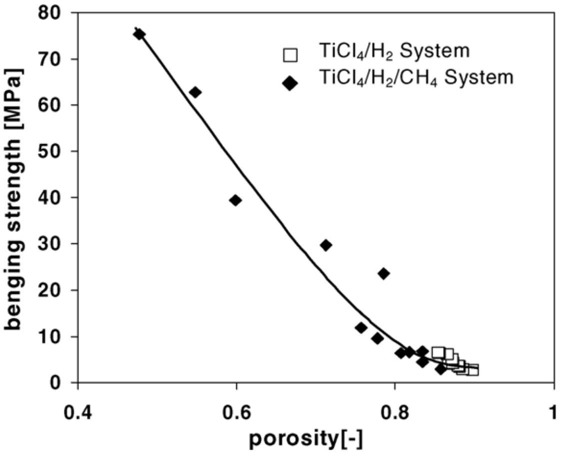

Fig. 7. Dependence of the bending strength on the porosity of the ceramics.

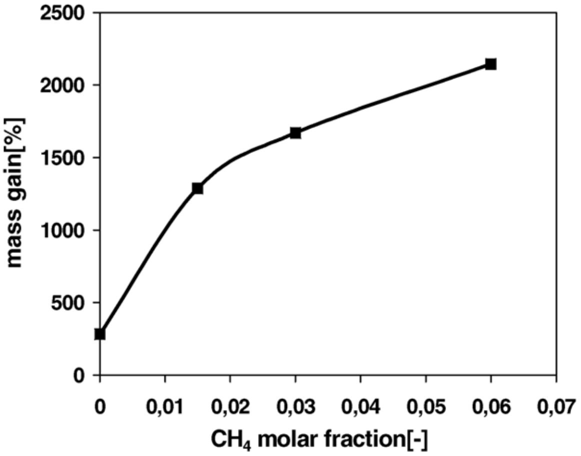

Fig. 8. Effect of the CH_4 molar fraction on the mass gain of the resulting ceramics with the $TiCl_4$-H_2-CH_4 system.

$$(x+y)TiCl_4 + xCH_4 + yC_b \xrightarrow{H_2} xTiC + yTiC_b + 4(x+y)HCl \qquad (2)$$

Based on the optimum infiltration conditions found with the $TiCl_4$-H_2 system, additionally the CH_4 molar fraction is varied to investigate its effect on the infiltration grade. Since the stoichiometric ratio of $TiCl_4$ to CH_4 for depositing TiC is 1:1 and the optimum $TiCl_4$ molar fraction determined for the $TiCl_4$-H_2 system is 0.03, the CH_4 molar fraction is varied in a region between 0.007 and 0.06, which corresponds to $TiCl_4/CH_4$ ratios in the range between 4 and 0.5.

Fig. 8 shows the mean mass gain after infiltration as a function of the CH_4 molar fraction. At the lowest CH_4 molar fraction of 0.007, a mean mass gain of only 344% is obtained, which lies under the theoretical value of 400% calculated for a complete conversion of the C_b-template into TiC. At CH_4 molar fraction of 0.01, the mean mass gain is 418%, increasing up to 600% at CH_4 molar fraction of 0.015. At higher methane concentration the voids between the fibres are filled with TiC because of the high deposition rate. The porosity decreases to 37% at mass gains above 2000%.

3.2.1. Characterization of the TiC ceramics

The infiltrated C_b-templates are characterized by XRD, showing for all samples sharp peaks for crystalline TiC.

Fig. 9 shows SEM micrographs comparing C_b-template infiltrated at CH_4 molar fraction of 0.015 having a mass gain of 819 and 75% porosity with that obtained at CH_4 molar fraction of 0.03 having a mass gain of 1520 and 61% porosity. It can be seen that the C_b-template with 819% mass gain is well infiltrated and there are still void spaces between the coated fibres. The fibres are coated by a coarse TiC layer, with a thickness of about 3–4 μm. Unconverted carbon core can also be seen (b). After 4 h infiltration the structure is almost filled with TiC (c and d). Thick TiC layers of 10 μm can be seen. The ceramic shows a relative low porosity of 61%.

