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Journal of the European Ceramic Society 27 (2007) 3433–3438
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Processing of biomorphic porous TiO_2 ceramics by chemical vapor infiltration and reaction (CVI-R) technique

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Received 19 November 2006; received in revised form 1 February 2007; accepted 10 February 2007
Available online 19 April 2007

Abstract

Porous biomorphic TiO_2 ceramics were manufactured from paper preforms by chemical vapor infiltration and reaction (CVI-R) in a three-steps process. First, the cellulose fibers of the paper were converted into carbon (C_b) by pyrolysis in an inert atmosphere. Then, C_b-template was infiltrated with a precursor system consisting of $TiCl_4$, CH_4 and H_2 to produce porous TiC ceramics, which were oxidized in a final step with air at temperatures in the range of 400–1200 °C. Depending on the conversion degree, TiC/TiO_2 or TiO_2 ceramics were obtained. The kinetics of the oxidation process was studied by thermal gravimetric analysis (TGA) and activation energies of 63 and 174 kJ mol^{-1} were estimated for the lower (400–800 °C) and higher (950–1200 °C) temperature regions, respectively. The TiO_2 ceramics were characterized by Raman spectroscopy (anatase/rutile ratio), SEM/EDX (morphology, composition) and nitrogen gas adsorption (pore structure). It was shown, that the anatase/rutile ratio as well as the pore structure of the resulting TiO_2 ceramics could be controlled varying the oxidation temperature. The TiO_2 samples obtained by oxidation of TiC biomorphic porous ceramics are lightweight but nevertheless have very good mechanical performances. Their bending strength varies between 30 and 40 MPa at a porosity of 65–70%. These structures have many potential applications, e.g. light structured materials, implants because of their bio-compatibility, catalyst support or catalyst for photo catalytic applications.

Keywords: CVI-R; TiO_2; Spectroscopy; Porosity; Structural applications

1. Introduction

Material synthesis from biological structures has become of increasing interest for the last decade. Various bio-templating high temperature techniques were developed to use natural grown structure, e.g. wood, natural fibers or paper as template for conversion into technical ceramics and ceramic composites. In previous works on the bio-templating we used the chemical vapor infiltration and reaction (CVI-R) technique to produce different biomorphic porous ceramics such as SiC,[1] TiC[2] and Si_3N_4[3] varying the precursor system and the conditions of the high temperature treatment.

More recent, extensive trials were directed to the fabrication of oxide-based biomorphic materials. Bio structure derived oxide ceramics like titanium oxide (TiO_2) is of particular importance for application as heat insulation, filter, catalyst or catalyst support in high temperature processes as well as for medical implants.[4]

Different biological structures were investigated in the literature to produce titanium oxide. Titanium oxide fibers could be prepared by infiltration of natural fibers such as sisal, jute and hemp fibers with $TiCl_4$ followed by a heat treatment in air.[5] Ota et al.[6] produced biomorphic porous TiO_2 ceramics by infiltration of wood with metal alkoxide like titanium isopropoxide (TTiP, $Ti[OCH(CH_3)_2]_4$). Huang and Kunitake[7] synthesized TiO_2 fibers from filter paper by a sol–gel process. This method was also used by Sieber and coworkers[8] for manufacturing porous TiO_2 ceramics with cellular morphology from native pine and rattan preforms.

In this work, the CVI-R technique was applied to produce biomorphic porous TiO_2 ceramics from paper preforms as shown in Fig. 1. First, the cellulose fibers of the paper were converted into carbon (C_b) by pyrolysis in inert gas atmosphere. Then, C_b-template was infiltrated with a precursor system consisting of $TiCl_4$, CH_4 and H_2 to produce porous TiC ceramics, which were oxidized in air at temperatures in the

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doi:10.1016/j.jeurceramsoc.2007.02.197

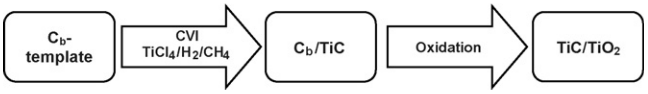


Fig. 1. Flow chart for the manufacturing of biomorphic porous TiO_2 ceramics from paper preforms.

range 400–1200 °C. Investigation was focused on the effect of the temperature on the kinetics of the oxidation process as well as on the microstructure of the resulting TiO_2 ceramics.

2. Experimental work

Biomorphic porous TiO_2 ceramics derived from paper preforms were produced by CVI-R technique in a three-step process.

