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Processing of porous TiO_2-ceramics from biological preforms

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Abstract

The manufacturing of porous TiO_2-ceramics with cellular morphology from biological preforms via sol–gel processing was investigated. Biological materials such as cellulose fiber felts, naturally grown wood as well as corrugated cardboard structures were vacuum infiltrated with a low viscous titania sol, which was prepared from titanium isopropoxide and modified with acetic acid. Pyrolysis in inert atmosphere at 800 °C and subsequent annealing in air resulted in the formation of highly porous, biomorphic TiO_2-ceramics with designed micromorphology. The microstructure and phase formation during processing as well as of the final material were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), density, and porosimetry measurements.

Keywords: Biotemplating; Porous TiO_2-ceramics; Sol–gel processing; Biomorphic ceramics

1. Introduction

Biotemplating of naturally grown preforms into ceramic structures represents an innovative technology for processing of microstructurally designed materials for technical and medical applications. In general, two different approaches have been applied to convert the biological preforms into non-oxide (transformation) as well as oxide (substitution) ceramics. In the transformation process, biological preforms were pyrolysed to yield porous carbon templates which were subsequently reacted with metal containing infiltrants to form carbide phases by melt, or vapor infiltration [1–4]. In the substitution process, native or pyrolysed biological preforms were internally coated with salts or metal organic precursors and subjected to oxidation to remove the carbon afterwards [5–8].

Porous TiO_2-ceramics are of interest due to the photocatalytic and bioactive properties of TiO_2. Imhof and Pine [9] reported the fabrication of TiO_2-foams via a sol–gel process. Haugen et al. [10] produced TiO_2-foams with fully open structure and more than 78% porosity by the polymer sponge method. TiO_2-fibers could be prepared by infiltration of natural sisal, jute, and hemp fibers with $TiCl_4$ following heat treatment in air [5]. Ota et al. [6] reported the manufacturing of biomorphic TiO_2-ceramics by infiltration of wood with titanium isopropoxide (TTiP, $Ti[OCH(CH_3)_2]_4$). Huang and Kunitake [11] synthesized TiO_2-fibers from filter paper by a surface sol–gel process. In our own work, biomorphic TiO_2-ceramics were prepared from rattan plants by sol–gel processing [8].

In this paper, a low viscous, stable TiO_2-sol was developed to produce porous TiO_2-ceramics, isomorphous to the initial native performs. The templates were derived from different kinds of biological preform (cellulose fiber felts, pine wood, rattan plant as well as corrugated cardboard structures). The infiltration behavior, ceramic phase formation, and microstructure development during processing will be reported.

2. Experimental

Specimens of cellulose fiber felts, native pine, and rattan and commercially available corrugated cardboards were dried (70 °C/24 h) and subjected to vacuum infiltration for 30 min with a low viscous TiO_2-sol. For preparation of the TiO_2-sol, TTiP ($Ti[OCH(CH_3)_2]_4$, 97+%, Alfa Aesar, Karlsruhe, Germany) was modified with acetic acid (CH_3COOH, 99%, Alfa Aesar) at the molar ratio of 1:8. A stable TiO_2-sol with a concentration of 1 M was obtained by hydrolysis the mixture with distilled water. Details of the TiO_2-sol preparation are described in previous work [8]. The gelation time

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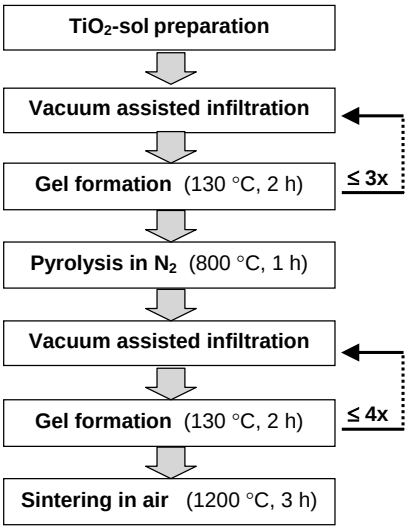

Fig. 1. Flow chart for the manufacturing of biomorphic TiO_2-ceramics from biological preforms.

of the sol was more than 12 days. The viscosity of the sol at room temperature was 14.5 ± 0.05 mPa s.

