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Ceramics International 30 (2004) 1967–1970

CERAMICS INTERNATIONAL

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Manufacturing of microcellular, biomorphous oxide ceramics from native pine wood

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Received 1 December 2003; received in revised form 10 December 2003; accepted 23 December 2003

Abstract

Pine wood was vacuum infiltrated with different low viscous alumina-, titania- and zirconia-sol. Subsequent pyrolysis in inert atmosphere at 800 °C and annealing in air up to 1550 °C resulted in the formation of porous, microcellular α-Al_2O_3, TiO_2 (rutile) and c-ZrO_2 (stabilized by 8 mol% Y_2O_3), respectively. The conversion process retained the microcellular anatomy of the initial pine wood. An anisotropic shrinkage during pyrolysis and annealing was observed for all samples. While after processing the small pores ($<1\ \mu m$) in the wood cell walls were vanished, the large pore channels—represented the earlywood and latewood tracheidal vessels—remained in the oxide ceramics and yielded an unidirected porous morphology on the micron level.

Keywords: D. Alumina; D. Titania; D. Zirconia; Biotemplating; Pine wood; Porous oxide ceramics

1. Introduction

Converting biological structures into ceramic materials has recently received increasing interest. While in biological growth and mineralization processes only very slow material synthesis rates occur, biotemplating techniques, in which biological materials are used directly as template structures for high-temperature conversion into technical ceramic materials, overcome this time rate problem [1]. The inherent open porosity in the natural plant structures is accessible for gaseous or liquid infiltration and subsequent high-temperature ceramic phase formation.

Previous work on biotemplating was focused mainly on the preparation of biomorphous carbide ceramics, e.g. SiC via a reaction of the biological material derived biocarbon with different Si-infiltrants such as Si-melt, Si/SiO-gas, Si-containing polymers as well as SiO_2-sols [2–6]. Several investigations have been also focused on the synthesis of biomorphous oxide ceramics. Yermolenko et al. [7] prepared Al_2O_3- and ZrO_2-fibers by oxidizing hydrated cellulose fibers impregnated with solutions of aluminum chloride and zirconium chloride. Patel and Padhi [8,9] manufactured Al_2O_3- and TiO_2-fibers by infiltration of natural sisal, jute and hemp fibers with $AlCl_3$ and $TiCl_4$, respectively. Ota et al. [10] produced biomorphous oxide ceramics by infiltration of wood materials with metal alkoxide, e.g. TTiP (titanium isopropoxide). After high-temperature treatment in air the wood structures were converted into porous TiO_2-ceramics. Shin et al. [11] synthesized hierarchical porous SiO_2-ceramics from wood by a surfactant-templated sol–gel process. In our own work, biomorphic Al_2O_3-, TiO_2-, ZrO_2- and mullite ($Al_6Si_2O_{13}$)-ceramics were prepared from rattan plants via a sol–gel process [12,13].

The present work deals with the manufacturing of biomorphous Al_2O_3-, TiO_2- and ZrO_2-ceramics from pine wood as biological template structure. Pine (*Pinus sylvestris*) is a coniferous wood with a nearly monomodal pore distribution and a mean pore diameter of about 20 μm. The macrostructure of the pine wood is characterized by the annual growth ring pattern with rings of a few millimetres in radial direction, formed from the earlywood and latewood regions. A sol–gel infiltration process of low viscous oxide precursors into pine wood was applied. After burn out of the biological preforms during sintering process, porous oxide ceramics, were obtained, which maintained the morphology of the pine wood.

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doi:10.1016/j.ceramint.2003.12.181

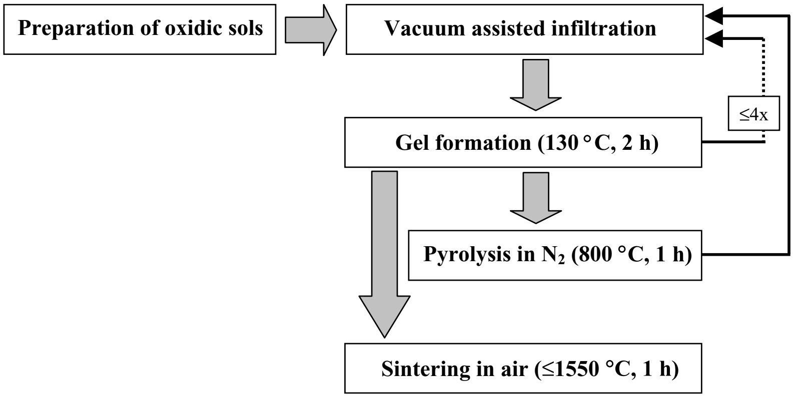

Fig. 1. Processing scheme for the manufacturing of microcellular, biomorphous oxide ceramics.