2.1. Pyrolysis

Flat paper samples (30 mm × 30 mm × 0.37 mm) were pyrolysed at 800 °C for 1 h in He atmosphere. At this temperature, cellulose, hemi cellulose and lignin were decomposed, leaving a porous carbon bio-template (C_b). Homogenous shrinkage in all dimensions was obtained during this step but keeping the initial microstructure of the paper. More details about the pyrolysis step were described in a previous work.[1]

2.2. Chemical vapor infiltration (CVI)

The carbon bio-template was converted into TiC porous ceramics by chemical vapor infiltration with $TiCl_4/CH_4/H_2$ according to the following equation:

$$(x+y)\mathrm{TiCl_4} + x\mathrm{CH_4} + y\mathrm{C_b} \xrightarrow[1150\,^{\circ}\mathrm{C}]{\mathrm{H_2}} x\mathrm{TiC} + y\mathrm{TiC_b} + 4(x+y)\mathrm{HCl} \qquad (1)$$

Methane acts as an additional carbon source.

The infiltration process was carried out at 1150 °C under atmospheric pressure with $x_{\mathrm{TiCl_4}} = x_{\mathrm{CH_4}} = 2\,\mathrm{mol\%}$ and a $H_2/TiCl_4$ ratio of 21. The infiltration time was 1–2 h resulting in a mass gain in the range of 600–1300%. Details of the processing of the biomorphic porous TiC ceramics by CVI-R technique were described in reference.[2]

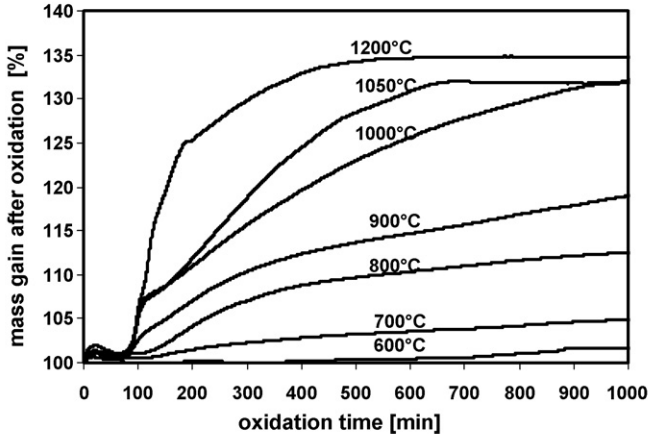


Fig. 2. Kinetic curves of TiC oxidation.

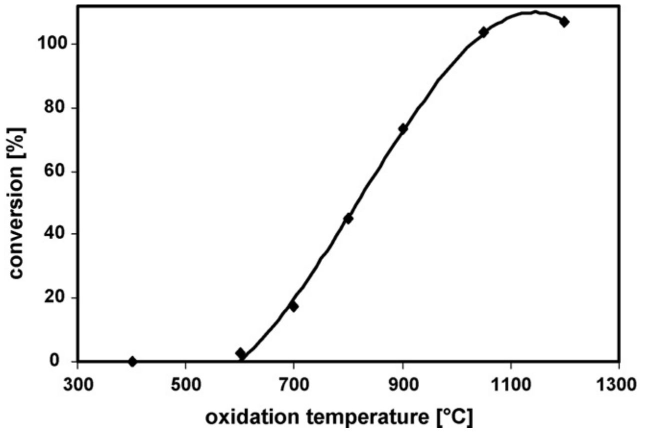


Fig. 3. Conversion of TiC porous ceramics into TiO_2 as a function of the temperature.

2.3. Oxidation

After the CVI process, the porous TiC ceramics were thermally treated in air at a temperature ranging from 400 to 1200 °C for 20 h at a flow rate around 2083 sccm resulting in porous TiO_2 ceramics according to the following equation:

$$\mathrm{TiC} + 2\mathrm{O_2} \rightarrow \mathrm{TiO_2} + \mathrm{CO_2} \qquad (2)$$

