

CHARACTERIZATION FOR SP²- AND SP³-BONDED CARBON IN WOOD CHARCOAL

Kengo Ishimaru, Daiwa House Industry Co. Ltd., Sakyo, Nara 631-0801, Japan

Toshimitsu Hata, Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji 611-0011, Japan

Paul Bronsveld, Department of Applied Physics, University of Groningen, 9747 AG Groningen, The Netherlands

Takashi Nishizawa, Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama-shi, Kanagawa 226-8503, Japan, Japan

Yuji Imamura, Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji 611-0011, Japan

Abstract

We have previously reported that the sp³-bonded carbons such as nano diamond in addition to sp²-bonded carbons are formed in wood during the carbonization process. The qualification of sp³-bonded carbons in carbonized wood has not been discussed extensively as of yet. In the present paper, the microstructural change of Japanese cedar precarbonized at 700°C in a laboratory-scale electric furnace and subsequently heated to between 1200 and 1800°C by pulse current heating was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and micro Raman spectroscopy.

The amount of amorphous phase decreases considerably with an increase in heat treatment temperature to 1400°C, while carbon crystallites develop clearly above this temperature, showing that 1400°C is a rather critical temperature at which the microstructure of carbonized wood undergoes drastic changes. The microstructure then consists of a combination of sp²- and sp³-bonded carbon. It is suggested that the sp³-bonded carbon is formed from an amorphous to a nano crystalline structure with the growth of polyaromatic stacks at temperatures mainly from 1400°C upwards.

Introduction

Carbon materials are classified in terms of their graphite-related and diamond-related carbon structures. The former is composed of stacking graphene layers based on sp²-bonded carbon atoms; the latter consists of sp³-bonded carbon atoms involved in tetrahedral bonding geometry. The microstructure of carbonized wood is partly amorphous and partly crystalline depending on heat treatment with cross-linking and oxygen-containing functional groups playing an important role.

We have previously reported that the sp³-bonded carbons such as nano diamond in addition to sp²-bonded carbons are formed in wood during the carbonization process (Ishimaru et al, 2001), but qualification of sp³-bonded carbons in carbonized wood has not been discussed extensively as of yet.

In the present study, the structural change of sp²- and sp³-bonded carbon in carbonized Japanese cedar wood with an increase of heat treatment temperature from 700° to 1800°C were characterized mainly by micro Raman spectroscopy.

Experimental

Wooden blocks of Japanese cedar (*Cryptomeria japonica*) with dimensions of approximately 20 (L) by 12 (R) by 12 (T) mm and organosolve lignin powder (passing 200 mesh, Alcell Technologies) dried at 105°C for 24 h were heated to 700°C with a heating rate of 4°C/min in a laboratory-scale electric furnace. The temperature was kept constant for 1 h in a N₂ gas flow and then the sample was cooled to room temperature. After this preheating treatment at 700°C in a graphite mold, the main heating was from room temperature to target temperatures of 1200°, 1400°, 1600°, and 1800°C at a heating rate of 15°C/min. Here the temperature was kept constant for 30min in a current-heating device (VCSP-II, S S Alloy, Hiroshima) under vacuum (Castro et al, 2004). The electric current was applied directly to the sample through a graphite die. Lignin powder preheated at 700°C was heated to only 1800°C.

Raman spectra of the carbonized samples were recorded at room temperature with a Renishaw in Via Raman spectroscopy equipped with an air-cooled CCD detector. An argon laser ($\lambda=514.5\text{nm}$) was adopted as an excitation source and was focused to approximately 1 μm in diameter at a power of less than 1 mW at the sample surface. The Raman spectra were recorded more than three times for each analysis point in order to check sample damage by laser irradiation and at three different points on the same sample under the same measuring condition to avoid spurious changes in spectral intensities. All Raman spectra were measured in the 1000-1800 cm^{-1} zone and fitted using five Gaussian/Lorentzian curves. The wave number was calibrated using the 520 cm^{-1} line of a silicon wafer.

Results and discussion

The carbon structure was characterized by micro-Raman spectroscopy. Figure 1a and 1b show the Raman spectra in the range of 1200-1800 cm^{-1} and 900-1300 cm^{-1} , respectively (Ishimaru et al, 2001). Two Raman bands for carbonized samples were distinctive at 1345-1355 cm^{-1} and 1585-1600 cm^{-1} , corresponding to the in-plane vibrations of sp²-bonded carbon with structural imperfections (D band for disorder) and the in-plane vibrations of sp²-bonded crystalline carbon (G band for

graphite), respectively (Katagiri, Ishida and Ishitani 1988). Indications for a D' band at 1620cm^{-1} and a D'' band in the range $1500\text{-}1550\text{cm}^{-1}$ were also detected in the Raman spectra. The D'' band around $1500\text{-}1550\text{cm}^{-1}$ is associated with an amorphous sp^2 -bonded carbon (Jawhari, Roid and Casado, 1995).