The TiO_2-sol infiltrated specimens were dried in air at 130 °C for 2 h to form a TiO_2-gel in situ. For the native pine and rattan specimens, this infiltration-and-drying procedure was repeated up to three times in order to increase the infiltrant content in the native samples. After the infiltration, the samples were pyrolysed at 800 °C for 1 h in N_2 atmosphere. At this temperature, the biopolymers of pine and rattan (cellulose, hemicellulose, and lignin) were decomposed, leaving a porous carbon char of about 25 wt.% of the initial wood preform. Further infiltration steps were performed into the porous char templates to increase the TiO_2-content in the specimen. Subsequently, the specimens were annealed in air up to 1200 °C for 1 h to remove the carbon template by oxidation and to increase the density of the TiO_2-struts by sintering. The cellulose fiber felts and cardboard specimens were directly annealed up to 1200 °C in air for 1 h after TiO_2-sol infiltration. The generic processing route to produce biomorphic TiO_2-ceramics is summarized in Fig. 1.

The phase formation during processing was identified by X-ray diffraction (XRD, D 500, Siemens, Karlsruhe, Germany). The microstructure of the highly porous, TiO_2-ceramics was observed by scanning electron microscopy (SEM, Phillips XL 30). Skeleton density was determined by He-pycnometry (Accu Pyk 1330, Micromeritics, Düsseldorf, Germany) and high-pressure Hg-porosimetry (Hg-porosimeter 2000, Carlo Erba Instruments, Milano, Italy).

3. Results and discussion

After three vacuum-infiltration and drying steps of the TiO_2-sol into the native pine wood and rattan preforms the weight remained constant for both specimens. The weight gain was 53 wt.% for pine and 41 wt.% for the rattan specimen. Due to the more open porosity of the pine wood compared to the rattan, the weight gain for the pine specimens was found to be slightly higher (about 12 wt.%). After pyrolysis at 800 °C in N_2 atmosphere, further TiO_2-sol infiltration yielded an additional weight gain of 27 wt.% for pine and 18 wt.% for rattan.

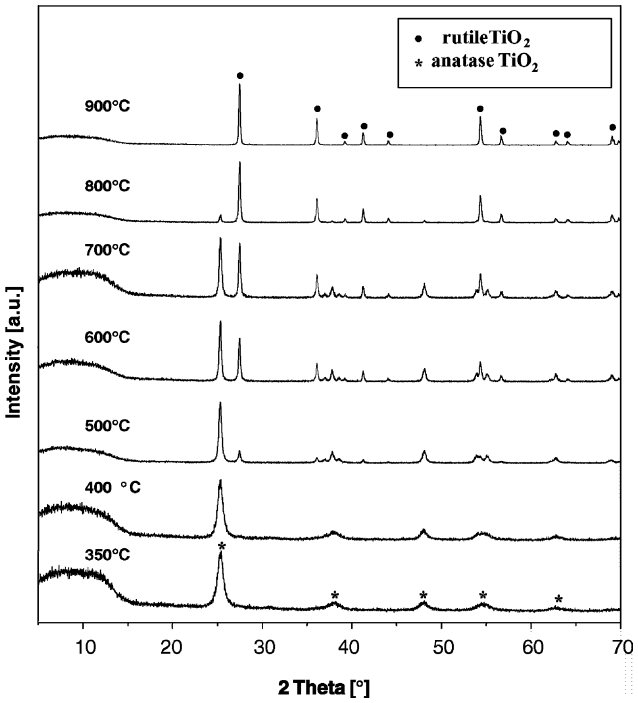

Fig. 2. XRD patterns of the titania sol infiltrated cellulose fiber specimens annealed at various temperatures in air.

The specimens of cellulose fiber felts and cardboard were infiltrated one and seven times, respectively. The final weight gain relative to the biological preforms was about 60 wt.% for the cellulose fiber specimen and about 140 wt.% for the cardboard specimen.

