1. Introduction

The development of highly porous ceramics with a cellular porosity has attracted increasing interest in the recent years. Due to their specific properties such as high surface area, high permeability, high-temperature stability, low weight and low thermal conductivity, porous ceramics are being investigated for a variety of applications including filters for molten metals and hot gases, light-weight structural components, electrodes, sensors, bioreactors, catalyst carriers, radiant burners as well as porous implants in the area of biomaterials [Gib/88, Mai/01].

In general, porous ceramics can be divided into two categories: reticulate ceramics and foam ceramics [Sag/92]. A reticulate ceramic consists of interconnected voids surrounded by a web of ceramic struts and is usually fabricated by infiltration and replication of a polymeric sponge preform. Infiltration of a ceramic slurry and sintering yields an open porous ceramic structure, characterized often by a hollow strut due to the burn out of the preform. A foam ceramic consists of closed and open pores within a continuous ceramic matrix and is usually made by foaming processes applying foaming agents [Col/02] or by powder consolidation using fugitive organic additives as pore formers [Lyc/98]. Both types of porous ceramics exhibit a nearly isotropic pore morphology but differ in the porosity, the size and shape of the pores and the permeability. Due to the larger pore size as well as the fully open pore structure, the permeability is usually high in reticulate ceramics and low in open/closed pore foam ceramics.

More recently, many efforts have been applied on converting biological structures into porous ceramic materials. 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 [Ota/95, Gre1/98, Gre1/01]. The inherent open porosity in the natural plant structures is accessible for gaseous or liquid infiltration and subsequent high-temperature ceramic phase formation. This technology offers a possibility to use the large variety of nature developments to produce microcellular ceramics, which are so far difficult to manufacture by conventional techniques.

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 [Gre2/98, Sie1/00, Vog/01, Zol/02, Vog2/02]. Several investigations have been also focused on the synthesis of biomorphous oxide ceramics. Yermolenko et al. [Yer/86] prepared Al_2O_3- and ZrO_2-fibers by oxidizing hydrated cellulose fibers impregnated with solutions of aluminum chloride and zirconium chloride. Padel and Padhi [Pat/90, Pat/93] 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. [Ota/00] 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. [Shi/01] synthesized hierarchical porous SiO_2-ceramics from wood by a surfactant-templated sol-gel process. Sieber et al. [Sie1/02, Sie2/02] prepared biomorphic Al_2O_3-, TiO_2-, ZrO_2- and mullite ($Al_6Si_2O_{13}$) ceramics from rattan plants via a sol-gel process.

The primary goal of this work was the preparation of highly porous biomorphous Al_2O_3-, TiO_2-, ZrO_2-ceramics, and the investigation of the infiltration behavior, ceramic phase formation and microstructure development during processing. High temperature cellular Al_2O_3-, TiO_2-, ZrO_2-ceramics with a hierarchical microstructure may be interesting for application as heat insulation structures, filters and catalyst carriers in high-temperature processes as well as for medical implant structures. The conversion of biological preforms (cellulose fiber felts, pine wood, rattan plant as well as corrugated cardboard structures) into highly porous, biomorphous Al_2O_3-, TiO_2-, ZrO_2-ceramics via sol-gel processing was performed. Vacuum infiltration of different kinds of low viscous, oxide sols into biological preforms and subsequent heat treatment were applied. Depending on the infiltrated biological preforms as well as on the processing parameters, the porosity and the pore morphology can be designed. The compression strength of the biomorphous Al_2O_3-, TiO_2-, ZrO_2-ceramics was analyzed with respect of orientation, porosity and strut microstructure.

2. Basic Principles

2.1 Biotemplating

Biotemplating represents an advanced technology for preparation of microcellular ceramic materials from native biopolymeric material through fast high-temperature processing [Ota/95, Gre1/98, Gre2/98, Gre/99, Sie/00]. The structural features of the initial biological materials are maintained in the ceramic product. In the biotemplating process, both native plant tissue e.g. wood and preprocessed technical products from cellulose fibers such as paper and cardboards, can be used as biological preforms for converting into highly porous, biomorphous ceramics. Naturally grown wood exhibits a hierarchically built anatomy, developed and optimized in a long-term genetic evolution process, while preprocessed technical products provide precursors with a more homogeneous microstructure.