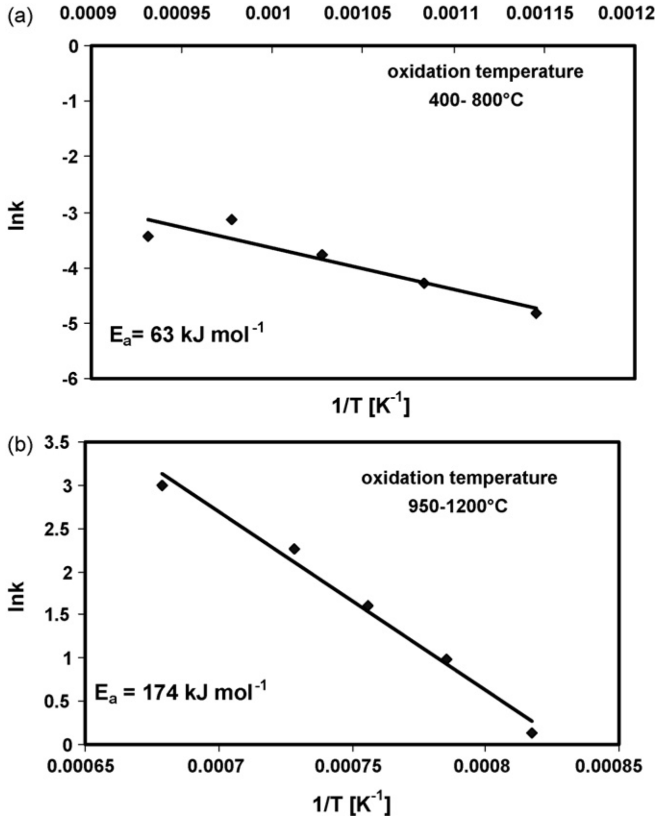


Fig. 4. Arrhenius plots for the oxidation of TiC: (a) low temperature region and (b) high temperature region.

Depending on the oxidation temperature, TiO_2 or TiC/TiO_2 ceramics were obtained.

2.4. *Kinetics of the oxidation process*

For the kinetic study, the mass change of the TiC ceramics during the isothermal oxidation in air flow (90 sccm) at temperatures between 400 and 1200 °C was monitored by thermal gravimetric analysis (TGA, Simultan-Thermo-Analysen-Gereat STA 409 Firma Netzsch-Gerätebau GmbH) and plotted as mass gain per sample surface area (mg/m^2) as a function of time.

2.5. *Characterization of the TiO_2 ceramics*

The produced TiO_2 ceramics were investigated by X-ray diffraction and Raman spectroscopy to verify the presence of anatase, rutile, unconverted TiC and free carbon. The ratio of anatase to rutile phase (A/R) in the samples was investigated by Raman spectroscopy and calculated using the following relation[9]:

$$\frac{A}{R} = \frac{I_{141}}{I_{440}} \tag{3}$$

where I_{141}, intensity of the anatase peak at 141 cm^{-1} and I_{440}, intensity of the rutile peak at 440 cm^{-1}.

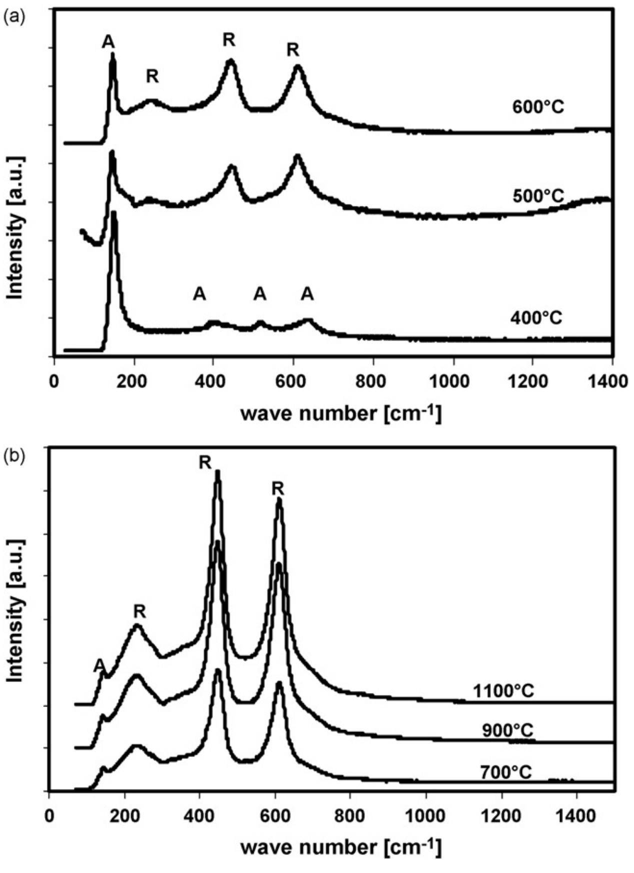


Fig. 5. Raman spectra of porous TiO_2 ceramics obtained from TiC at different oxidizing temperatures: (a) low temperatures and (b) high temperatures.