The TiO_2-phase formation during heat treatment in air was monitored by XRD analysis of the cellulose fiber specimens between 350 to 900 °C (Fig. 2). Anatase is observed to be formed after heating up to 350 °C. The phase transformation from anatase to rutile started at 500 °C and was completed at 900 °C. Due to small impurities of Ca and K in the biological preforms (ash contents of CaO and K_2O were determined to be less than 0.1 wt.% of the initial pine wood weight), a small amount of $CaTiO_3$ and $K_2Ti_6O_{13}$ were detected in the biomorphic TiO_2-ceramics derived from pine, rattan and cardboard.

Fig. 3 shows SEM micrographs of biomorphic TiO_2-ceramics derived from pine, rattan, cellulose fiber felts, and cardboard. As can be seen, all of the feature of the initial cellular anatomy of the biological preforms were well reproduced in the TiO_2-reaction product after sintering at 1200 °C for 1 h. Few lumps of TiO_2 were observed in the vessels,

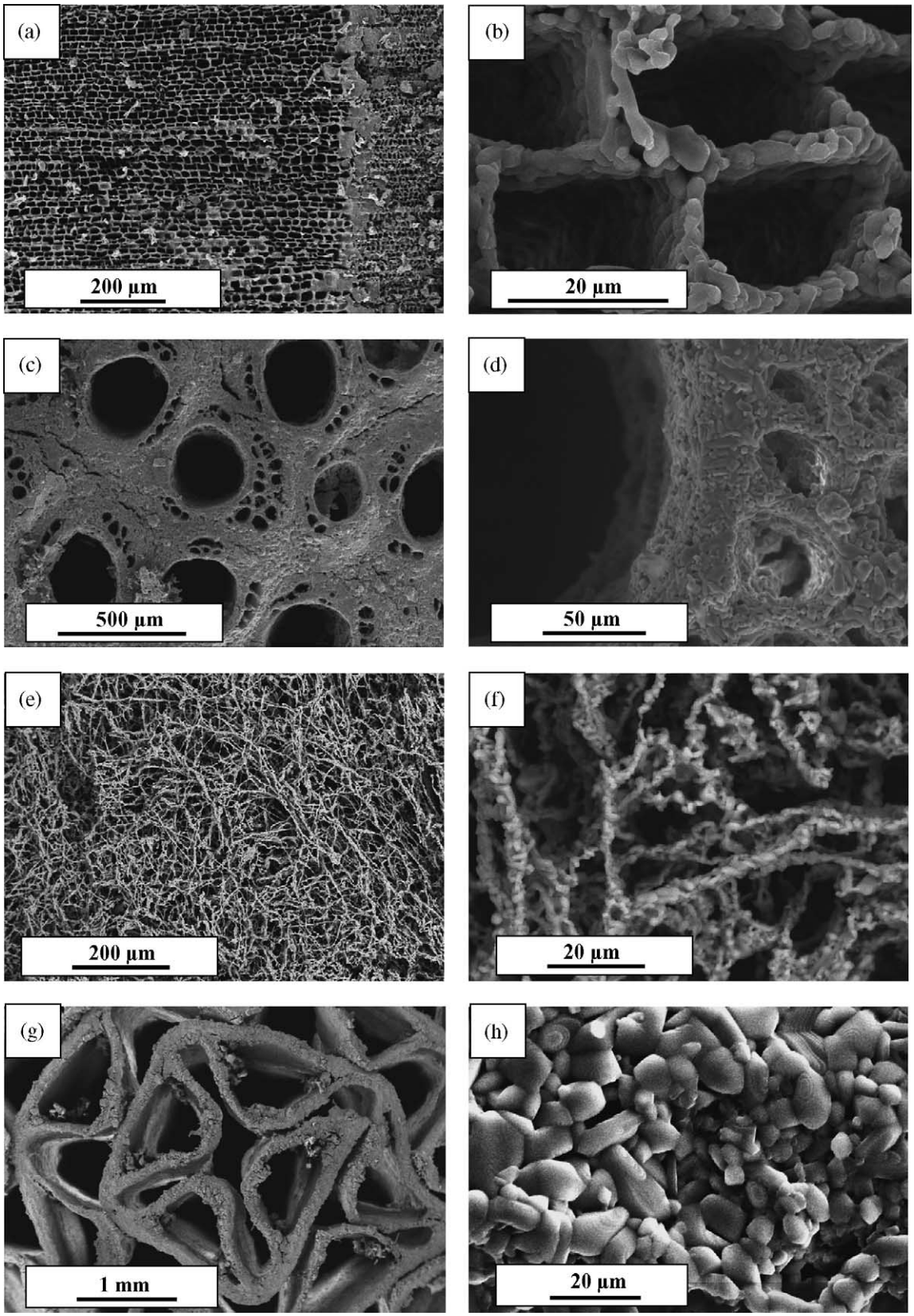

Fig. 3. SEM micrographs of biomorphic TiO_2-ceramics derived from (a and b) rattan, (c and d) pine, (e and f) cellulose fiber felts, and (g and h) cardboard after sintering at 1200 °C/1 h in air, axial section.

Table 1
Physical properties of the native and sintered rattan, pine, cellulose fiber, and cardboard specimens

	Rattan		Pine		Cellulose fiber		Cardboard	
	Native	Sintered	Native	Sintered	Native	Sintered	Native	Sintered
Geometrical density (g/cm^3)	0.5	0.45	0.54	0.86	0.30	0.79	0.22	0.85
Skeleton density (g/cm^3)	1.3	4.25	1.4	4.26	1.62	4.26	1.68	4.01
Relative density (%)	0.38	0.11	0.39	0.20	0.19	0.19	0.13	0.21
Total porosity (%)	62	89	61	80	81	81	0.87	79

most of the vessels remained open after the conversion into TiO_2-ceramic. The cell diameter in the earlywood region is about 20 μm, and about 5 μm in the latewood region. The size of TiO_2-grains is about 5 μm.

The biomorphic TiO_2-ceramic derived from rattan exhibits a homogeneous microstructure in which large pores of about 200–300 μm are surrounded by smaller pores of about 50 μm (Fig. 3b–d). Some cracks on the cell walls were formed during drying, pyrolysis, and annealing processes. While the large vessels remain open, the smaller pores are fully or partially closed with TiO_2-grains. The distances between the large vessels and the pore diameters were reduced due to the large shrinkage of 49%.

