

# PROCESSING OF CARBIDE-DERIVED CARBON (CDC) USING BIOMORPHIC POROUS TITANIUM CARBIDE CERAMICS

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## Abstract

Biomorphic porous TiC and TiC/TiO<sub>2</sub> ceramics were covered with highly porous carbon, so-called carbide-derived carbon (CDC), by selective etching of Ti from TiC with chlorine containing gas in a temperature range 400-1000°C. The etching rate of TiC is strongly affected by the chlorine concentration, but only slightly by the reaction temperature. No correlation was found between etching rate of TiC and specific surface area (SSA) of the resulting CDC with respect to temperature. Kinetic investigations show that up to 80 minutes the etching process is controlled by the chemical reaction. At longer times diffusion limitation has to be taken into account. Addition of hydrogen to the etching gas enhances the diffusion of the chlorine molecules, so that no diffusion limitation was observed. The CDC produced by chlorination of TiC at 400°C is amorphous. Increased reaction temperature and addition of hydrogen to the chlorine gas lead to formation of regions with higher order like onion carbon and graphitic ribbons. The CDC coated TiC/TiO<sub>2</sub> ceramics with predominantly anatase phase show enhanced photo catalytic activity.

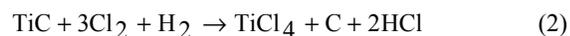
## Introduction

Carbide-derived carbon (CDC) process represents a new class of nanoporous carbons, produced by selective thermochemical etching of inorganic carbon containing materials such as metal carbides. The structure of the CDC can be templated by the initial carbide structure, with the opportunity for further structural modifications by controlling the process parameters like temperature, total pressure, etching agent type and concentration.

Review of the literature data on CDC shows that the etching process is possible using variety of carbides like B<sub>4</sub>C [Dash, 2004], Ti<sub>2</sub>AlC [Hoffmann], TiC [Dash, 2006], SiC [Cambaz], Ti<sub>3</sub>SiC<sub>2</sub> [Yushin, 2005a]. Among them is SiC the most investigated template for this process.

Titanium carbide (TiC) is also a very promising candidate for producing of CDC. TiC as starting material shows a small and uniform carbon-carbon distance and this may lead to a highly porous carbon with narrow pore size distribution [Yushin, 2005b]. Results on CDC from TiC show that amorphous carbon is produced and that the specific surface area increases with etching temperature in a temperature range from 400 – 1000°C. After 3h treatment in chlorine atmosphere a specific surface area of 1200 m<sup>2</sup>/g up to 1800 m<sup>2</sup>/g is reached at 400°C and 800°C, respectively. At higher temperatures a graphitisation of carbon results in a small decline in SSA. In general, etching temperatures below 1000°C result in amorphous carbon whereas temperatures above 1000°C lead to graphitisation of the carbon resulting in a decrease of the SSA. Further investigations on pore size and pore size distribution were made which show that micro pores (< 2 nm) are formed in a temperature range of 400 – 700°C [Dash, 2006; Zheng]. With increasing chlorination temperature the average pore size is increased and for reaction temperatures higher than 1000°C the pore size distribution is broadened and mesopores are detected [Dash, 2006]. Most investigations on the field of CDC are based on metal carbides in form of powder. The reaction kinetics and conditions for diffusion limitations are studied poorly. Further on, almost no information is published about the influence of temperature, etching agent and time on the etching rate.

In this work, porous carbons were prepared by CDC approach according to reactions (1) and (2) using porous TiC and TiC/TiO<sub>2</sub> structures produced from paper preforms by chemical vapor infiltration and reaction (CVI-R) technique [Ghanem].



It is important to point out that the formation of carbon on the surface is uniform and doesn't change the shape of initial TiC and TiC/TiO<sub>2</sub> ceramics allowing preparing structures with complex geometry and high mechanical stability. The idea is to use these structures as adsorbent, catalyst or catalyst support because of their easier separation from the reaction mixture. CDC coated TiC/TiO<sub>2</sub> porous ceramic is expected to show enhanced photo catalytic activity because of high specific surface area.

## Experimental

### Processing of biomorphic porous ceramics by CVI-R technique

Biomorphic porous TiC and TiC/TiO<sub>2</sub> ceramics derived from paper preforms were produced by chemical vapour infiltration and reaction (CVI-R) technique in a three-steps process according to the following schema (Figure 1). Details are given in [Ghanem, Popovska].

