Porous ceramics prepared by mimicking silicified wood

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Abstract

Porous titania, alumina and zirconia ceramic woods with wood-like microstructures, analogous to that of silicified wood, were prepared from natural woods as templates. The production of these ceramic woods was performed by the following process: (1) infiltration of metal alkoxide into wood specimens, (2) hydrolysis of the alkoxide in the cell structure to form titania, alumina or zirconia gels, (3) firing in air to form titania, alumina or zirconia ceramic woods. The resulting titania, alumina and zirconia ceramic woods were studied by means of an X-ray diffractometer, a mercury porosimeter and a scanning electron microscope. The microstructure of these ceramic woods retained the same structure as that of the raw wood: with the pore sizes corresponding to those of the original wood, and the major pores being unidirectionally connected.

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1. Introduction

In recent years, porous ceramics have become important materials for a variety of applications such as thermal and/or sound insulation, absorption, filtration, and as catalysts. Various materials and methods have been studied regarding the preparation of porous ceramics. Generally speaking, the preparation methods can be classified into two, i.e. the foaming method and the polymeric-sponge method [1]. In the former method, porous ceramics are prepared by mixing ceramic powder with organic materials as a pore-forming agent, which are subjected to combustion into carbon oxide gas, resulting in the formation of pores within the ceramic body, during the firing process. In the latter method, a polymeric spongy material infiltrated with ceramic slurry is burned out leaving a porous ceramic. We have been trying to prepare porous ceramics from wood instead of sponge [2–5].

The wood structure is characterized by cells and vessels that are filled with water, with 3–0 and 3–1 connectivities [6], respectively. The term connectivity is defined as the dimensionality of the connections for each individual phase in a composite. The 3–0 connectivity means that one phase (water in a cell) is isolated in zero-dimension, while the cells are connected in three-dimensions. Water contained in vessels showed the 3–1 connectivity pattern, with water in a vessel being the one-dimensionally connected phase and the wood body being the three-dimensionally connected phase. The size of the cells and the diameter of the vessels both vary with the species. These features in wood make it an attractive template for making special porous ceramics such as filters, absorbent and catalyst carriers, and lightweight structural ceramics. In the natural world, a wood made of ceramics has been recognized, known as fossil wood or silicified wood. Although, the mechanism of the fossilization process has not been clarified completely yet, it is considered that deposition of mineral silica within the wood texture and replacement of their cells and tissues produce silicified wood [7]. Leo et al. [8] reported on the artificial
fossilization of wood by means of the infiltration of tetraethyl orthosilicate (Si(OEt)_4). The infiltrated Si(OEt)_4 was hydrolyzed to deposit an amorphous silica in the texture of wood. He found that a microstructure of the artificial silicified wood was comparable to that of natural fossil wood.

We have so far studied the preparation of porous ceramics using natural woods as templates. Si(OEt)_4 was vacuum-infiltrated into a wood specimen and hydrolyzed to form silica gels in cell walls and then fired in an argon atmosphere, resulting in porous silicon carbide ceramics retaining the porous structure of the original wood [2,3]. When titanium isopropoxide (Ti(iPr)4) was used instead of Si(OEt)_4, firing in air resulted in porous titania ceramics [4,5]. We call these ceramics, that are prepared by the use of natural woods as starting materials and that have external and/or internal forms similar to the original woods, ‘ceramic woods’. In addition, Niihara et al., Nishida et al. and Greil et al. [9–11] prepared silicon carbide ceramic woods by infiltrating molten silicon or gaseous silicon oxide. Furthermore, Greil et al. [12] tried to prepare some kinds of porous oxide ceramic woods by the sol–gel method. In this paper, preparation of porous alumina and zirconia ceramic woods using aluminum isobutoxide (Al(iPr)3) and zirconium n-propoxide (Zr(nPr)4), in addition to titania ceramic woods have been presented.

2. Experimental procedure

2.1. Materials

Employed reagents and solvents were the highest grade available. The kinds of wood used were as follows: coniferous trees such as Japanese cedars (Sugi), Japanese cypress (Hinoki) and firs (Momi); broad-leaved trees such as the Japanese Judas tree (Katsura), horse chestnut (Tochi), paulownia (Kiri) and matoa (Banryugan). Pieces of raw wood were cut (e.g. 15 mm x 10 mm x 10 mm) and dried thoroughly at 110 °C for 12 h.