Similar results were obtained from the cellulose fiber and cardboard specimens. After burn out of the biological preforms during the sintering process, the microcellular fiber structure (Fig. 3e and f) as well as macrostructures of cardboard specimen (Fig. 3g and h) is retained. Due to the higher content of impurities, the grain size of TiO_2-cardboard is about 10 μm, while it is only 1–2 μm in the TiO_2-fiber specimen.

Table 1 summarizes the results of the density and porosity measurements of the biomorphic TiO_2-ceramics. The porosities were derived from the differences between the skeleton and geometrical densities measured by He-pycnometry. The rattan derived TiO_2-ceramic shows a higher geometrical porosity compared to the pine samples, due to the smaller weight gain during TiO_2-sol infiltration. The skeleton densities of the rattan and pine derived TiO_2-ceramics are close to the theoretical density of TiO_2 (4.26 g/cm^3), indicating only small amounts of residual porosity. On the contrary, the cardboard specimen shows lower density due to the impurity phases as well as a higher formation of closed pores.

4. Summary

Biological materials can be used as structural preforms for processing of highly porous biomorphic TiO_2-ceramics. Infiltration of the biological preforms with a stable TiO_2-sol and subsequent heat treatment in air offers a simple processing scheme for manufacturing of biomorphic TiO_2. Depending on the preform porosities as well as on the processing parameters, porosity and pore morphology of the TiO_2 can be designed. An unidirected pore morphology, high surface area, high-temperature stability, low weight and low thermal conductivity make biomorphic TiO_2 an interesting candidate for applications as filters, catalyst, and photocatalyst materials, as well as medical implant structures.

Acknowledgements

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