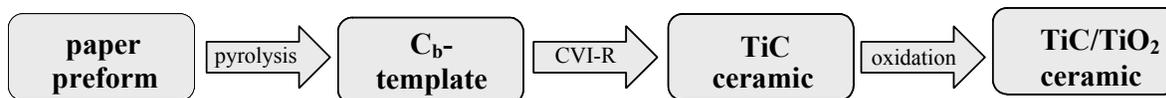
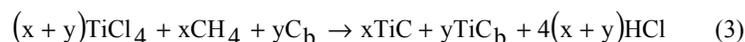


Figure 1. Overall scheme for production of porous TiC and TiC/TiO<sub>2</sub> ceramics

The paper preform consisting mainly of cellulose fibres was converted into carbon biotemplate (C<sub>b</sub>) by pyrolysis in inert atmosphere, followed by chemical vapour infiltration at 1100°C and atmospheric pressure with TiCl<sub>4</sub>/CH<sub>4</sub>/H<sub>2</sub> as precursor system according to the following equation [Popovska]:



The last processing step was oxidation of TiC in order to produce TiC/TiO<sub>2</sub> ceramics. The oxidation was conducted in air flow for 20 h at 400°C.

### Processing of carbide-derived carbon (CDC) by selective etching of TiC ceramics

The TiC ceramic was covered with carbon layer by selective etching in chlorine or chlorine/hydrogen gas mixtures at temperatures in the range 400 – 1000°C at atmospheric pressure. The gas mixtures consist of helium with 0.020 or 0.026 mol/h Cl<sub>2</sub> without or with addition of H<sub>2</sub> (Cl<sub>2</sub>/H<sub>2</sub>=4). The chlorination times vary between 20 minutes and 4 hours (Figure 2).

The TiC/TiO<sub>2</sub> mixed ceramic was treated with chlorine/hydrogen gas mixture for a short time of 10 minutes at low temperature of 400°C in order to obtain thin carbon layer retaining the catalytic active anatase modification of TiO<sub>2</sub> (Figure 2).

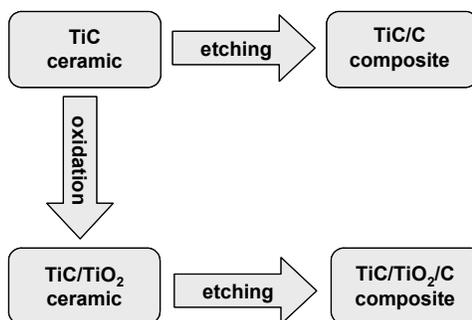


Figure 2. Processing scheme for CDC coated TiC and TiC/TiO<sub>2</sub> ceramics

The TiC samples were placed in the isothermal zone of a horizontal hot-wall tubular flow reactor operated at atmospheric pressure and heated up to the reaction temperature by 5 K/min under a helium flow. Once the desired temperature was reached, chlorine or chlorine/hydrogen gas mixture was passed through the alumina tube with 3.2 cm inner diameter and a heated length of 100 cm. After chlorination, the furnace was cooled down to room temperature in helium/hydrogen atmosphere. The etching rate was calculated as mass loss (mg) per unit time (h).

### Characterisation methods

The resulting carbon-ceramic composites (C-TiC and C-TiC/TiO<sub>2</sub>) were characterised by Raman Spectroscopy. Raman spectra from 100 to 2000 cm<sup>-1</sup> were collected using Raman spectrometer equipped with an Ar<sup>+</sup> laser (λ= 633 nm) at 50x magnification in order to investigate the structure of the carbon formed.

Gas sorption analysis was performed using a Gemini 2370 from Micromeritics GmbH with nitrogen as adsorbates at -195.8°C. It was used to calculate the specific surface area (SSA) and the pore volume. The porosity of the ceramics was determined by Hg-porosimetry with Carlo Erba Mercury Intrusion Porosimeter 2000.