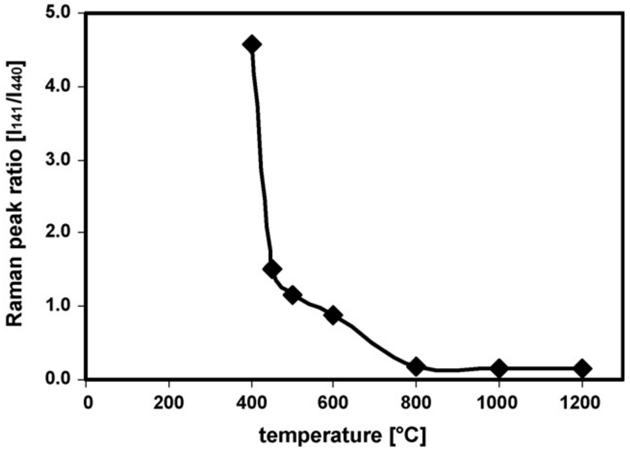


Fig. 6. Anatase/rutile ratio in the TiO_2 ceramics obtained by oxidation of TiC at different temperatures.

The morphology and the composition of the TiO_2 ceramics were investigated by Scanning Electron Microscopy coupled with an Energy Dispersive X-ray Analysis (Philips SEM/EDX, XL 30). Their pore structure was determined by low temperature nitrogen adsorption in a volumetric system (Gemini 2370 from micrometrics GmbH) whereas the porosity of the ceramics was determined by mercury porosimetry (Carlo Erba Mercury Instrusion Porosimeter 2000).

The bending strength of the TiO_2 ceramics was determined by a double ring bending test (INSTRON Model 4204) according to DIN52292.[10] A scheme of the double ring bending test and the measurement calculations are presented in reference.[1]

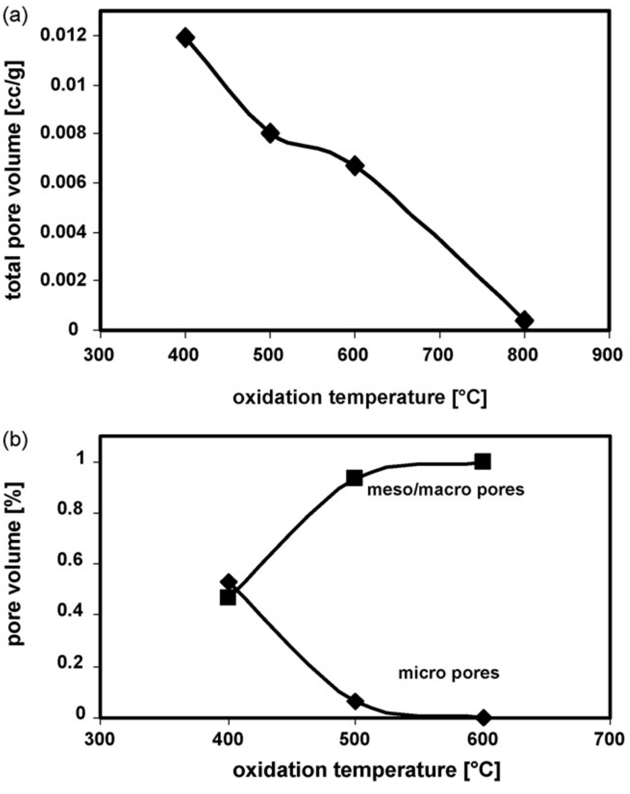


Fig. 7. (a) Total pore volume and (b) volume of micro, meso and macropores as function of the oxidation temperature.