2.2. Preparation of porous ceramic woods

Titania ceramic woods were prepared as described previously [2,3]. Alumina ceramic woods were prepared as follows. Pieces of dried and acetylated [5] wood were infiltrated in 25–75 vol% of Al(iPr)3 solution, which was diluted with 2-butanol, in reduced pressure for 1 h. The infiltrated Al(iPr)3 was hydrolyzed with 1 vol% of water in 1-propanol, using an ultrasonic generator for 20 min. to form alumina gel in situ. The specimens that contained gel were dried at a temperature of 110 °C for 24 h. The treatment process of infiltration, hydrolysis and drying was repeated several times to increase the yield of alumina gel, and then the specimens were fired at 1300 °C for 4 h in air.

In the case of zirconia ceramic woods, pieces of dried wood were infiltrated in 10–20 vol% of Zr(nPr)4 solution in 1-propanol. In order to prepare calcium stabilized zirconia ceramic woods, the pieces containing zirconia gel were infiltrated in calcium nitrate aqueous solution in reduced pressure for 1 h and dried at a temperature of 110 °C for 24 h. The process of infiltration and drying was repeated until the ratio of calcium to zirconium became 3–18 mol%, and then the specimens were fired at 800–1300 °C for 2 h in air.

2.3. Measurements

The products were identified using an X-ray diffractometer (XRD) (Model RINT 1100, Rigaku Co., Tokyo, Japan) and observed via a scanning electron microscope (SEM) (Model JSM-6100, JEOL, Tokyo, Japan) and an energy dispersive X-ray spectrometer (EDS) (Model JED-2001, JEOL, Tokyo, Japan). Pore size distribution was measured with a mercury porosimeter (Model PASCAL 140 and 240, AMCO Inc., Tokyo, Japan).

3. Results and discussion

3.1. Gel fixation in wood

As the treatment process (infiltration, hydrolysis and drying) was repeated, the weight of specimens increased. Fig. 1 shows weight changes of various woods treated with 30 vol% of Ti(iPr)4 solution. The rate of weight increase differed greatly depending on the type of wood. With the coniferous and broad-leaved trees, the weight changes saw an increase of 76–96 and 13–28% for six treatments, respectively. It is considered that the amounts of fixed gel were related to the microstructure as shown in Fig. 2.

![Fig. 1. Weight change of various specimens, relative to the increasing number of treatments of Ti(iPr)4 (30 vol% solution) infiltration, hydrolysis and drying.](image-url)
Fig. 2. SEM images of carbonized wood. Broad-leafed trees: (a) Kiri, (b) Tochi; needle-leaved trees, (c) Sugi, (d) Momi.

Fig. 3. SEM images and EDS analysis (cross-sectional view) of Sugi fixed with titania gel five times (treated with 30 vol% solution). (a) SEI, (b) BEI and (c) EDS.
The secondary electron image (SEI), back scattered electron image (BEI) and titanium mapping image (EDS) of Sugi fixed with titania gel five times are shown in Fig. 3. Titania gel is shown as a bright image in Fig. 3(b) and dots in Fig. 3(c). It is evident that titania gel has become fixed to the surface of the cell walls. Consequently, the amount of gel fixation became relatively small in broad-leaved trees with large vessels (Fig. 2(a) and (b)), compared with coniferous trees with fine tracheids (Fig. 2(c) and (d)). Similarly, when Al/B and Zn/P solutions (Fig. 4) were used, the rate of gel fixation to coniferous trees was higher than that of broad-leaved trees.

3.2. Crystalline phase

In the titania ceramic woods, anatase was formed by firing at temperatures below 800 °C. Crystallization of rutile was observed to coexist with anatase, at temperatures higher than 800 °C. At temperatures above 1000 °C, rutile formed exclusively [4]. In the alumina ceramic woods, α-alumina was formed by firing at 1300 °C.