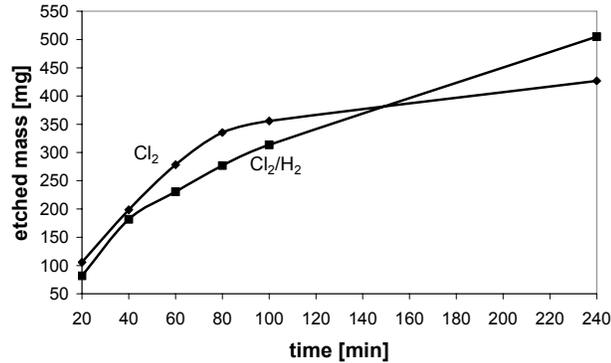
The morphology of the samples was investigated by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis (SEM/EDX, JSM-6400) to determine the composition of the surface layer.

## Results and discussion

### Parameter screening of the etching process of TiC ceramic

#### Kinetics of the chlorination of TiC

The kinetics of the chlorination process was investigated at 400°C and presented in Figure 3 plotting the etched mass as a function of reaction time for chlorine and chlorine/hydrogen as etching agent. According to the literature [Yushin, 2005b], the CDC layer thickness increased linear with the reaction time indicating no control by diffusion. Looking at the curves in Figure 3, it can be seen that it is the case only at etching times in the region up to 80 minutes, where the amount of etched titanium is nearly linearly increased from 106 mg in 20 minutes up to 336 mg in 80 minutes. At longer reaction time the process is limited by diffusion of the reactive gas through the formed carbon layer in order to react with TiC.

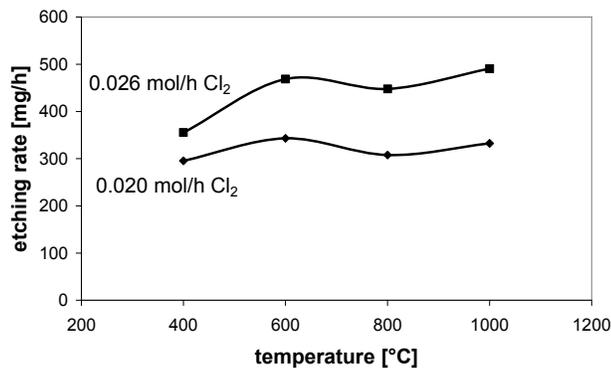


**Figure 3.** Kinetic curves of the etching reaction with chlorine and chlorine/hydrogen ( $\text{Cl}_2/\text{H}_2=4$ ) mixture at 400°C

Addition of small amount hydrogen to chlorine gas ( $\text{Cl}_2/\text{H}_2=4$ ) results in a 20 -25% lower etching rate due to the lower reactivity of the HCl as etching agent. The progression of the kinetic curve looks also different. No clear diffusion limitation seems to occur up to 240 minutes reaction time. Hydrogen enhances the diffusion of the chlorine molecules as described in the literature [Cambaz] and enlarges the specific surface area of the carbon formed. Thus, hydrogen addition can avoid diffusion limitation and it is useful especially at longer etching times to achieve high etching rate and CDC with high SSA.

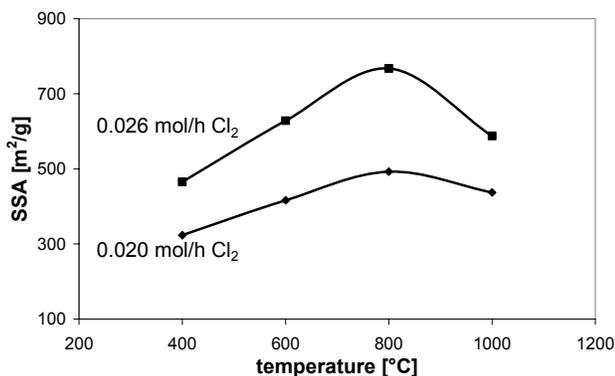
#### Effect of temperature and chlorine concentration on the etching rate of TiC and the SSA of the resulting CDC

The etching rate of TiC at different temperatures and chlorine concentrations is presented in Figure 4. Increasing the temperature up to 600°C leads to higher etching rates especially at higher chlorine concentration. However, in the range 600-1000°C almost no temperature dependence of the etching rate could be observed. Thus, the temperature has less effect on the etching process than chlorine concentration.