2.1.1 Characteristics of Wood

2.1.1.1 Anatomy of Wood

Wood is a natural grown composite with a complex hierarchical cellular structure [Fin/70, But/80, Gib/92]. It provides mechanical strength to the tree as well as performs functions such as liquid transport and nutrition storage. The cells of wood are usually elongate fibrous structure. All wood cell types are, therefore, arranged into “along-the-axis” (termed axial) or “across-the axis” (termed radial) systems. The elongated tubular cells which aligned with the axis of the tree trunk, are referred to as longitudinal cells, or fibers. Perpendicular to those are ray cells which are aligned from the center of the trunk radially outwards to the bark.

For the macroscopic and microscopic identification of wood, the cellular structure of wood is usually studied in three basic planes of orientation: axial, tangential and radial. In transverse section (axial cutting), all the longitudinally running elements like vessels and fibers (grains) are cut transversely. In tangential and radial sections, however, all the longitudinally running elements are cut longitudinally. The difference between tangential and radial sections lies in the orientation of the rays. While the tangential section is cut perpendicular to the ray direction, the radial section is cut parallel to the rays, Fig. 2.1.1.

Most woody plants grow periodically rather than continuously. The seasonal pattern of growth is reflected in the formation of a series of growth increments or growth rings in the wood [Cor/79, Har/85]. Earlywood, or springwood, is formed early in a growing season. Earlywood cells have large diameters and thin cell walls. Latewood, or summerwood, is formed toward the end of the growing season and the latewood cells are thick-walled cells with smaller diameters. Due to changes in the size and shape of the cells and the thickness of their cell walls within the growth ring, mantle-like layers of growth ring are discernible to the naked eyes in transverse section, Fig. 2.1.1.

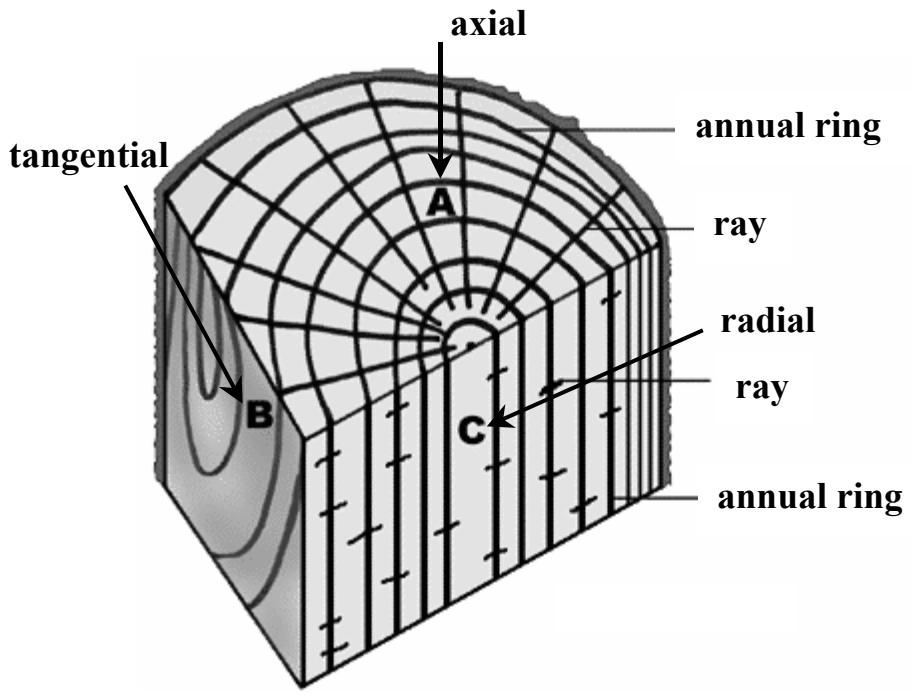

Fig. 2.1.1: Schematic sketch of the definition of the three basic planes of wood with respect to the growth direction [Col/02].

