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ORIGINAL ARTICLE

Koei Nishimiya · Toshimitsu Hata · Hikari Kikuchi
Yuji Imamura

Effect of aluminum compound addition on graphitization of wood charcoal by direct electric pulse heating method

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Abstract The catalytic effect of aluminum on graphitization of wood charcoal was examined. Wood charcoal impregnated with aluminum triisopropoxide to various levels was subjected to direct electric pulse heating. Electric conductivity and heat conductivity of the products showed strong, systematic dependence on the amount of aluminum added. X-ray diffractometry indicated that these effects result from a larger degree of graphitization. Because the amount of aluminum in the final product was negligible, aluminum, before being lost by vaporization, apparently catalyzed graphitization at a lower temperature than is used for conventional treatments.

Key words Direct electric pulse heating method · Charcoal · Graphitization · Aluminum

Introduction

Wood charcoal or wood-based biomass carbon is an important functional material[1] for its adsorption[2] and thermal or electrical properties. Developing these properties of carbonization of wood at high temperatures is required because highly graphitized biomass carbon can be obtained only at high temperature. The thermal and electrical properties of wood charcoal are closely related to the degree of graphitization. When the carbonizing temperature is high or the heating rate is low, more time and energy are needed to prepare the charcoal. If equipment makes it possible to carbonize wood samples at a higher heating rate than in a conventional furnace, the cost of graphitization would be greatly reduced.

In this study we applied direct electrical pulse heating to the carbonization of charcoal samples at a high temperature to achieve such an aim.[3,4] Direct electric pulse heating is a novel powder consolidation method used to produce permanent magnets, ceramics, alloys, and so on. Plasma is generated among the metal or ceramic powder when pulsed current is applied while densifying materials within a short time at high temperature and high current discharge. There are three advantages to this method: segregation of the minimum molecular chain, purification of the growth of crystallites, and prevention of oxidation at boundaries among particles.

Furthermore, it is important for saving energy to reduce the temperature for graphitization of wood charcoal. When metal is added as a catalyst, graphization occurs at a lower range of temperatures. The aluminum compound solution was chosen because of the catalytic ability[5] of aluminum during graphitization and the simplicity of treating and impregnating it into wood charcoal, with the expectation of creating new ceramics from the biomass carbon.

We studied the properties of wood charcoal carbonized with aluminum triisopropoxide by direct electric pulse heating. X-ray diffraction and X-ray photoelectron spectroscopy (XPS) were used to monitor the graphitization.

Materials and methods

A wood sample of Japanese cedar (*Cryptomeria japonica*) was ground into particles of 1.27 mm or less. The wood powder was carbonized at 500°C in a conventional electric

K. Nishimiya[1] (✉) · T. Hata · Y. Imamura
Research Institute for Sustainable Humanosphere, Kyoto University, Uji 611-0011, Japan

H. Kikuchi
S.S. Alloy Co., Higashihiroshima 739-0046, Japan

Present address
[1]Hokkaido Forest Products Research Institute, 1-10 Nishikagura, Asahikawa 071-0198 Japan
Tel. +81-166-75-4233 (ext. 393); Fax +81-166-75-3621
e-mail: kouei@fpri.asahikawa.hokkaido.jp

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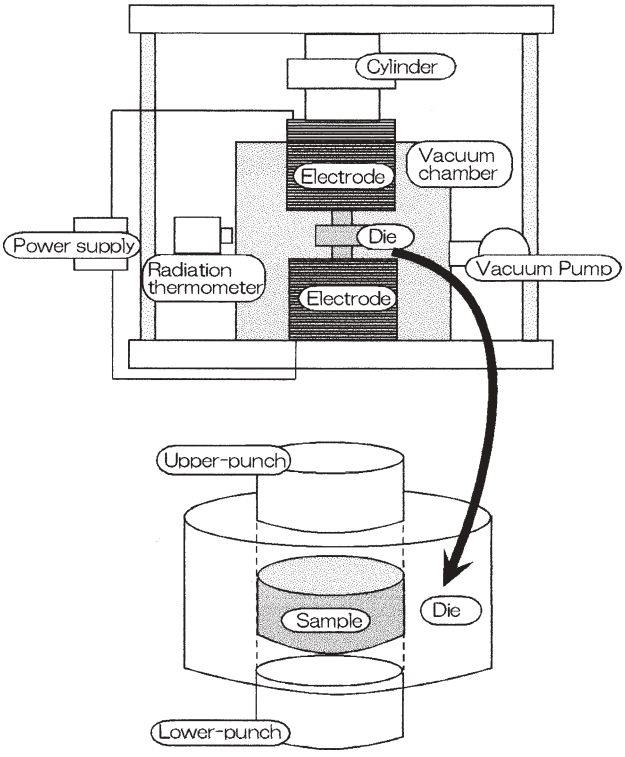