2. Experimental procedure

Low viscous, stable oxide sols were prepared for the infiltration process. The properties of the different sols (concentration, viscosity) were adjusted for an optimized infiltration behavior into the pine wood preform. The gelation time was never less than 7 days. More details of the sol preparation procedure are described in previous work [10,11].

For preparation of the alumina sol, aluminum *iso*-propoxide ($Al[OCH(CH_3)_2]_3$, ≥98%, Alfa Aesar, Karlsruhe, Germany) was hydrolyzed in distilled H_2O and peptized with HNO_3. Titania sol was obtained by modification of titanium *iso*-propoxide (TTiP, $Ti[OCH(CH_3)_2]_4$, 97%, Alfa Aesar) with acetic acid (HOAc, 96%, Alfa Aesar) and subsequent hydrolysis in distilled H_2O. Zirconia sol was obtained from zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, 99.9%, Alfa Aesar). For stabilization of the cubic ZrO_2-phase, 8 mol% yttrium nitrate ($Y(NO_3)_3 \cdot 6H_2O$, 99.9%, Alfa Aesar) was added.

Cylindrical samples of 25 mm in diameter and 5 mm in thickness were cut perpendicular to the native pine wood axis. The samples were dried at 70 °C for 24 h, and subsequently vacuum infiltrated with the different sols. The infiltrated samples were dried in air at 130 °C for 2 h to form oxide gels in situ. This procedure was repeated up to three times to increase the precursor content in the native pine samples (first infiltration process). After infiltration, the samples were pyrolyzed at 800 °C for 1 h in N_2-atmosphere. At this temperature the biopolymers (cellulose, hemicellulose and lignin) of pine wood were decomposed, leaving a porous carbon char of about 25 wt.% of the initial pine wood. Further infiltration/drying steps were performed with the porous char templates (second infiltration process). Finally the samples were annealed in air to remove the carbon template by oxidation and to increase the density of the Al_2O_3-, TiO_2- as well as ZrO_2-struts by sintering. The sintering temperatures of Al_2O_3-, TiO_2- and ZrO_2-samples are 1550, 1200 and 1500 °C for 1 h, respectively. The processing scheme is summarized in Fig. 1.

The microstructure of the Al_2O_3-, TiO_2- and ZrO_2-ceramics and the phase formation during processing were examined by X-ray diffraction (XRD, D 500, Siemens, Karlsruhe,

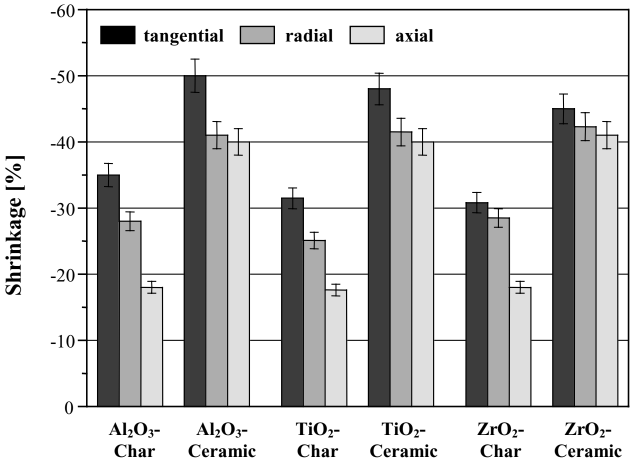

Fig. 2. Shrinkage of the pine wood samples infiltrated with alumina, titania or zirconia sol after pyrolysis (800 °C/1 h, N_2) and sintering (up to 1550 °C/1 h, air) in axial, radial and tangential directions.

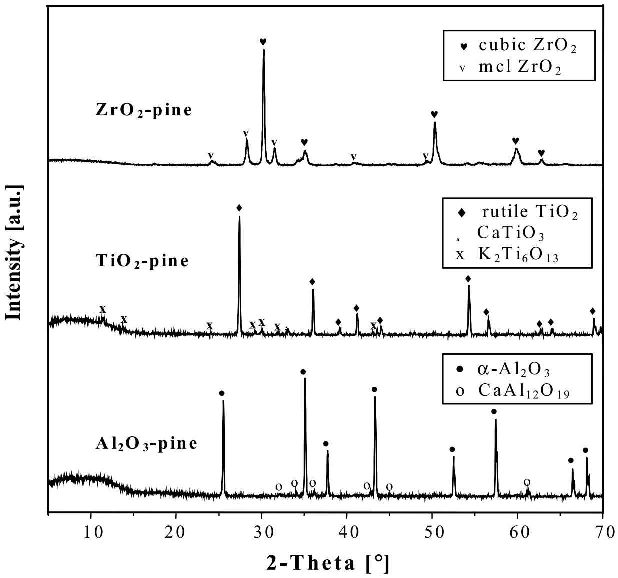

Fig. 3. XRD patterns of the biomorphous Al_2O_3-, TiO_2- and ZrO_2-ceramics derived from pine wood after annealing at 1550, 1200 and 1500 °C for 1 h in air, respectively.

