

CARBON MODIFIED FIBROUS TiO₂ CERAMIC COMPOSITES WITH ENHANCED PHOTO CATALYTIC ACTIVITY

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Introduction

Biomorphic porous ceramics are a new class of materials, which combine low density with high strength and shape stability. These properties make them suitable for a wide range of technical applications, including catalyst supports, filters for molten metals or radiant burners. Titanium oxide (TiO₂) is a particularly versatile material for use as photo catalyst, photovoltaic material, gas sensor, and optical coating.

Biomorphic TiO₂ ceramic composites were produced by chemical vapor infiltration and reaction (CVI-R) technique using pyrolyzed paper preforms as templates. In order to improve the photo catalytic activity the amount of the anatase phase as well as the specific surface area of the composites has been enhanced by modification with carbon applying the carbide-derived carbon (CDC) approach.

Experimental

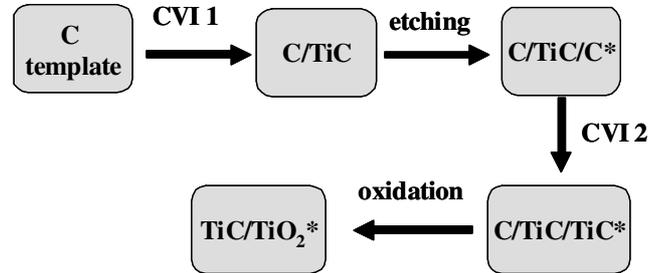
Biomorphic TiO₂ composite ceramics were produced from paper preforms by CVI-R technique (Fig. 1). First the paper was converted into carbon template by pyrolysis up to 800°C in inert gas atmosphere, followed by CVI with a precursor system consisting of TiCl₄, CH₄ and H₂ at 1150°C, depositing a TiC layer on the carbon fibers of the template [1]. The final step is a partial oxidation of the biomorphic TiC ceramics in the temperature range 400-1000°C to obtain TiO₂ composite ceramics with different crystalline microstructure.



Fig. 1. Flow chart of processing of biomorphic TiO₂ ceramic composites by CVI-R technique

The objective of this work was to enhance the SSA of the TiO₂ ceramic composites by integration of the CDC approach into the CVI-R technique as shown in Figure 2. In CDC (carbide derived carbon) the metal is removed selectively from the metal carbide lattice by chlorination at high temperature thus generating highly porous carbon on the surface. By CDC approach, the TiC ceramic was firstly exposed to chlorine containing atmosphere at elevated temperatures for different reaction times up to 1h (eq. 2), where TiC/C* composite ceramics with high SSA up to 460 m²/g have been obtained compared to the 0.74 m²/g of the initial TiC. Then by further infiltration step via CVI 2 using TiCl₄/H₂ system at 1100°C (Eq. 3), the

C* from the etching process reacts with the decomposed Ti forming highly porous TiC/TiC* or TiC/C*/TiC* composites. Finally an oxidation step in air flow at 400°C for 10 hours leads to TiO₂ composite ceramics with high SSA (TiO₂*).

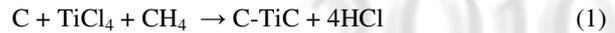


C*: carbon with enhanced SSA

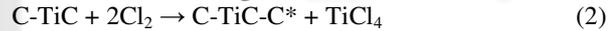
TiO₂*: titanium oxide with enhanced SSA

Fig. 2. Processing of biomorphic TiO₂ by integrated CDC approach (etching)

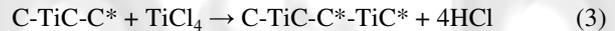
CVI 1



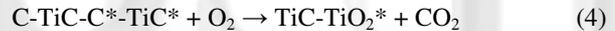
Chlorination (etching)



CVI 2



Oxidation



The produced TiO₂ composite ceramics were investigated by Raman Spectroscopy to verify the presence of anatase and rutile phase as well as non-reacted free CDC. The ratio of anatase to rutile phase (A/R) in the samples was calculated using the following relation [2]:

$$A / R = I_{141} / I_{440} \quad (5)$$

whith

I₁₄₁: Intensity of the anatase peak at 141 cm⁻¹

I₄₄₀: Intensity of the rutile peak at 440 cm⁻¹

The morphology and the composition of the TiO₂ ceramic composites 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.

Results and Discussion

The oxidation temperature has a strong influence on the phase structure of the TiO₂ ceramics. Temperature as low as 400°C leads to formation of high amount of anatase as can be

seen in Fig. 3. Moreover, it is clearly to be seen that A/R ratio is much higher using combined CDC/CVI-R approaches compared to CVI-R alone, which proves that the presence of carbon stabilizes the anatase phase. However, no significant change of the A/R ratio was observed at 800°C where the rutile form of TiO₂ is predominantly produced.