3. Results and discussion

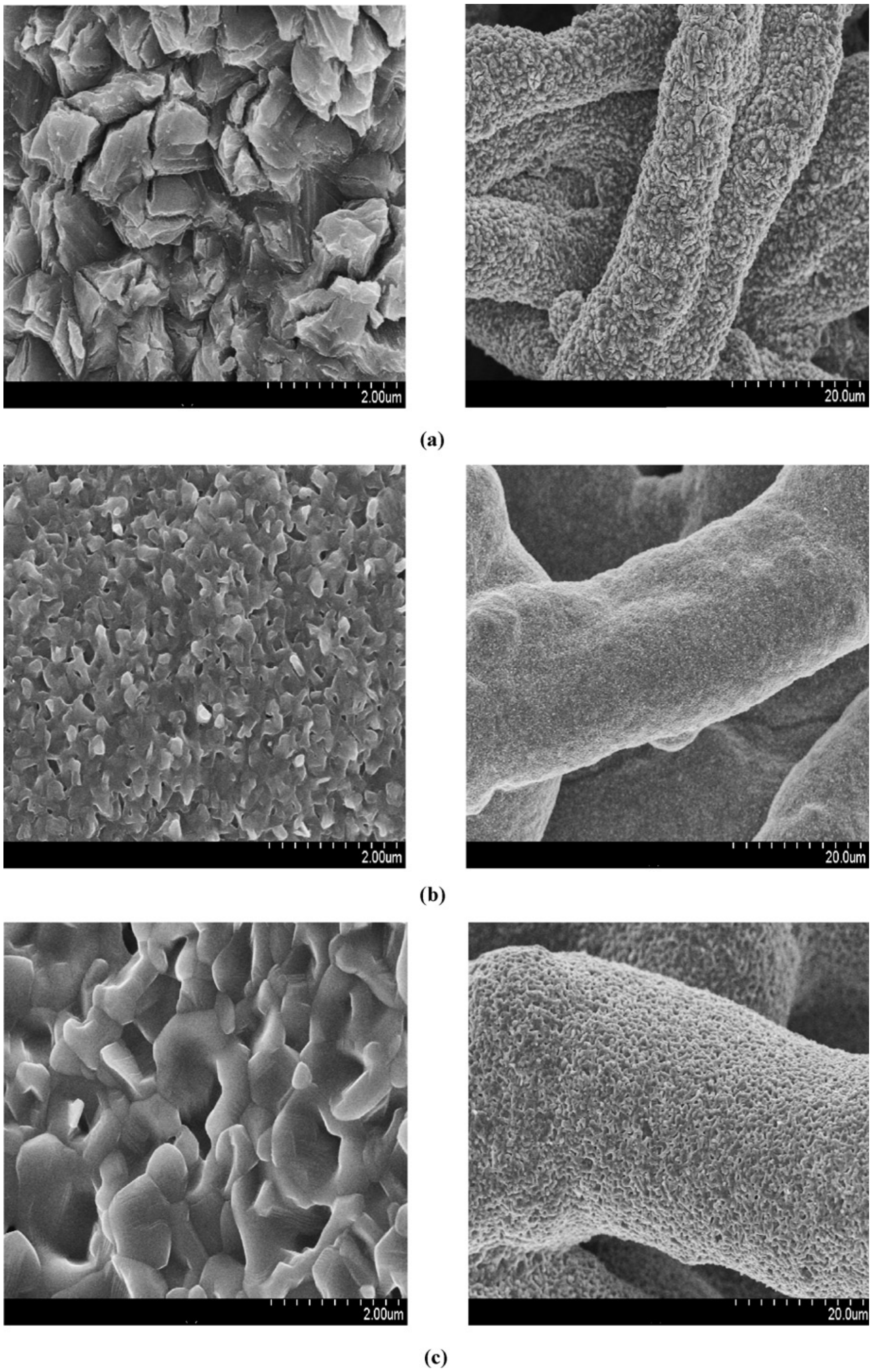
3.1. Oxidation kinetics of TiC

The kinetics of oxidation of TiC expressed as mass gain per sample unit area as a function of time as well as its conversion degree into TiO_2 at temperatures ranging from 400 to 1200 °C are presented in Figs. 2 and 3, respectively. As can be seen, the conversion degree of TiC ceramics into TiO_2 is relative low up to 800 °C then it increases rapidly with the temperature until 1000 °C, where 100% conversion is reached. The conversion values were obtained by dividing the measured weight increase by the theoretical one, which was calculated according to Eq. (2).

The mass gain data presented in Fig. 2 up to 1200 °C indicate that the oxidation behaviour obeys parabolic rate law which can be expressed as:

$$\Delta m = (kt)^{0.5} \quad (4)$$

where Δm, t, k are the mass gain per unit sample area, time and rate constant, respectively.



(a)

(b)

(c)

Fig. 8. Microstructure of the biomorphic porous TiO_2 ceramics obtained at: (a) 400 °C, (b) 600 °C and (c) 800 °C.

Therefore, the k values at different oxidation temperatures can be estimated as a slope of the plots $(\Delta m)^2$ versus t. The rate constant of the oxidation reaction, k follows an Arrhenius relation:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{5}$$

where E_a is the activation energy for the oxidation process, k_0 the pre-exponential coefficient, T the oxidation temperature (K) and R is the universal gas constant.

