Surface Structure of Woodceramics Manufactured from Cedar

Yutaka Sawada¹, Sachiko Sezaki¹,*, Riko Ozao², Yuko Nishimoto³, Toshihiro Okabe⁴, Mieko Ide⁵ and Azusa Shida⁵

¹Tokyo Polytechnic University, Atsugi 243-0297, Japan
²SONY Institute of Higher Education, Atsugi 243-8501, Japan
³Kanagawa University, Hiratsuka 259-1293, Japan
⁴Industrial Research Institute of Aomori Prefecture, Aomori 030-0113, Japan
⁵Yokohama City Center for Industrial Technology and Design, Yokohama 236-0004, Japan

Systematic morphological observations and surface analyses were completed in order to clarify the surface structure of “woodceramics”, i.e., carbon-carbon composite materials consisting of plant-originated carbon reinforced by carbon generated from phenol resin. The woodceramic material was made from cedar sawdust at various temperatures (650°C, 700°C, 800°C, 1000°C and 1200°C) in a nitrogen atmosphere. The microstructure was not affected by the manufacturing temperatures; bundles of the micro-tubes of the original plant (cedar) were preserved. The nanostructure was also unaffected by the manufacturing temperatures except for the one manufactured at the highest temperature (1200°C). Fine needles (fibers) on the surface of the 1000°C-prepared specimen were incorporated into the substrate for the 1200°C-prepared specimen. The oxygen/carbon atomic ratio (0.14) determined by XPS was approximately constant for all specimens manufactured at various temperatures. This value agreed with that of the bulk composition (0.12) except for the one (0.07) manufactured at the highest temperature (1200°C). The binding energy of C1s (284.1 eV) was attributed to elementary carbon. The binding energies of C1s and O1s (532.4 eV) were unchanged by the manufacturing at different temperatures. The specimens manufactured at low temperatures (650°C, 700°C and 750°C) showed high hydrogen/oxygen atomic ratios (2.6, 2.0 and 1.9, respectively) while those manufactured at high temperatures (1000°C and 1200°C) had the lower values (1.3 and 1.4, respectively). The X-ray diffraction analysis indicated an amorphous phase with weak halos at 23.7°/C14 and 43.1°/C14 (d-spacings; 0.375 and 0.210 nm, respectively). The weak peaks at 30.41°/C14, 35.30°/C14 and 50.84°/C14 (d-spacings; 0.2937, 0.2541 and 0.1795 nm, respectively) that appeared eventually were attributed to a minute amount of impurities.

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1. Introduction

The “woodceramics” are defined as carbon-carbon composite materials consisting of plant-originated amorphous carbon reinforced by glassy carbon generated from phenol resin. Woodceramics are usually manufactured by impregnating phenol resin into wood-based (lignocellulosic) materials, such as cedar (Cryptomeria japonica, SUGI in Japanese), pine (Pseudotsuga menziesii, MATSU in Japanese), AOMORI HIBA (Thujopsis dolabrata), MDF (medium density fiber) boards, waste paper, apple wastes, etc. before heating in an inert gas atmosphere or in vacuum.

The structure of the original plant is preserved or reflected in the resulting woodceramics. Therefore, woodceramics are basically porous and used in filters and heat-shielding materials. The structure of the woodceramics can be controlled to some extent by changing the parameters of the carbonization process; the porosities (densities) and the particle sizes (surface areas) affect most of the properties.

A unique characteristic of the woodceramics is that reinforcement by glassy carbon provides a high mechanical strength in spite of the porous nature of the woodceramics.¹ The glassy carbon generated from the artificial origin (phenol resin) eliminates the fluctuation and instability caused by the amorphous carbon generated from the natural origin (wood). The porous nature of the woodceramics is also expected for tribological application for lubricated sliding contacts.² Woodceramics are electrically conductive and applicable as a flat panel heater for snow melting tiles,³ and the shielding of electromagnetic waves.⁴,⁵ The high emissibility of far-infrared rays is also important for heater applications.³,⁶ The surface conditions of woodceramics seemed to affect the properties of gas adsorbents and gas sensors.⁷ Industrial wastes such as sawdust can be utilized for the easy and inexpensive production of woodceramics. Recently, much attention has been paid to woodceramics as environmentally-benign materials or so-called “ecomaterials”. The organic compounds evolved from plants during the heating process can be used instead of phenol resin as Ozao and Okabe⁸ reported. Woodceramics can be easily disposed by combustion; this advantage is prominent for other ceramic materials.

As mentioned above, previous papers have mainly focused on the application of woodceramics. Most of the processing parameters seemed to be empirically determined. Clarification of the surface structure of the woodceramics is important to understand the formation mechanism as well as to control the properties for a wide variety of applications. Okabe et al.⁹ reported the original morphology of cedar sawdust remaining after carbonization. Ozao et al.¹⁰ reported needles on the surface of cedar-based woodceramics manufactured from MDF board. However, the SEM (scanning electron microscope) observations was limited to the specimens manufactured at 800°C. In the present study, a systematic observation by scanning electron microscope (SEM) was executed for woodceramics manufactured from cedar sawdust heated at various temperatures. The surface composition determined by X-ray photoelectron spectroscopy (XPS) was
compared to the bulk composition. The chemical state of carbon and oxygen was examined by XPS. The crystalline state evaluated by an X-ray diffraction analysis was also discussed.