Germany) and scanning electron microscopy (SEM, Phillips XL 30). Skeleton density was determined by He-pycnometry (Accu Pyk 1330, Micromeritics, Düsseldorf, Germany).

3. Results and discussion

Due to the decomposition of the biopolymers in the pine wood during pyrolysis and the burn out of the carbon during sintering, large shrinkages have been found in all samples. The shrinkage exhibited an anisotropic behavior for all samples. In the tangential direction of the alumina sol infiltrated pine samples, the shrinkage after pyrolysis was about 35%. After sintering in air, the shrinkage increased to 50%. For the radial and axial direction, the shrinkages were 28 and 18% after pyrolysis, 41 and 40% after sintering, respectively. Similar results have been obtained in the titania sol as well as zirconia sol infiltrated pine samples (Fig. 2).

After sintering, the infiltrated pine samples were converted into biomorphous Al_2O_3-, TiO_2- and ZrO_2-ceramics. Fig. 3 illustrates the XRD pattern of the biomorphous oxide ceramics. The main crystalline phases are α-Al_2O_3, rutile TiO_2 and cubic ZrO_2 (stabilized by Y_2O_3 with a trace of monoclinic ZrO_2). Due to impurities of Ca and K in the pine wood, a small amount of $CaAl_{12}O_{19}$, $CaTiO_3$, $K_2Ti_6O_{13}$ and $Ca_{0.2}Zr_{0.8}O_{1.8}$ (coincides with the pattern of cubic ZrO_2) were detected in the biomorphous oxide ceramics.

Fig. 4 shows the cellular microstructure of the biomorphous oxide ceramics derived from pine wood in axial direction. As may be seen, the initial cellular anatomy was