Fig. 1. Apparatus used for direct electric pulse heating method

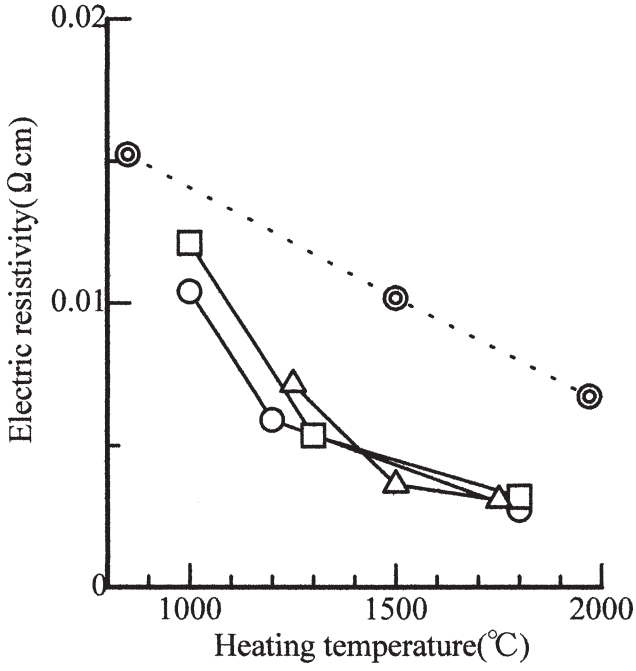

Fig. 2. Electrical resistivity of carbonized wood charcoal (CWC) *Circles*, Al 10%; *squares*, Al 20%; *triangles*, Al 30%; *double circles*, charcoal only. These symbols pertain also in Figs. 3–5

furnace under N_2 gas flow to remove the tar. The charcoal powder was then treated with aluminum triisopropoxide as follows: 2.0 g of the charcoal powder was dipped into an isopropanol solution of aluminum triisopropoxide for 24 h. The amounts of dissolved aluminum triisopropoxide were 10%, 20%, and 30% of the weight of dry wood charcoal as aluminum. After dipping, the powder was dried at 105°C for 24 h and then heat-treated by the direct electric pulse heating method.

The charcoal (0.3–0.4 g) impregnated with aluminum triisopropoxide was set into a graphite die and carbonized using Plasman II (S S Alloy, Hiroshima, Japan) by direct electric pulse heating. A schema of the heating equipment used is shown in Fig. 1. The thermal constants and electric resistivity of carbonized wood charcoals were measured. The thermal constants, such as thermal diffusivity, specific heat capacity, and thermal conductivity were measured by TC-7000H (Shinku Riko, Tokyo, Japan). The electric resistivity was measured by the four probes method using Roresta MCP-T410 (Mitsubishi Petrochemical, Tokyo, Japan). X-ray photoelectron spectroscopy and X-ray diffraction analysis were used to analyze the electrical and thermal behavior of the carbonized wood charcoal affected by changes in the crystal structure. X-ray diffraction was measured at a tube voltage of 35 kV and a tube current of 100–300 mA by the reflection method using Rigaku Geigerflex RAD2C. For X-ray photoelectron spectroscopy, the photoelectron spectrum of the carbonized wood charcoal was measured using AXIS-HS-1 (Shimadzu/KRATOS, Kyoto, Japan).

Results and discussion

Electrical resistivity of carbonized wood charcoal

The relation between the electric resistivity and heating temperature of carbonized wood charcoal (CWC) with aluminum is shown in Fig. 2. The electric resistivity of CWC with aluminum decreased as the heating temperature increased, similar to wood charcoal alone. The heating temperature strongly influences the electrical resistivity of CWC because there is more energy for crystallizing carbons at high temperatures. Although the addition of aluminum improved the electrical conductivity of CWC, no clear correlation was found between the electric resistivity and aluminum content. The electric resistivity of CWC with aluminum was much lower than that of the original wood charcoal with increasing heating temperature. The improvement in electrical conductivity of CWC was influenced by the presence of aluminum but not by its content.