Besides peaks for sp^2 -bonded carbons also a shoulder assigned to sp^3 -bonded carbon was observed. Similar results for sp^3 -bonded carbon have been reported before in carbon black and wood charcoal (Ishimaru et al, 2001; Pantea, 2001). It has been suggested that the microstructure of non-graphitic carbon is most often made of sp^2 - and sp^3 -bonded carbons (Kaneko et al, 1992; Schroeder, 2002). The sp^3 -bonded carbons are closely related to the cross-linking between adjacent carbon crystallites (Kercher and Nagle, 2003). The orientation and growth of carbon crystallites are then impeded by the cross-linking between the carbon atoms at temperatures as high as 2000°C (Franklin, 1951). Oxygen-rich and hydrogen-poor carbon precursors such as wood form hard carbon due to the development of cross-linking at the early stages of carbonization (Oberlin, Villey and Combaz, 1980). The oxygen content of wood is much higher than that of other carbon precursors of hard carbons which are rich in oxygen, such as lignin, polyfurfuryl alcohol, and phenolic polymers (Ishimaru et al, in press b); Fitzer and Schafer, 1970). The Raman spectra of carbonized lignin at 1800°C , as seen in Figure 2, show sharp G and D bands and no sp^3 band. The FWHM of the Raman G band of carbonized lignin at 1800°C is only 21 cm^{-1} , compared with 50 cm^{-1} for carbonized wood which means that carbonized wood contains much more disordered carbon crystallites than do other hard carbons such as lignin. Thus, sp^3 -bonded carbons develop due to cross-linking in the microstructure of carbonized wood and disturb the graphitic ordering of the carbon crystallites even at high temperature.

In conclusion, the initial amount of the amorphous phase in carbonized wood decreases considerably with an increase in heat treatment temperature up to 1400°C , while carbon crystallites develop clearly above this temperature, showing that 1400°C is a rather critical temperature at which the microstructure undergoes drastic changes. The microstructure consists of a combination of sp^2 - and sp^3 -bonded carbon. It is suggested that the sp^3 -bonded carbon is formed from an amorphous to a nano crystalline structure with the growth of polyaromatic stacks being dominant at temperatures mainly from 1400°C upwards, while cross linking being a minor opposing factor.

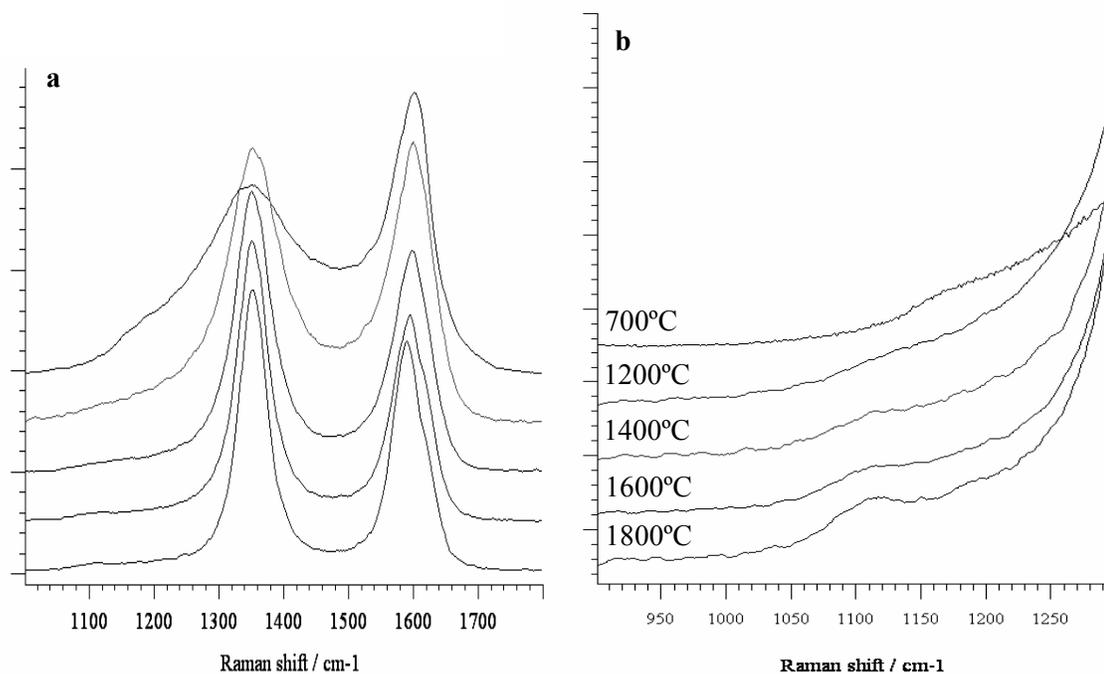


Figure 1. Raman spectra of carbonized wood in the range from 1000 to 1800 cm^{-1} (a) and 900 to 1300 cm^{-1} (b) (Ishimaru et al, in press a).

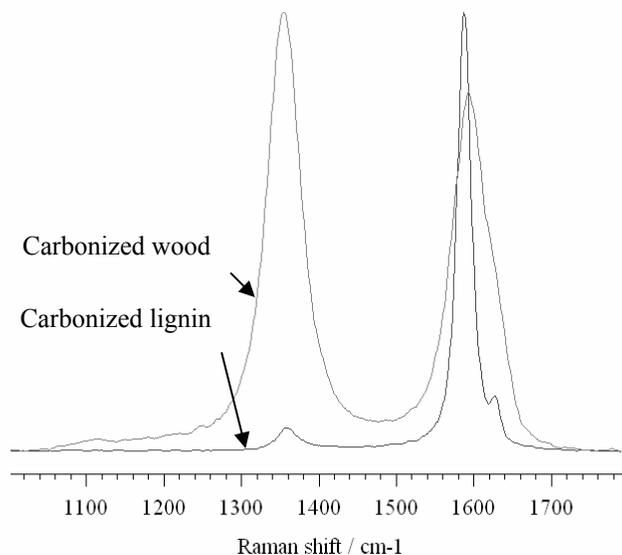


Figure 2. Raman spectra of carbonized wood and lignin at 1800°C (Ishimaru, et al in press a).

Acknowledgements

This research was carried out with support from Grant-in-Aid for Scientific Research (14002121 and 18380107) from the Ministry of Education, Science, and Culture of Japan.

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