Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electron microscopic study on catalytic carbonization of biomass carbon: I. carbonization of wood charcoal at high temperature by al-triisopropoxide

Toshimitsu Hata [a], Yuji Imamura [a], Koei Nishimiya [b], Paul Bronsveld [c], Tomas Vystavel [c], Jeff De Hosson [c] & Hikari Kikuchi [d]

[a] Wood Research Institute, Kyoto University, Uji, Kyoto, 611-0011, Japan

[b] Hokkaido Forest Products Research Institute, Nishikagura 1-10, Asahikawa, Hokkaido, 071-0198, Japan

[c] Materials Science Centre, University of Groningen, Nijenborgh 4, Groningen, 9747 AG, The Netherlands

[d] S S Alloy, Kagamiyama, Higashi Hiroshima, 739-0046, Japan

Version of record first published: 18 Oct 2010

Mol. Cryst. Liq. Cryst., Vol. 386, pp. 33–38

1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113150

ELECTRON MICROSCOPIC STUDY ON CATALYTIC CARBONIZATION OF BIOMASS CARBON: I. CARBONIZATION OF WOOD CHARCOAL AT HIGH TEMPERATURE BY AL-TRIISOPROPOXIDE

Toshimitsu Hata and Yuji Imamura
Wood Research Institute, Kyoto University, Uji, Kyoto 611-0011, Japan

Koei Nishimiya
Hokkaido Forest Products Research Institute, Nishikagura 1-10, Asahikawa, Hokkaido 071-0198, Japan

Paul Bronsveld, Tomas Vystavel, and Jeff De Hosson
Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Hikari Kikuchi
S S Alloy, Kagamiyama, Higashi Hiroshima 739-0046, Japan

Currently, carbonized materials from wood or waste have been focused upon as raw materials for carbons. These carbons are important for the production of artificial graphite. First hand observation was done on the growth of long parallel graphite structures in wood charcoal [1]. A comparison is made between graphitization in pure biomass carbon and catalytic graphitization in biomass carbon suspended in Al-triisopropoxide. Both types of samples were carbonized during 5 min under an argon pressure of 50 MPa at temperatures up to 2500 Kelvin. Catalytic graphitization was developed by formation and dissociation of plate like Al_4C_3, but only at temperatures higher than 2000 K.

Keywords: catalytic graphitization; transmission electron microscopy; direct pulse heating; Al-triisopropoxide; wood charcoal

INTRODUCTION

The carbonization of wood or waste wood is important in the production of artificial graphite. Wood charcoal transforms into graphite at temperatures around 2700 K rather easily. In the presence of such catalysts as Fe, Co and

Ni the graphitization accelerates and runs at a lower temperature, in the case of solid phase graphitization even below 1700 K [2].

A process of hydrocarbon decomposition and CO disproportionation on Fe-, Co- and Ni- containing catalysts must take place during the carbonization. Similarly, during heating a compressed powder mix of biomass carbon and aluminum graphitization develops by formation and dissociation of plate like Al_4C_3. The well-known structure of merging and interlinking of graphite fibrils was observed preferentially at the higher heat treatment temperatures. At lower temperatures, onion-like graphite was observed, consisting of concentric rings of (002) graphite planes, a distance of 0.34 nm apart [3]. The processing temperature for catalytic graphitization of biomass carbon has been extensively studied [4–6]. The effect of a catalyst is not obvious, while especially contamination by the catalyst itself should be avoided. In the present paper, results are reported on the graphitization of biomass carbon suspended in a solution of Al-triisopropoxide and heat treated at temperatures up to 2500 K.

MATERIALS AND METHODS

Materials

Sugi (*Cryptomeria japonica*) powder was preheated in an electric furnace, increasing the temperature by 4 K/min from room temperature to 773 K in an Argon atmosphere. After the target temperature was reached, the temperature was kept constant for 60 min, and then the furnace was switched off to cool down. Graphitization was studied in the powderized wood charcoal prepared by suspension mixing with Al-triisopropoxide.

Treatment Method

The wood charcoal powder was soaked in 40% isopropyl alcohol solution of aluminum triisopropoxide. After soaking for 24 hrs, the specimen was dried at 378 K for 24 hrs, sieved with a 1.27 mesh size pass, and then graphitized by the direct pulse heating apparatus.

The specimens were given a heat treatment by a direct pulse heating apparatus (Plasman, S S Alloy, Hiroshima). The principle is depicted in Figure 1. Electric pulses and pressure were directly applied to the wood charcoal powder inside the dye. The weight percentage of aluminum was 0, 10, 20 and 30% based on the weight of dry wood charcoal. The graphitizing temperature was from 973 to 2473 K, the reaction time was 5 min and the pressure was 50 MPa.