Thermal diffusivity, specific heat capacity, and thermal conductivity of wood charcoal are shown in Figs. 3–5, respectively. The thermal diffusivity of CWC improved as the carbonizing temperature increased. The increase in aluminum content increased the thermal diffusivity, especially at high heating temperatures; this tendency is different from that of electric resistivity. The specific heat capacity declined less at high heating temperatures. Specific heat capacity had little relation to aluminum content. Thermal conductivity is calculated by multiplying the density, thermal diffusivity, and specific heat capacity. With 10% alumi-

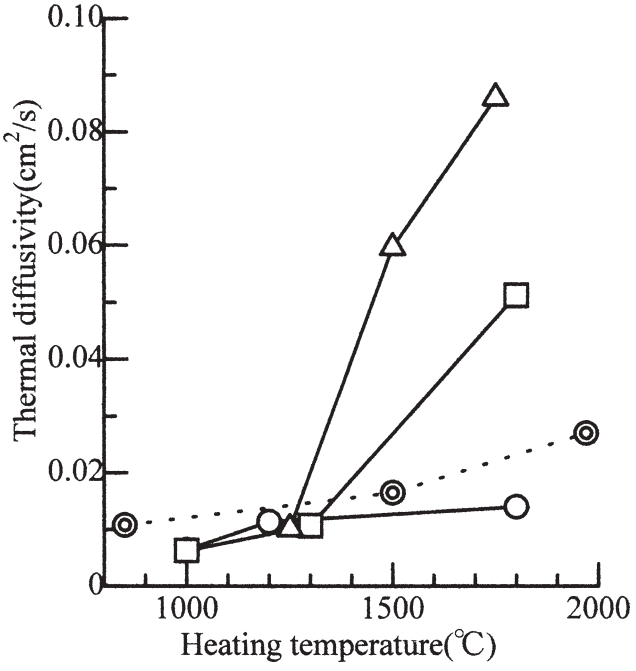

Fig. 3. Thermal diffusivity of CWC

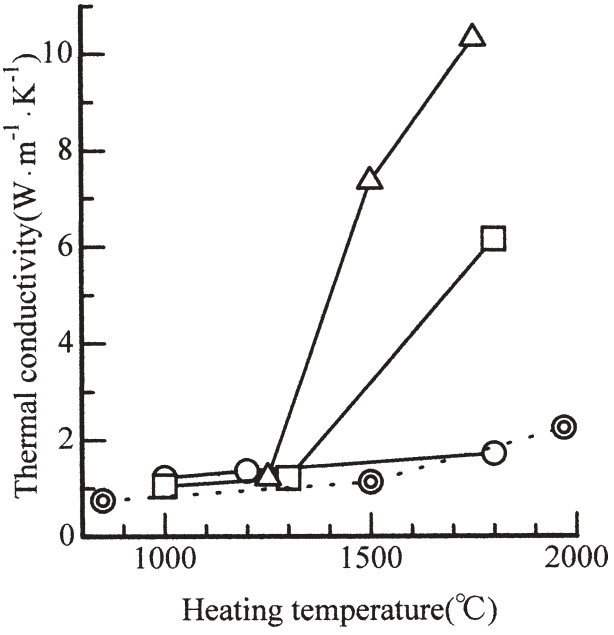

Fig. 5. Thermal conductivity of CWC

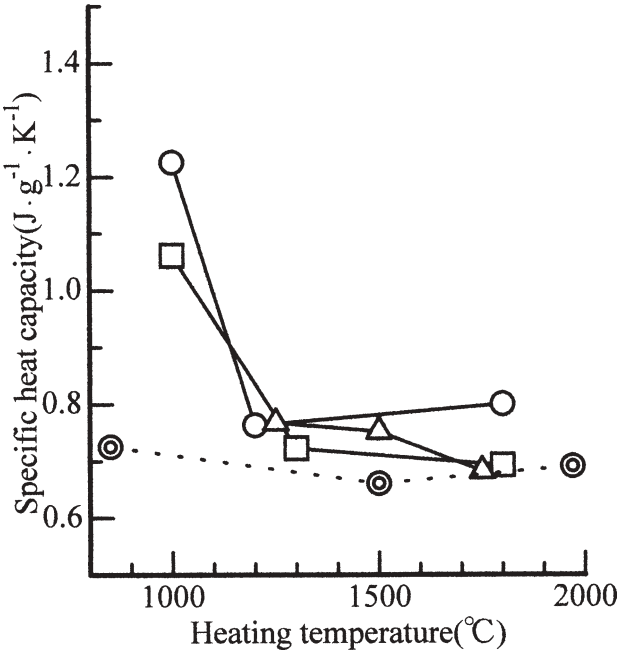

Fig. 4. Specific heat capacity of CWC

num treatment there was little difference compared to the original wood charcoal. However, with 30% aluminum treatment, a drastic increase in the thermal conductivity of CWC was observed; it was almost 10-fold that of the original charcoal. Thus, the thermal properties were effectively enhanced by the addition of aluminum.