The effect of the oxidation temperature on the SSA of TiO₂ composites is similar to that on the A/R ratio. Specific surface area up to 101 m²/g and 40 m²/g was achieved for samples prepared by CDC/CVI-R and CVI-R, respectively. This makes CDC combined with CVI-R a promising technique to enhance the specific surface areas of both TiC and TiO₂. The SEM micrographs (Fig. 4) show a shape stability of the produced TiO₂ ceramic composites.

In order to prove the stabilizing effect of free carbon on the anatase phase, two biomorphic TiC ceramic samples were chlorinated under the same conditions, followed by CVI 2 for 45 min and 90 min respectively, using TiCl₄/H₂ precursor (Eq. 3) to produce TiC/C*/TiC* composites with different amount of free C* (Tab. 1). Subsequently, the samples* were oxidized in airflow at 400°C for 10 hours to obtain TiO₂. The Raman spectra of the samples exhibited A/R ratio of 5 and 3.5, respectively. Additionally, the amount of residual non-reacted carbon after CVI 2 step was calculated to be 17 % and 0 % for TiC/C₄₅*/TiC* and TiC/C₉₀*/TiC* (Tab. 1). The free carbon in the TiO₂ sample obtained after CVI 2 of 45 min was responsible for the enhanced A/R ratio of 5 compared to 3.5 where no free carbon was available.

The photo catalytic activity of biomorphic TiO₂ ceramic composites obtained by different processing routes (Fig. 1 and Fig. 2) was evaluated by measuring the degradation kinetics of 4-chlorophenol (4-CP) by irradiation with UV light. The sample, which was modified by CDC approach, shows much higher rate constant of the photo degradation reaction due to the enhanced amount of anatase phase and high SSA (Tab. 2).

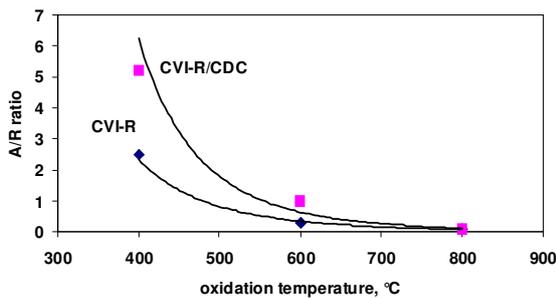


Fig. 3 A/R ratio of TiO₂ obtained by oxidation of TiC (CVI-R) and TiC/C*/TiC* (CDC/CVI-R) as a function of the oxidation temperature in airflow for 10h

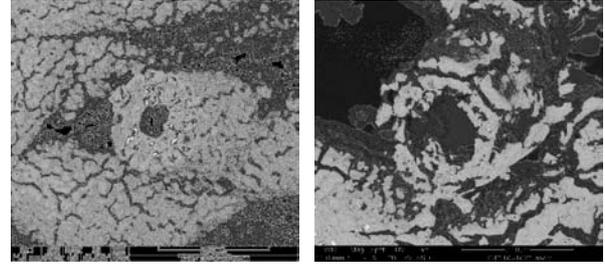


Fig. 4 Morphology of TiO₂ composites obtained by oxidation of TiC (CVI-R) and TiC/C*/TiC* (CDC/CVI-R) in airflow at 400°C for 10h

Table 1: Effect of the carbon content in the TiC/C*/TiC* on the properties of the corresponding TiO₂ ceramics

Items	TiC/C*/TiO ₂ * CVI 2: 45 min	TiC/TiO ₂ * CVI 2: 90 min
non reacted CDC after CVI 2 [%]	17	0
conversion of TiC to TiO ₂ [%]	30	67
Anatase/Rutile	5.0	3.5
SSA [m ² /g]	43	77

Table 2. Pseudo-first order rate constant of degradation of 4-CP, SSA and catalyst loading of TiO₂ obtained by different routes

Typ of TiO ₂	k [hr ⁻¹]	SSA [m ² /g]	Catalyst loading [mg/m ²]
CVI-R	0.09	40	213
CVI-R/CDC	0.70	101	443

Conclusions

Biomorphic TiO₂ ceramics were modified with carbon by integrating the CDC approach into the conventional CVI-R technique. Free carbon stabilizes the anatase phase leading to high A/R ratio and high SSA. The result is enhanced photo catalytic activity compared to TiO₂ ceramics obtained by the conventional CVI-R technique.

References

- [1] Popovska, N., Almeida Streitwieser, D., Chen Xu, Gerhard H. Paper Derived Biomorphic Porous Titanium Carbide and Titanium Oxide Ceramics Produced by Chemical Vapor infiltration and Reaction (CVI-R). J. Eur. Ceram. Soc. 2005; 25(6): 829-836.
- [2] Reinaldo J., Raman, Infrared, X-ray and EELS studies of Nanophase Titania, Dissertation, Blacksburg, Virginia Polytechnique Institute and State University, 1996.