In the zirconia ceramic woods, only the monoclinic-phase was formed at temperatures above 1000 °C, although the metastable tetragonal-phase was formed by firing at 800 °C as shown in Fig. 5. The obtained specimen could not hold its original form owing to the large volume of change by phase transition between the monoclinic- and tetragonal-phase as shown in Fig. 6(a'). On the other hand, the specimens retained the form of the original wood when the cubic-phase was stabilized by calcium as shown in Fig. 6(b'). Fig. 7 shows powder XRD patterns of calcium doped zirconia woods fired at 1300 °C. The more calcium was doped, the more the crystal system changed from monoclinic to cubic and CaZrO₃.

![Fig. 4. Weight change of various specimens, relative to the increasing number of treatments of Zn/P (30 vol% solution) infiltration, hydrolysis and drying.](image)

![Fig. 5. Powder XRD patterns of zirconia Sugi specimens fired at various temperatures following treatment (treated with 20 vol% solution). (a) 800 °C, (b) 1000 °C and (c) 1300 °C. (●) monoclinic ZrO₂ and (▲) metastable tetragonal ZrO₂.](image)

![Fig. 6. Photographs of raw woods and zirconia ceramic woods from Sugi (treated with 20 vol% solution). (a) and (b) raw woods, (a') monoclinic zirconia ceramic wood and (b') cubic zirconia ceramic wood (Molar ratio of Zr:Ca is 82:18 at the preparation).](image)

![Fig. 7. Photographs of raw woods and zirconia ceramic woods from Sugi (treated with 20 vol% solution). (a) and (b) raw woods, (a') monoclinic zirconia ceramic wood and (b') cubic zirconia ceramic wood (Molar ratio of Zr:Ca is 82:18 at the preparation).](image)
3.3. Microstructure

The microstructure of the products remained unaltered from the raw wood as well as the external forms shown in Fig. 8.

Fig. 9 shows SEM images of titania ceramic woods from a broad-leaved tree and a coniferous tree. In broad-leaved tree ceramic woods (Fig. 9(a) and (b)), there were two kinds of pore size, one is 30–80 μm, and the other 5–20 μm. The former originated from vessels, the latter from vasicentric tracheids, respectively (Fig. 2(a) and (b)). In coniferous tree ceramic woods (Fig. 9(c) and (d)), there were pores with a regular size of about 10–20 μm originating in tracheids (Fig. 2(c) and (d)).

The walls of the vessels, vasicentric tracheids and tracheids were almost replaced by single-grain layers. In addition, it turned out that the pores were unidirectionally connected as shown in Fig. 9(e). There are some micropores of a few micrometers in the walls composed of the single-grain layers. It is considered that these micropores developed during the sintering process. Consequently, the ceramic woods also had second or third pores that did not originate from the wood textures.

Fig. 10 shows the pore size distributions of titania ceramic woods from Kiri and Sugi. Although both the cumulative volume of Kiri and Sugi ceramic woods were almost the same (about 1200 mm³ g⁻¹), there was a characteristic difference in pore size distribution. Kiri ceramic wood (Fig. 10(a)) had two peaks at around 10 and 70 μm, while Sugi ceramic wood (Fig. 10(b)) had a single peak at around 15 μm. These pore sizes exactly corresponded to those of the vessels and vasicentric tracheids in broad-leaved trees, and the tracheids in coniferous trees, respectively.

Fig. 11 shows SEM images of alumina and calcia-stabilized zirconia ceramic woods. The microstructures of these ceramic woods retained those of the original woods. However, the textures of these ceramic woods are composed of thinner walls, showing a thinner fixation of zirconia and alumina gels than the titania gel.

4. Conclusions

A new type of porous ceramic was prepared by mimicking silicified wood. Titania, alumina and zirconia ceramic woods were prepared by the sol–gel method, using natural woods as templates. These ceramic woods retained exactly the same microstructure as that of raw wood, where the representative pore sizes were about 10 and 70 μm for broad-leaved trees, and about 15 μm for coniferous trees. Including micropores developed by sintering, the ceramic woods had hierarchical pores of two or three different sizes. They could be used as a 3–1 composite material composed of ceramic and pore, since the major pores were unidirectionally connected.
Fig. 9. SEM images of titanified woods from (a) Kiri, (b) Tochi, (c) Hinoki, (d) and (e) Momi (treated with 30 vol% solution). (a)–(d) were observed perpendicular to vessels, (e) was observed parallel to vessels.

Fig. 10. Pore size distributions in the titania ceramic woods from (a) Kiri and (b) Sugi.
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