Role of aluminum investigated by XRD and XPS

X-ray diffractograms of CWC are shown in Fig. 6 to investigate the degree of graphitization of CWC. With 10% aluminum treatment (Fig. 6a) the diffraction peaks at all heating temperatures were detected at about 25°C. These peaks were not particularly sharp, especially at low temperatures, and they originated from the precursor of graphite. Graphitization was not sufficient over this range of temperatures and aluminum content. With 20% treatment (Fig. 6b), a sharp graphite peak was detected at 1800°C. On the other hand, the diffraction peak became dull as the heating temperature dropped. The diffraction peak at 1750°C was the sharpest among all the samples (Fig. 6c). A strong peak was obtained even at a low heating temperature of 1500°C. This suggested that graphitization occurred at a low temperature because of the effect of the aluminum. It was certain that the heating temperature had a marked effect on the progress of graphitization in CWC. However, no peaks originating from aluminum or aluminum carbide were detected in any case. This means that the state of aluminum in CWC was not determinable by X-ray diffraction.

There was no proof of bonding between carbon and aluminum. It seems that the graphitization of CWC may depend on the catalytic effect of alumina, or the carbon-aluminum compound had already disappeared from the sample during the reaction based on the results of XPS described below. This result explains why aluminum has an effect as catalyst for graphitization. It became clear that the graphitization of wood-based carbon was promoted by alumina.

The change agreed well with the changes seen in the behavior of electric resistivity and thermal conductivity. In

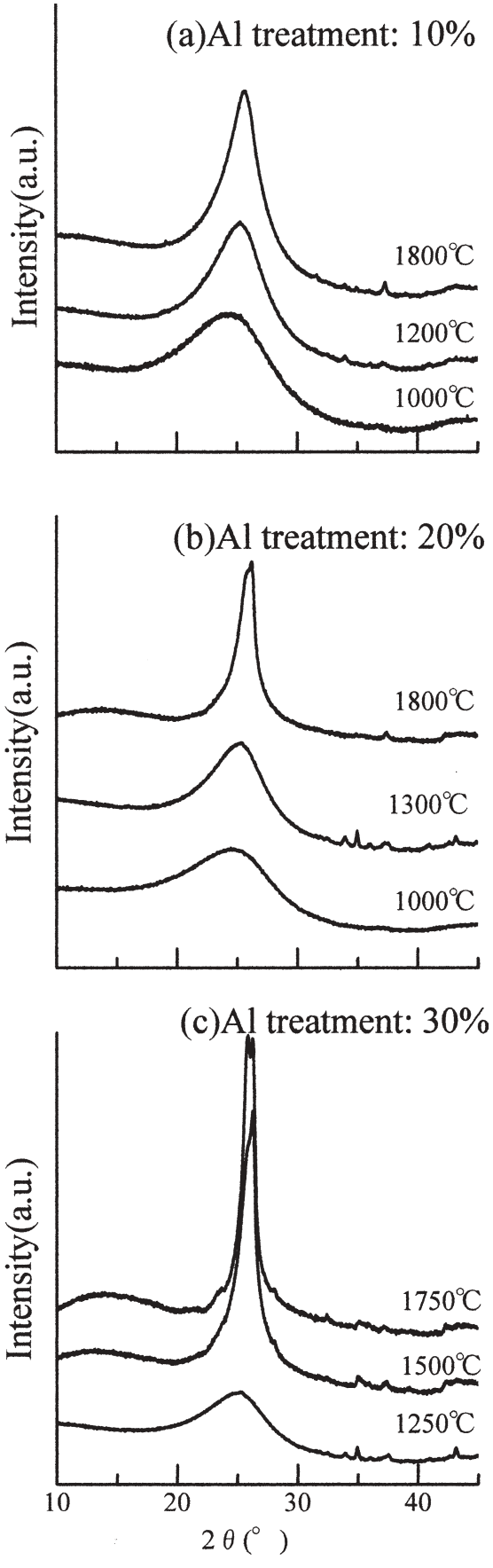

Fig. 6. X-ray diffractograms of CWC

short, the more the graphitization progressed, the more the electric resistivity declined. The electrical and thermal characteristics of CWC are related to the degree of graphitization.