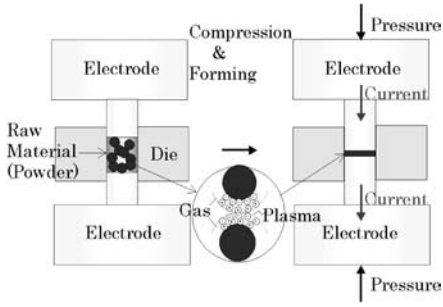

FIGURE 1 Direct pulse-heating apparatus.

Analysis

Composition and nanostructure of the biomass carbon ceramic were examined by transmission electron microscopy (JEOL 2010F with GATAN Imaging Filter and JEOL 4000EX/II) and by scanning electron microscopy (FEI XL30S) to monitor the graphitization of the biomass carbon.

RESULTS

SEM and TEM Analysis

Figure 2 shows the SEM image of pure wood charcoal carbonized at 2273 K for 5 min. Stacking of cell walls were observed. The typical porous wood structure is better maintained at lower temperatures. Figure 3 shows the SEM image of a sample with 20 wt.% aluminum heat treated at 2073 K. The individual droplets are molten aluminum, identified by energy dispersive X-ray spectroscopy. Figure 4 is a SEM image of a sample containing 30 wt.% aluminum heat treated at 1573 K. Judging from this picture one can say

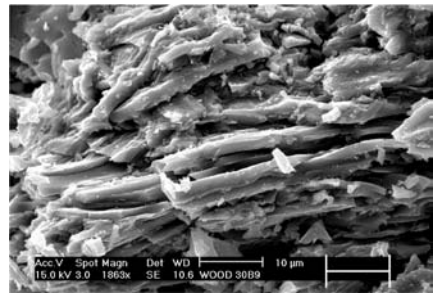

FIGURE 2 Pure charcoal; 5 min at 2273 K.

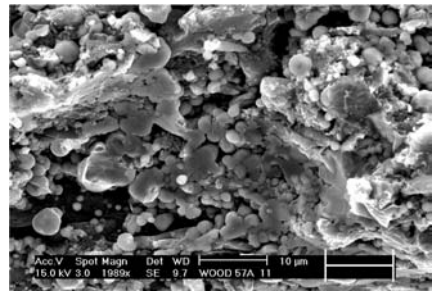

FIGURE 3 Charcoal with 20% Al-triisopropoxide; 5 min at 2073 K.

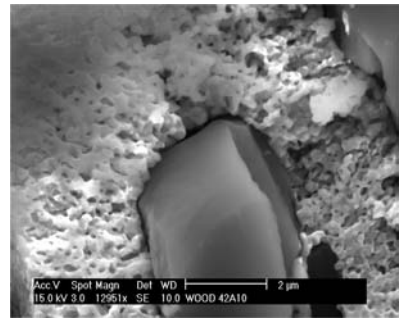

FIGURE 4 Carbon particle surrounded by Al_2O_3 in charcoal with 30% Al-triisopropoxide; 5 min at 1573 K.

that wetting or even a reaction between carbon and aluminum has not taken place. Also TEM images were collected revealing the effect of aluminum reacting with carbon at several concentrations and temperatures.

Figure 5 is the EFTEM image of wood charcoal with 20% Al-triisopropoxide carbonized at 1573 K for 5 min. Evidently, Al_2O_3 has been formed. Wetting of the wood particles with aluminum is the most important parameter. Below 2073 K wetting of carbon with aluminum is problematic, as can be concluded from a comparison of Figure 3 with Figure 6 and from Figure 4 with Figure 5. However, it does not constitute a problem at 2473 K as can be appreciated from a comparison between Figures 7 and 8.

High-resolution electron micrographs of the 002 lattice fringes of graphene were imaged in all samples. The well-known structure of merging and interlinking of graphitic fibrils was observed preferentially at higher heat treatment temperatures (Fig. 6). Even at a temperature of 2473 K (Fig. 7), a random structure was observed, typical for wood charcoal. However, in the sample containing 10% Al-triisopropoxide and carbonized

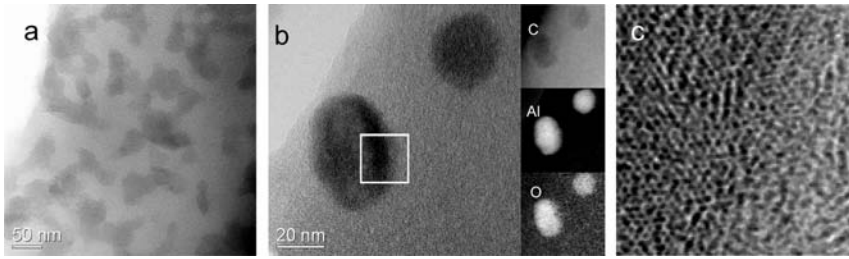

FIGURE 5 Charcoal with 20% Al-triisopropoxide; 5 min at 1573 K, a) overview showing dispersed catalytic particles; b) two Al_2O_3 particles and elemental mapping for Carbon, Aluminum and Oxygen; c) detail from Figure b (white frame).