**Figure 4.** Etching rate of TiC at different temperatures and chlorine concentrations for 1h etching time

The effect of the etching conditions on the specific surface area (SSA) of the resulting CDC is shown in Figure 5. The curves show similar temperature dependence of the SSA, independent from the chlorine concentration used. In both cases SSA is linearly increased raising the reaction temperature up to 800°C, where a maximum value of SSA is achieved. A further increase of the temperature results in CDC with lower SSA due to changes in the microstructure as well as in the pore structure. Comparing Figure 4 and Figure 5 it can be concluded, that there is no correlation between etching rate of TiC and SSA of the resulting CDC.

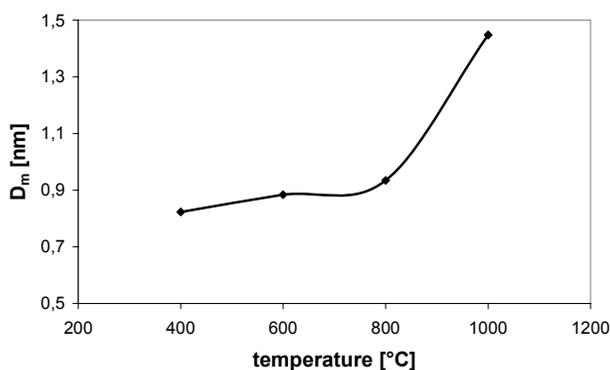


**Figure 5.** Specific surface area (SSA) of CDC obtained at different etching conditions for 1h etching time

### *Microstructure of CDC*

#### Pore structure

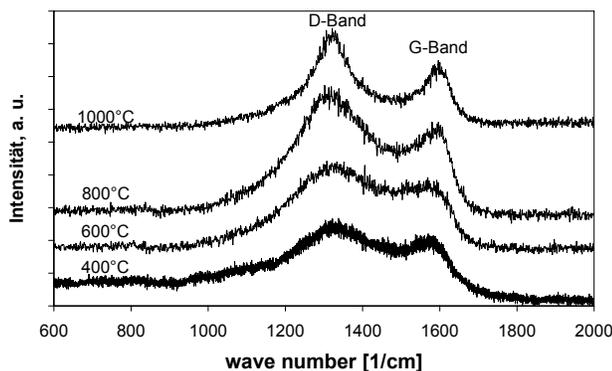
The pore structure of CDC derived from TiC at different reaction temperature in the range 400-1000°C was investigated by low temperature nitrogen adsorption. The adsorption isotherms of samples chlorinated at 400, 600 and 800°C are of type I of the Brunauer classifications [Webb], which is consistent with a microporous material with pore size less than 2 nm. The adsorption isotherm at 1000°C shows a hysteresis and therefore is of type IV in the same classification scheme, indicating presence of mesopores. The sample etched at low temperature shows narrow distribution, whereas broadening of the curves with the temperature was found. The mean diameter of the pores ( $D_m$ ) increases with increasing the chlorination temperature (Figure 6). The observed differences in the pore size are due to changes in the CDC microstructure increasing the reaction temperature.



**Figure 6.** Mean pore diameter for CDC obtained at different temperatures

#### Raman spectroscopy

The CDC structure was examined by Raman spectroscopy (Figure 7). The spectra show the two characteristic peaks for carbon- the D band at 1330 – 1342  $\text{cm}^{-1}$  and G band at 1585 – 1600  $\text{cm}^{-1}$ .