Wood is divided into two main groups [Pan/80, Hoa/80]: hardwoods (deciduous wood which is botanically classified as *dicotyledonous angiosperms*) and softwoods (coniferous wood or *gymnosperms*):

Hardwood

The majority component of hardwood species is vessel elements (tracheas). The main function of pores in the tracheas is water conduction. According to the distribution of the pores in the cross section, hardwood can be divided in two large classes: *ring-porous* and

diffuse-porous wood. In the *ring-porous* wood, e.g. oak and beech, the large pores are localized in the earlywood while the latewood is made up of smaller pores, thus the earlywood/latewood transition occurs abruptly and is very distinct, Fig. 2.1.2a. In *diffuse-porous* wood, e.g. poplar and birch, the pores are distributed throughout the growth rings, Fig. 2.1.2b. Other cell types are present, notably fibers (thick-walled mechanical support cells), ray parenchyma (small, think-walled food transport and storage cells), and axial parenchyma (food storage cells which are vertically elongated in a standing tree stem). The size of these cells and their distribution varies considerably among different species of wood as well as among trees of a given species and within a single tree [Pan/80].

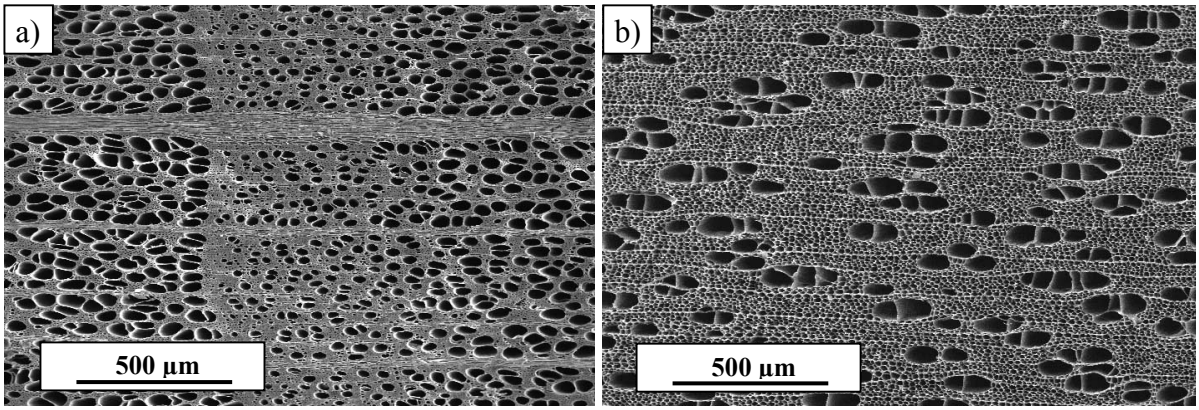

Fig. 2.1.2: SEM-graphs of (a) ring-porous wood e.g. beech and (b) diffuse-porous wood e.g. poplar.

Softwood

Comparing to the hardwood structure, softwoods are less complex. Softwoods contain fewer cell types with less variation in the size and arrangement of those cell types in the wood structure. They do not have the vessel elements and a single cell type, the longitudinal tracheid, occupy about 90-95% of the total volume of most types of softwood. These longitudinal tracheids are usually 1 to 5 mm long and 15 to 80 µm in diameter [Côt/80, Pan/80, Har/85]. Tracheid walls are pierced by numerous pits, which form the majority pathway for water and solution from one cell to another. Another important type of cells in softwood is ray cells, which include ray tracheids and ray parenchyma arranged in radial strands perpendicular to the grain direction. Softwood rays are from one to many cells in height but are usually only one cell wide. Ray cells are smaller compared to the longitudinal tracheids. Softwood can be categorized by the presence or absence of resin canals and