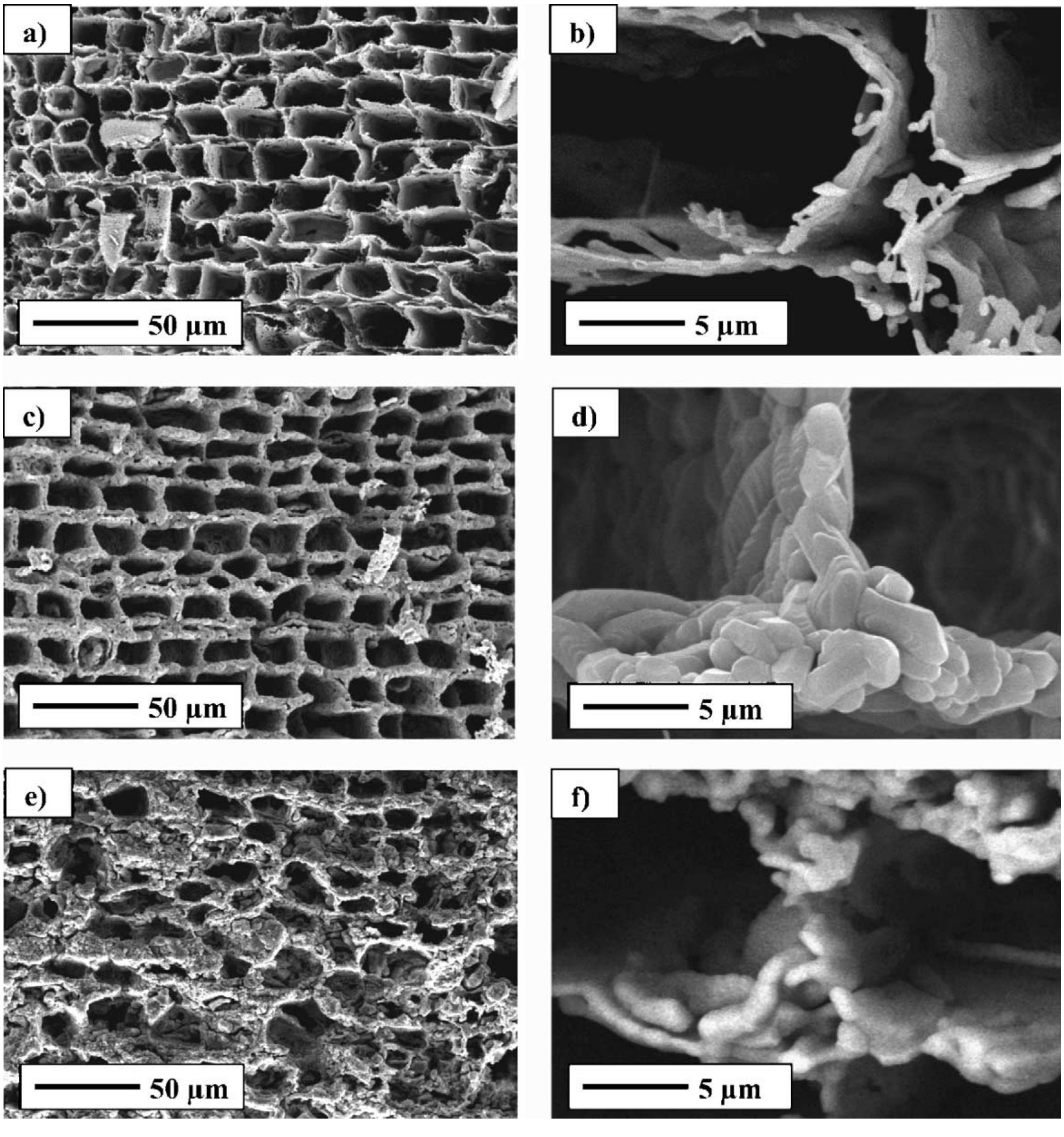

Fig. 4. SEM micrographs of biomorphic oxide ceramics from pine wood after sintering at different temperatures in air: (a, b) Al_2O_3-pine (1550 °C/1 h), (c, d) TiO_2-pine (1200 °C/1 h), and (e, f) ZrO_2-pine (1500 °C/1 h).

Table 1
Materials properties of the biomorphic oxide ceramics derived from pine wood

	Ceramic phase	Density (g/cm^3)		Porosity (%)
		Geometrical	Skeleton	
Al_2O_3	α-Al_2O_3	0.22	3.93	94
TiO_2	Rutile TiO_2	0.86	4.26	80
ZrO_2	Cubic ZrO_2	1.11	5.81	81

reproduced in the ceramic products. In the biomorphous Al_2O_3-ceramics, the carbon burn out of pine wood cell walls left only small holes in the earlywood regions. Due to the smaller cell diameter and thicker cell walls in the earlywood region, the morphology is characterized by a hollow fiber structure, separated by voids of up to 5 μm (Fig. 4a and b). In contrast to Al_2O_3 samples, the cell walls of pine wood were replaced by dense layers of TiO_2 in the biomorphous TiO_2-ceramics. Most of the vessels are kept open after ceramic conversion (Fig. 4c and d). The microstructure of biomorphous ZrO_2-ceramics appears similar to that of biomorphous Al_2O_3- and TiO_2-ceramics (Fig. 4e and f). The size of the Al_2O_3-, TiO_2- or ZrO_2-grains is about 3–5 μm.

Table 1 shows the material properties of the biomorphous oxide ceramics. The porosity was calculated from the differences between the geometrical and skeleton densities measured by He-pycnometry. The skeleton density of biomorphous Al_2O_3- and TiO_2-ceramics are very close to the theoretical density of Al_2O_3 (3.97 g/cm^3) and TiO_2 (4.26 g/cm^3), respectively, indicating only small amount of closed porosity. Due the content of monoclinic ZrO_2 (theoretical density 5.68 g/cm^3) and impurities, the skeleton density of the biomorphous ZrO_2 is only 5.81 g/cm^3 (theoretical density: 6.7 g/cm^3).

4. Summary

Infiltration of pine wood preform with low viscous oxidic sols such as Al_2O_3-, TiO_2- and ZrO_2-sols offers a versatile method to manufacture novel oxide ceramics with a unique unidirected microcellular microstructure. Depending on the infiltrated wood specimen as well as on the processing parameters, the porosity and the pore morphology can be designed. The anisotropic properties of the biomorphous oxide ceramics may be interesting for application as heat insulation structures, filters and catalyst carriers in high-temperature processes as well as for medical implant structures.

Acknowledgements

The financial support from the Volkswagen Foundation under contract I/73 043 is gratefully acknowledged. C.R. Rambo also thanks the CAPES Foundation, Brazil for the scholarship.

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