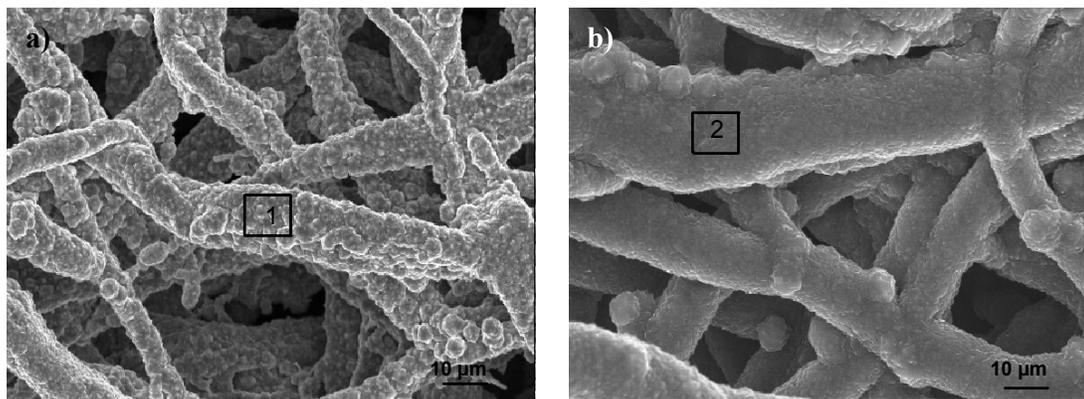


**Figure 7.** Raman spectra of samples chlorinated at different temperatures

A much higher intensity of disordered-induced D-band compared with G-band, corresponding to in plane vibration of carbon atoms in graphite, suggests in all cases a nanocrystalline and disordered structure of CDC. However, increasing the chlorination temperature results in a decrease of full width at half maximum (FWHM) of D- and G-band indicating a substantial increase of ordered carbon in particular above 800°C.

#### Morphology of CDC

The surface morphology of TiC-ceramics before and after chlorination at 600°C was investigated by Scanning electron microscopy (SEM) and presented in Figure 8.



**Figure 8.** SEM images of a) TiC ceramic and b) CDC-TiC ceramic

A difference in the fibre structure can easily be recognized. Whereas the TiC-fibres look quite irregularly in size and thickness, the CDC-TiC fibres seem to be bloated because of the porous structure. The element composition of the layer was estimated by EDX analysis at the marked positions in the images (Table 1).

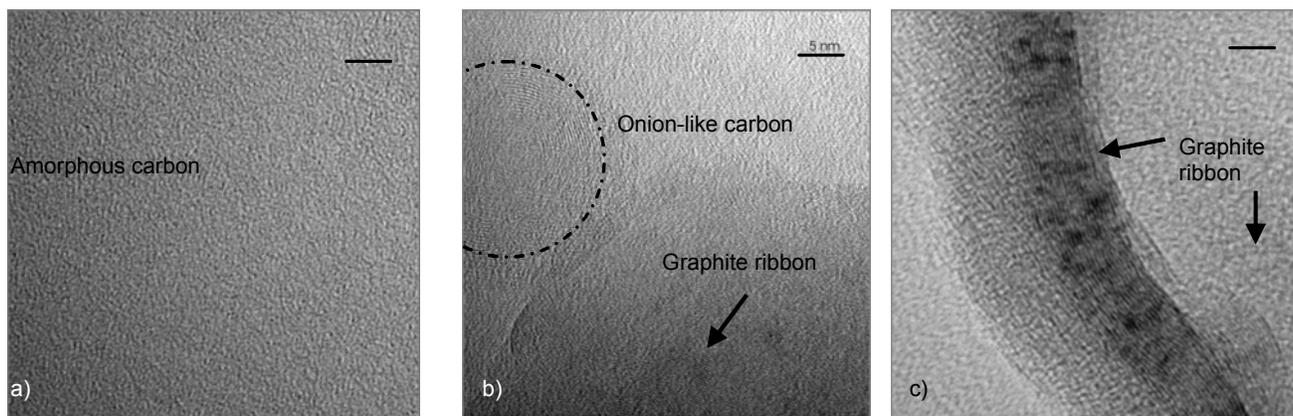
**Table 1.** EDX analysis of element composition of TiC (pos. 1) and CDC-TiC (pos.2)

at. %	pos. 1	pos. 2
<b>C</b>	58.5	94.5
<b>O</b>	-	2.7
<b>S</b>	-	0.8
<b>Ti</b>	41.5	2.0

After chlorination of the TiC samples the Ti content decreases from 41.5 to 2.0 at. % and they consist mainly of carbon. Oxygen and sulphur impurities were detected in small amount as well.