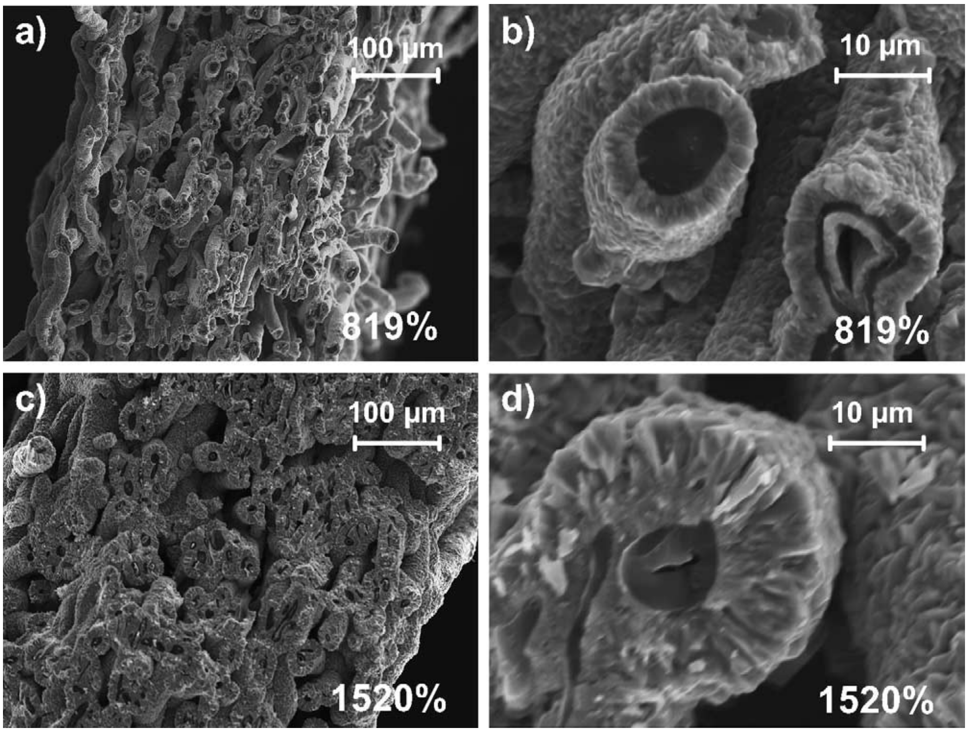

Fig. 9. SEM micrograph of a sample infiltrated with $TiCl_4$-H_2-CH_4 system with 819% mass gain: (a) 200× and (b) 2000× magnification and 1520% mass gain: (c) 500× and (d) 2000× magnification.

The bending strength of the TiC ceramics obtained using different precursor systems as a function of the porosity is shown in Fig. 7. As already mentioned, the lower is the porosity, the higher is the bending strength of the ceramics. High values of the bending strength up to 50 MPa could be obtained at a mass gain of about 1600%, corresponding to 60% porosity. For the infiltrated C_b-templates with a mass gain in the range between 600 to 800% corresponding to 80–75% porosity bending strength values up to 25 MPa can be achieved.

Summarizing the results of the infiltration of C_b-templates with the $TiCl_4$-H_2-CH_4 system, it can be concluded that due to the higher deposition rate the pores of the C_b template are filled with TiC, which leads to denser structures. At such conditions the carbon from the template cannot react completely to TiC. However, the methane as additional carbon source contributes to an improved mechanical stability of the obtained porous TiC ceramics.

3.3. *CVI-R of TiC from carbon biotemplates in two step process (Route 3)*

In order to combine the advantages of the both processing routes described above, a two step procedure is investigated. Two steps infiltration of the C_b-templates, first with $TiCl_4$-H_2 followed by $TiCl_4$-H_2-CH_4 is applied to produce biomorphic porous TiC ceramics achieving high infiltration grade combined with good mechanical properties.

- Step:1 Eq. (1)
- Step:1 Eq. (2)

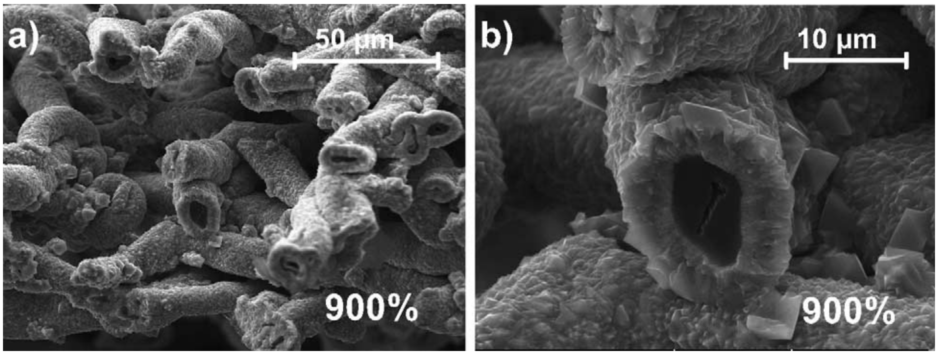

Fig. 10. SEM micrographs of the samples infiltrated by two step process: (a) 500× and (b) 2000× magnification.