2. Experimental

2.1 Specimen

The preparation of the woodceramics was reported elsewhere.11) The present specimens were prepared from the sawdust (1.0–1.7 mm) of cedar and phenol resin with the mass ratio of 6:4. The solution of phenol resin (resin content, approx. 30%; Model PX-1600, Honen Corp.) was ultrasonically impregnated into the cedar sawdust. The phenol resin was first hardened in an oven first at 60°C for 8 h then at 135°C for 8 h before heating in a nitrogen atmosphere of a carbonization furnace at 650°C, 700°C, 800°C, 900°C, 1000°C or 1200°C.

2.2 Evaluation

The micro- and nano-structures of the as-prepared specimens were observed by SEM (Model 5310, JEOL) with the acceleration voltage of 20 kV. Secondary electron images were clearly obtained without depositing gold.

The specimens were pulverized with an agate mortar and evacuated at room temperature for approximately 1 day before XPS analysis using magnesium X-ray radiation (model APEX, Phi; 20 kV, 20 mA); the as-prepared specimens and the specimens argon-etched for 15 s were compared. The surface compositions of the woodceramics were approximately calculated from the XPS peak areas and the relative sensitivity factors assuming the specimens consisted of only carbon and oxygen and were homogeneous.

The bulk composition (content of carbon and hydrogen) was determined by gas chromatography using a CHN analyzer (model 2400, Perkin-Elmer); the specimen was completely combusted using a catalyst at 920°C in an oxygen-containing atmosphere and the evolved carbon dioxide and water vapor were carried by helium to the thermal conductivity detector. The oxygen content in the woodceramic was tentatively estimated from the residual mass (which will mainly be attributed to metal oxides) after the combustion based on the assumption that the specimen except the residue consisted of carbon, hydrogen and oxygen.

The X-ray diffractometry spectra for the pulverized specimens were measured using a rotating copper target (acceleration voltage, 40 kV; electron beam current, 300 mA) and a graphite monochrometer (Model RINT-2500T, Rigaku).

3. Results and Discussion

3.1 Micro- and nanostructure

The SEM photographs of typical surface structures of the cedar-based woodceramics are indicated in Figs. 1 and 2 at different magnifications. The morphology of the original plant (cedar) was preserved although probably accompanied by some shrinkage. Bundles of the micro-tubes were clearly observed but the phenol resin was undistinguishable in the SEM photos.

The specimen manufactured at 1000°C is shown in Fig. 1.

Fig. 1 SEM photographs of cedar-based woodceramics manufactured at 1000°C. (a) The SEM photographs (low magnification) (b) The SEM photographs (medium magnification) (c) The SEM photographs (high magnification).

The low-magnification photo [Fig. 1(a)] shows the shape of the original material, i.e., the sawdust of cedar. The medium-magnification photo [Fig. 1(b)] shows many round-shaped
windows or holes on the tubes walls. The high-magnification photo [Fig. 1(c)] shows fine needles (fibers) which seemed to grow by a chemical vapor deposition process of the volatile organic compounds. Similar fibers were reported by Ozao et al.\textsuperscript{10} for the woodceramics manufactured from MDF board of cedar impregnated with 55% phenol resin and sintered at 800°C. Small particles were observed on the tube walls. The SEM photos of the cedar-based woodceramics manufactured at lower temperatures were not indicated in the present paper since the surface morphology was approximately identical to that manufactured at 1000°C except for the small particles and the fibers.

The specimen manufactured at the higher temperature (1200°C) is shown in Fig. 2. The low-magnification photos [Fig. 2(a)] indicated that the morphologies were similar to those [Fig. 1(b)] manufactured at 1000°C. However, the medium-magnification photo of the tube surface [Fig. 2(b)] showed a different structure; the round-shaped windows [shown in Fig. 1(b)] combined to form a larger square-shaped window. A part of the thin walls was rolled up to form a rod-like structure. The high-magnification photo [Fig. 2(c)] shows that the fibers and particles prepared at 1000°C [Fig. 1(c)] disappeared and were incorporated into the substrate; this should be interpreted as a kind of sintering behavior by which the surface energy was reduced.

3.2 Surface composition and the state of carbon

The XPS spectra for the present specimens were approximately identical. A strong C1s XPS peak supported the fact that the carbon predominated on the surface of the present woodceramics. A strong O1s peak suggested that the surface was covered with oxygen or oxygen-containing molecules. Metal elements such as iron, nickel, chromium, and aluminum should be attributed to the natural origin of woodceramics or the contamination during the manufacturing process or preparation process for the surface analysis. Chlorine, sulfur, nitrogen were also detected. The peak intensity of these minor elements fluctuated between the specimens. The total amount of these elements except carbon and oxygen was approximately 2–3 at% and independent of the manufacturing temperatures. Hydrogen was undetectable by XPS.