#### TEM

TEM studies of CDC-TiC reveal their microstructure at atomic scale. Whereas etching with chlorine at 400°C results in formation of mainly amorphous carbon (Figure 9a), chlorination at 600°C with chlorine/hydrogen gas mixture results in formation of more ordered carbon structures (Figure 9b). The main part consists of amorphous carbon but the addition of hydrogen to the reactive gas favours the formation of onion-like carbon. The TEM micrograph shows also some isolated sites of well-ordered graphitic sheets within amorphous carbon. Literature review confirms the formation of onion-like carbon but it is described for temperatures about 900°C in pure chlorine atmosphere [Zheng]. Admixture of hydrogen promotes the creation of better ordered structures such as onion-like carbon. A HRTEM micrograph of a sample treated at 1000°C shows a well-ordered graphitic ribbon within amorphous carbon (Figure 9c). The ribbon has a thickness of about 5 nm, which corresponds to 15 graphene layers. Curved graphitic structures were not found in this sample and no complete graphitisation is visible. This result agrees well with the results of Raman spectroscopy, where the D-peak is still better pronounced as the G-peak. All analyses suggest small improve of the grade of order of CDC with increasing reaction temperature.



**Figure 9.** HRTEM micrographs of CDC-TiC chlorinated for 1h at a) 400°C, b) 600°C and c) 1000°C

***Processing of carbon coated TiO<sub>2</sub> by selective etching of TiC/TiO<sub>2</sub> ceramics***

The CDC approach was also applied on the TiC/TiO<sub>2</sub> ceramics in order to generate carbon layers with high specific surface area. It is expected, that carbon coated TiO<sub>2</sub> will show enhanced photo catalytic activity as reported in the literature [Lettmann]. In previous work [Ghanem] the processing of biomorphic TiC/TiO<sub>2</sub> ceramics was studied in details. It was found, that the oxidation temperature of TiC affects the anatase/rutile ratio of the resulting TiO<sub>2</sub> samples. The catalytic more active anatase phase is formed at temperatures below 600°C. Therefore, the TiC/TiO<sub>2</sub> ceramics produced by oxidation of biomorphic TiC at 400°C in air flow [Ghanem] were etched for 10 minutes at 400°C in Cl<sub>2</sub>/H<sub>2</sub> mixture to produce a thin carbon layer within the TiO<sub>2</sub> surface. The amount of carbon is calculated to be 1.8 wt%. As a result, the specific surface area (SSA) of the resulting ceramic composite was increased significantly as shown in Table 2.

**Table 2.** Specific surface area (SSA) of biomorphic ceramics

Sample	TiC	TiC/TiO <sub>2</sub>	C-TiC/TiO <sub>2</sub>
SSA, m <sup>2</sup> /g	0.7	17.7	63.4

The CDC coated TiC/TiO<sub>2</sub> ceramics show enhanced photo catalytic activity by degradation of 4-chlorophenol (4-CP) under UV light due to the improved adsorption capacity. The results will be presented in a separate paper.

**Conclusions**

Biomorphic porous TiC and TiC/TiO<sub>2</sub> ceramics produced from paper preforms by chemical vapor infiltration and reaction (CVI-R) technique can be covered with highly porous carbon by selective etching of Ti from TiC with chlorine containing gas in a temperature range 400-1000°C.

The etching rate of TiC is affected by the chlorine concentration, but only slightly by the reaction temperature. Kinetic investigations have shown that up to 80 minutes the etching process is controlled by the chemical reaction. At longer treatment times diffusion limitation has to be taken into account. Addition of hydrogen to the etching gas enhances the diffusion of the chlorine molecules, so that no diffusion limitation was observed. Thus, hydrogen addition can avoid diffusion limitation and it is useful especially at longer etching times to achieve high etching rate and CDC with high SSA.

The pore structure of CDC can be tuned by the etching temperature. Microporous carbon with narrow pore size distribution was obtained at temperatures ranging from 400 to 800°C. Treatment at higher temperatures leads to formation of mesopores. No correlation was found between etching rate of TiC and specific surface area (SSA) of the resulting CDC.

The CDC produced by chlorination of TiC at 400°C is amorphous. Increased reaction temperature and addition of hydrogen to the chlorine gas lead to formation of higher ordered regions like onion carbon and graphitic ribbons as shown by Raman spectroscopy and TEM.

The CDC coated TiC/TiO<sub>2</sub> ceramics with predominantly anatase phase show enhanced photo catalytic activity due to the high SSA of 64 m<sup>2</sup>/g.

The produced carbon-ceramic composites are mechanically stable. These structures can be used as adsorbent, catalyst or catalyst support because of their easier separation from the reaction mixture.

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