XPS spectra of the CWC are demonstrated in Figs. 7 and 8. Typical carbon 1s spectra of CWC are shown in Fig. 7. The carbon 1s peak was detected at 284.6 eV in both samples (a) and (b). No difference was detected in the carbon 1s spectra, and the peak pattern was similar to that of the graphite.[6] The spectra of carbon 1s had no relation to the observed positions of the samples. It seems that the graphitization occurred at all areas of the sample. The aluminum 2p spectra are shown in Fig. 8. The peak at 74 eV was thought to have originated from Al_2O_3 (alumina) judging from the chemical shift of the aluminum. Other peaks related to aluminum were not detected. Based on this result, it was clear that the carbon composite with aluminum did not exist. It thus seems that aluminum has a catalytic effect during graphitization. This deduction derives from the improvement in the electrical and thermal characteristics of CWC. In addition, the aluminum peak was not detected at all points of the CWC. It seems that aluminum was localized in the CWC.

Conclusions

The changes in the properties of CWC on addition of aluminum were detected as follows.

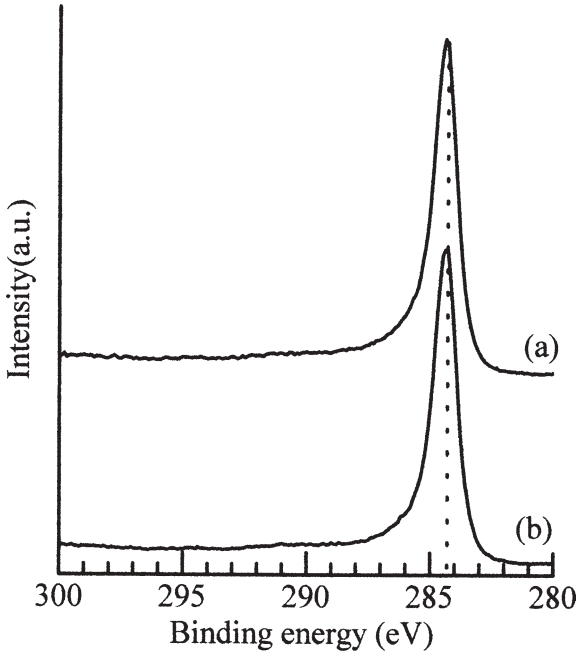

Fig. 7. Carbon 1s spectra of CWC. **a** 20% Treatment, 1800°C. **b** 30% Treatment, 1750°C

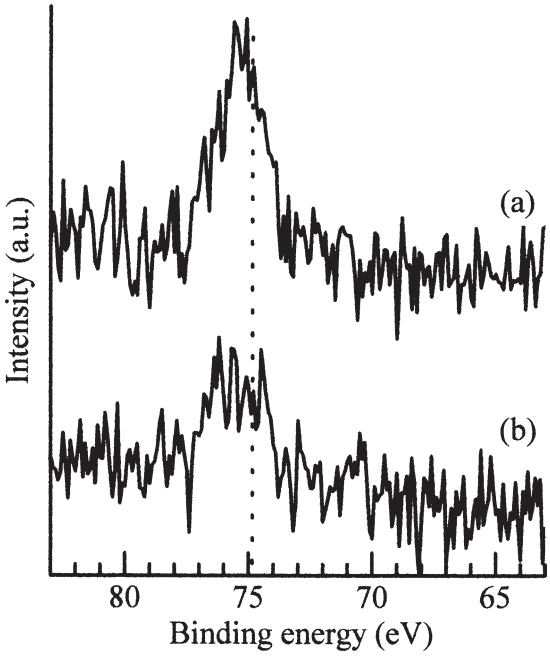

Fig. 8. Al 2p spectra of CWC. **a** 20% Treatment, 1800°C. **b** 30% Treatment, 1750°C

1. On addition of aluminum, the electric resistivity of carbonized wood charcoal (CWC) decreased and the thermal conductivity increased at the same heating temperature. Notably, the thermal conductivity was about 10 times that of normal CWC, confirming that the properties of CWC (especially electrical and thermal properties) were able to be controlled by the addition of metals.
2. Graphitization of the carbon matrix of CWC was closely involved with these property changes. Based on X-ray diffraction analysis, it was clear that the graphitization occurred at a lower temperature after addition of aluminum. The amount of aluminum also influenced the graphitization.
3. XPS analysis clearly showed that a carbon-aluminum composite was not left in the sample. This result indicated that the changes in the properties of CWC depend not on the composite of aluminum but on the catalytic effect of aluminum on the graphitization.

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