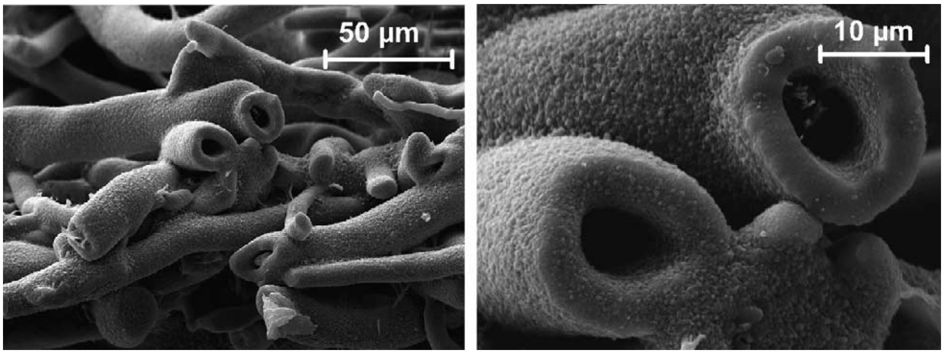

Fig. 11. SEM micrographs of the TiO_2 ceramics: (a) 500× and (b) 2000× magnification.

During the first step with the $TiCl_4$-H_2, the carbon fibres of the biotemplate are converted into TiC by reductive $TiCl_4$ decomposition and a subsequent reaction between titanium and C_b (Eq. (1)). In the second step (Eq. (2)), CH_4 is introduced as additional carbon source and reacts with the decomposed titanium to TiC, reinforcing in this way the porous ceramic structure.

The two steps infiltration is carried out by combining the optimum infiltration conditions found for both $TiCl_4$-H_2 and $TiCl_4$-H_2-CH_4 system established above. Fig. 10 shows the SEM micrographs of infiltrated C_b-template by two steps procedure. The sample has a mass gain of about 900% at dwell time of 1 h for every step, corresponding to a porosity of 74%. It can be seen, that the initial porous structure of the carbon biotemplate is retained in the resulting ceramic. The carbon fibres are covered with a thick TiC layer of about 5 µm. Additionally, faceted crystal TiC particles on the fibres can be seen (b). The bending strength of the porous ceramics produced by the two step process lies at about 25 MPa.

4. Processing of TiO_2 porous ceramics

First results on the processing of biomorphic porous TiO_2 ceramics by oxidation of biomorphic TiC ceramics in air flow are presented. White colored TiO_2 ceramic is obtained at 850 °C, air flow velocity of 10 cm/s and oxidation time 6 h. Using XRD it is shown, that the rutile modification of TiO_2 is formed.

In Fig. 11 SEM micrographs of the TiO_2 ceramics are shown. As it can be seen the fibrous structure of the original C_b-template is retained. Though, through the higher molecular weight of TiO_2 compared to that of TiC the structures seems bloated out.

The bending strength of the TiO_2 porous ceramics depends on the quality of the previous TiC ceramic and lies in the same range at 10 MPa for a TiO_2 ceramic obtained from a TiC ceramic with 372% mass gain. The porosity of the TiO_2 ceramics is a little bit higher than that of the corresponding TiC ceramics. For example a TiC ceramic with 442% mass gain has a porosity of 82%, while the same TiO_2 ceramic lies at 85%.

5. Conclusions

Porous TiC ceramics with good mechanical properties, derived from carbonized paper (C_b-template) can be produced by CVI in a two steps process. In a first step, the pores of the carbon biotemplate are infiltrated with $TiCl_4$ in excess of hydrogen, where reductive thermal decomposition and chemical reaction to TiC takes place on the fiber surface simultaneously. A complete conversion of the C_b-template to TiC is limited by the slow solid–solid diffusion of the reactants titanium and carbon through the grown TiC layer, leading to poor mechanical properties of the resulting ceramics. For this reason, in a second processing step, methane is added to the reaction gas as an additional carbon source. The additional deposited TiC strengthens the porous structure, resulting in improved mechanical properties of the obtained ceramics.

Porous TiO_2 ceramics as rutile modification can be produced by oxidation of the TiC ceramics at 850 °C in air flow. The fibrous structure of the original C_b-template is retained after processing

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