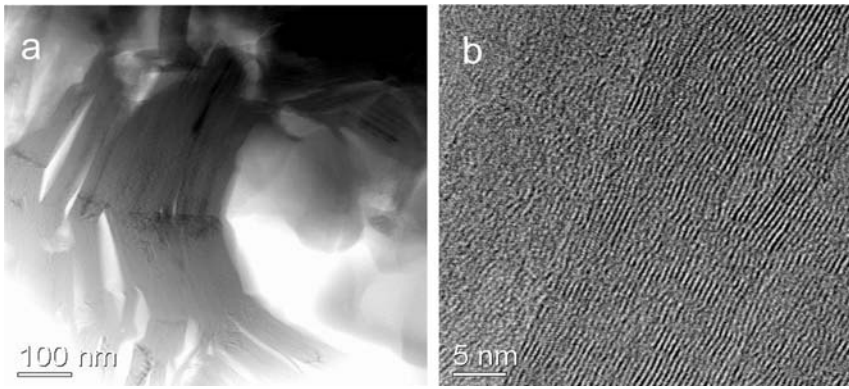

FIGURE 6 Charcoal with 20% Al-triisopropoxide; 5 min at 2073 K. a) overview; b) graphitized structure.

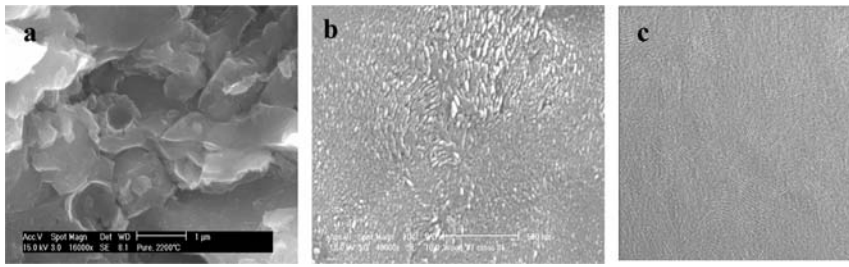

FIGURE 7 Pure charcoal; 5 min at 2473 K. a) top view, b) side view, c) random structure.

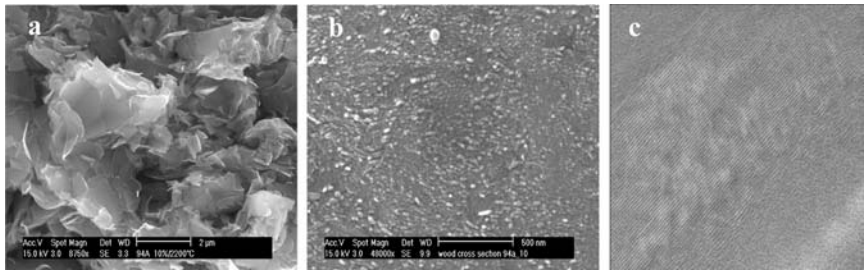

FIGURE 8 Charcoal with 10% Al-triisopropoxide; 5 min at 2473 K. a) top view, b) side view, c) graphitized structure.

at 2473 K (Fig. 8), one could observe graphite crystallites while almost all aluminum has disappeared.

DISCUSSION

According to Yu *et al.* [7] graphitization develops catalytically by formation and dissociation of plate like Al_4C_3.

$$2Al_2O_3 + 9C(s) \rightarrow Al_4C_3(s) + 6CO(g) \quad (1)$$

$$Al_4C_3(s) \rightarrow 4Al(g) + 3C\ gr(s) \quad (2)$$

The most important point is to establish the equilibrium condition [7] as written explicitly in Eqs (1) and (2). It is important to force the wood particles to transform into the plate like Al_4C_3 while CO is being formed. The high temperature–high pressure carbonising step may be instrumental in achieving the same result with Al_2O_3 powder particles as was obtained with Al triisopropoxide.

REFERENCES

[1] Hata, T., Yamane, T., Kobayashi, E., Imamura, Y., & Ishihara, S. (1998). *J. Wood Science*, *44*, 332–334.
[2] Krivoruchko *et al.* (2000). *Carbon*, *38*, 1075–1082.
[3] Hata, T., Imamura, Y., Kobayashi, E., Yamane, T., & Kikuchi, K. (2000). *J. Wood Science*, *46*, 89–92.
[4] Oya, A., Yamashita, R., & Otani, S. (1978). High Temperatures–*High Pressures*, *10*, 511–520.
[5] Oya, A., Yamashita, R., & Otani, S. (1978). High Temperatures–*High Pressures*, *10*, 521–526.
[6] Oya, A. & Marsh, H. (1982). *J. Materials Science*, *17*, 309–322.
[7] Yu, J. K., Ueno, S., Li, H. X., & Hiragushi, K. (1999). *J. Eur. Cer. Soc.*, *19*, 2843–2848.