The Arrhenius plots of $\ln k$ versus $(1/T)$ at a temperature range 400–1200 °C are shown in Fig. 4(a and b). The plots change their slopes at around 900 °C. Therefore, two values for the activation energy can be calculated, 63 kJ mol^{-1} in the low temperature region (650–800 °C) and 174 kJ mol^{-1} at higher oxidation temperatures (950–1200 °C). Most of the reports in the literature about oxidation of TiC concern temperatures above 800 °C, where values for the activation energy of 179,[11] 193[12] or 181 kJ mol^{-1}[13] were calculated, which is in good agreement with our results in the high temperature region. However, the oxidation of TiC at temperatures below 800 °C is of great importance in order to obtain anatase phase with high photo catalytic activity.

3.2. Characterization of the TiO_2 ceramics

Titanium oxide exists in three crystalline forms anatase, rutile and brookite. Rutile is the thermodynamically more stable phase possessing smaller band gap energy of 3.0 eV than the anatase modification (3.2 eV).

Raman spectroscopy was found to be more sensitive in detecting structures of poor crystallinity than XRD especially for TiO_2 crystal structures obtained at low oxidation temperatures. Fig. 5(a and b) presents the Raman spectra of TiO_2 ceramics obtained from TiC at different oxidation temperatures. Anatase shows characteristic peaks at 638, 515 and 141 cm^{-1}, whereas rutile peaks appear at 610, 448 and 249 cm^{-1}. It can be seen that anatase was formed predominantly at temperatures below 600 °C (Fig. 5a). At higher oxidation temperatures the samples consist mainly of rutile (Fig. 5b). The anatase/rutile ratio (R) in the TiO_2 ceramics was estimated by Raman spectroscopy using Eq. (3) and plotted versus the oxidation temperature as shown in Fig. 6. Maximum amount of anatase ($R = 5.5$) was obtained at 400 °C. It decreases with the temperature and at 800 °C the samples consist mainly of rutile ($R = 0.3$).

The oxidation temperature affects also the pore structure of the resulting TiO_2 as can be seen in Fig. 7(a and b). Anatase-TiO_2 obtained by oxidation at 400 °C shows a maximum pore volume, corresponding to a BET surface area of 17 m^2/g, whereas only 0.8 m^2/g was measured for rutile-TiO_2 produced at temperatures above 800 °C. Anatase phase is generally known to have a higher specific surface area compared to rutile phase. Nearly, equal micro/mesopore ratio was found at 400 °C compared to 100% of mesopores obtained at temperatures above 600 °C (Fig. 7b).

Fig. 8 shows the SEM micrographs of biomorphic porous TiO_2 ceramics obtained by oxidation of TiC at 400, 600 and 800 °C. The surface of the samples after oxidation at 400 and 600 °C was composed of TiC/TiO_2, whereas complete conversion into TiO_2 was found at temperatures above 800 °C, as shown in Fig. 3 and confirmed by EDX analysis. Cracks and voids are clearly to be seen at 400 °C, which provide easy paths for gas transport of oxygen, leading to enhance conversion of TiC into TiO_2 porous ceramics. Increasing the oxidation temperature leads to denser structure with larger grain size and lower specific surface area.

The TiO_2 samples obtained in the present work by oxidation of TiC biomorphic porous ceramics are light but at the same time with very good mechanical properties. Their bending strength varies between 30 and 40 MPa at a porosity of 65–70%. These structures have many potential applications, e.g. light structured materials, implant because of their bio-compatibility, catalyst support or catalyst for photo catalytic applications.

4. Conclusions

Highly porous TiO_2 ceramics with high mechanical performances can be produced by oxidation of biomorphic porous TiC ceramics derived from paper preforms by CVI-R technique. The oxidation temperature affects strongly the conversion degree as well as the anatase/rutile ratio and the pore structure of the resulting ceramics. Anatase phase with high specific surface area and equal amount of micro and mesopores was obtained at oxidation temperatures around 400–500 °C. Under these conditions the conversion of TiC is low and the activation energy of the oxidation reaction is 63 kJ mol^{-1}, low, compared to that above 800 °C. In this temperature region with activation energy of 174 kJ mol^{-1} complete conversion of TiC into rutile-TiO_2 with low specific surface area but predominantly mesopores was observed. The TiO_2 structures with predominantly anatase phase are very promising candidates for photo catalytic applications in a continuous process with low pressure drop and easy separation of the products.

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