The surface compositions (oxygen/carbon atomic ratios) of the woodceramics determined by XPS are shown in Fig. 3.

![Fig. 3 Compositions of cedar-based woodceramics manufactured at various temperatures.](image-url)
The bulk compositions are plotted in this figure for reference. The specimen was mainly composed of carbon and lower amounts of hydrogen and oxygen. The XPS results should be understood as a rough estimation. With uncertainties in mind, the surface composition was constant and independent of the manufacturing temperature. The average oxygen/carbon atomic ratio (0.14) was approximately identical with that of the manufacturing temperature. The average oxygen/carbon ratio (0.12) except for the one manufactured at the highest temperature. An exceptionally low oxygen/carbon atomic ratio (0.07) for the high manufacturing temperature seemed to be attributed to formation of pure carbon. The hydrogen/oxygen atomic ratios were approximately 2 and 1, respectively, for the specimens manufactured at low temperatures (650°C, 700°C and 800°C) and high temperatures (1000°C and 1200°C). This suggested that the specimens manufactured at low temperature contained hydrocarbons and/or adsorbed water (hydrogen/oxygen = 2) rather than hydroxyl groups (hydrogen/oxygen = 1), adsorbed oxygen and carbon dioxide.

A typical XPS spectrum for the cedar-based woodceramics manufactured at 1200°C is shown in Figs. 4 and 5 for the C1s and O1s peaks, respectively. The binding energy of the present analysis was not calibrated since the measured value for graphite (284.5 eV) agreed with the reported value (284.6 eV). The binding energy determined at the peak top of C1s (284.1 eV) was constant for all the specimens manufactured at various temperatures with and without the argon-etching. The carbon should not be attributed to the compounds, but to elementary carbon. The peak had a tail at the higher binding energy; this suggested the coexistence of carbon compounds such as phenols at 286.1 eV, a carbonyl group at 287.3 eV and a carboxyl group at 288.7 eV. The binding energy of O1s (532.4 eV) was unaffected by the preparation temperature although the assignment was abandoned. Argon ion etching for 15 s produced a new O1s peak with a lower binding energy (530.4 eV).

The X-ray diffraction spectra of the cedar-based woodceramics manufactured at various temperatures are shown in Fig. 6. The present specimens were amorphous or glassy. A weak halo (extremely broad peak) and much weaker one were observed at 23.7 and 43.1°; and the corresponding d-spacings were 0.375 and 0.210 nm, respectively. These peaks presumably represent the {002} and {100} planes of the graphite-like layers; Dahn et al. reported a similar spectrum for a typical specimen prepared by pyrolysing sugar at 1050°C. The intensity and the width of these hallos were not correlated with the manufacturing temperatures. The short distance order between the carbon atoms seemed to be similar. A smaller peak at 29.5° was reported for another woodceramic manufactured from MDF board. The present spectra were taken from a low diffraction angle (3.0°) so that a remarkably high background was observed for the specimen manufactured at 1200°C; the high intensity should be attributed to X-ray scattering caused by the long range order of the carbon atoms. Weak peaks at 30.41°, 35.30° and 50.84° (d-spacings, 0.2937, 0.2541 and 0.1795 nm, respectively) eventually appeared and disappeared when measured. This should be attributed to a minute amount of impurities although the assignment was impossible at the present time.

4. Conclusions

The woodceramics manufactured from cedar at various temperatures (650°C, 700°C, 800°C, 1000°C and 1200°C) were observed by SEM. The microstructure was not affected by the manufacturing temperatures; bundles of the micro-tubes of the original plant (cedar) were preserved. The nanostructure was also unaffected by the manufacturing temperatures except for the one manufactured at the highest temperature.
Fine needles (fibers) on the surface of the 1000°C-prepared specimen were incorporated into the substrate for the 1200°C-prepared specimen.

The oxygen/carbon atomic ratio (0.14) determined by XPS was approximately constant for all specimens manufactured at the various temperatures and approximately agreed with that of the bulk specimen. The binding energy of C1s (284.1 eV) was attributed to elementary carbon. The binding energies of C1s and O1s (532.4 eV) were unchanged by the manufacturing at the different temperature. The hydrogen/oxygen atomic ratios were approximately 2 and 1, respectively, for the specimens manufactured at low temperatures (650°C, 700°C and 800°C) and high temperatures (1000°C and 1200°C).

The X-ray diffraction spectra of the present specimens were amorphous with a weak halo (extremely broad peak) and a much weaker one observed at 23.7° and 43.1°; d-spacing of 0.375 and 0.210 nm, respectively. The weak peaks at 30.41°, 35.30° and 50.84° (d-spacings; 0.2937, 0.2541 and 0.1795 nm, respectively) that appeared eventually were attributed to a minute amount of impurities.

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