

Raman spectroscopy of wood-based C-C composite materials (woodceramics)

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Structure of wood-based C-C composite materials, which is called as woodceramics, was studied by raman spectroscopy and X-ray diffraction. Samples were prepared by heating the Medium-Density-Fiber (MDF) boards impregnated with phenol resin at the temperature ranging from 600 to 1200°C in an evacuated electric furnace. Ordered structures were discussed by measuring powder X-ray diffraction. The samples prepared in this study had amorphous structure with only short-range order along *c*-axis. Disordered structures were studied by raman spectroscopy. In this study, the samples prepared at low temperature contain three kinds of carbon: crystallized graphite-like carbon, amorphous carbon and polycyclic aromatic compound. Fraction of these components varied with increasing heat treatment temperature. At the temperature range between 600 and 800°C, fraction of the amorphous components increased with increasing heat treatment temperature and the graphite components neither increase nor decrease. Two unknown peaks were obtained in these raman spectra. It is likely that these peaks are caused by adsorbed molecule.

Key words: raman spectroscopy, woodceramics

1. INTRODUCTION

Wood-based C-C (Carbon-Carbon) composite materials called as "Woodceramics" are new carbon materials, developed by Okabe *et al* [1]. This C-C composite is prepared by heating the Medium-Density-Fiber (MDF) boards, which are generally used for furniture, impregnated with phenol resin in an evacuated furnace. This composite material has two different components. One is the porous carbon originated from the wood. The other is a kind of "hard carbon" originated from phenol resin. The composite with two different structure of carbons shows various properties: mechanical [2], electrical [3], electromagnetic [4] *etc.*

Recently, the frequency range of the EM-wave used by various consumer electronics products has increased for broadband communication and high speed signal processing. Consequently, it is needed for industries to develop the method to control the EMI (Electro Magnetic Interference) at high frequency (above GHz band). There is fear for the damage in the security, health, safety and economy, which is caused by the unnecessary EM-wave. One of the solutions for this problem is to absorb the unnecessary EM-waves with the materials, which can transform the electromagnetic energy to thermal energy. Thus, the development of EM-wave absorbing materials suitable for the frequency above GHz band is important.

We have previously reported the EM-wave absorption characteristics at the frequency above GHz band of the wood-based C-C composite materials [5,6], synthesized at relatively low temperature. The crystal structure, electric properties and microstructure of these C-C composite materials has already investigated, and

reported as follows that the remarkable EM-wave absorption characteristics were caused by micro electric polarization in the C-C composite materials and the composite is one kind of artificial dielectric system [6].

However, the relation of the EM-wave absorption characteristics with structure of materials is still not fully understood because of crystal structure, which determined from measurement of X-ray diffraction, of these C-C composite materials are nearly amorphous, and hard to discuss the structural difference between samples prepared at different conditions.

In the present paper, short-range correlated structure of these C-C composite materials is investigated by raman spectroscopy. Structural change of these materials as a function of heat treatment temperature, and the relation of electromagnetic properties with structure are also discussed.

2. EXPERIMENTAL PROCEDURE

The samples were prepared by heating the Medium-Density-Fiber (MDF) boards impregnated with phenol resin at the temperature range between 600°C and 800°C for 4h in an evacuated (~50mmHg) electric furnace. Powder X-ray diffraction measurements were carried out for determination of crystal structures of the prepared samples with the diffractometer (Model RINT-1500, Rigaku), using Cu-K α radiation. Raman spectroscopy measurements were carried out for characterization of short-range ordered structure in two-dimensional graphite layers with the Raman spectrometer (Model T64000, Jobin Yvon), using Ar ion laser ($\lambda=514.5\text{nm}$). Electrical resistivity was measured for the samples with a typical dimension of 3.0 x 3.0 x 20.0 mm³, with a DC current *I* of 0.001 ~ 5 mA in a

four-probe configuration. Microstructures were observed with the Scanning Electron Microscope (Model JSM-5310, JEOL). Material's response to RF were determined from measurements of S -parameter at the frequency range between 50 MHz and 18 GHz with the vector network analyzer (Model 8720ES, Agilent Technology). The S -parameter measurements were performed by coaxial method for the cylindrical shaped samples with inner diameter of 3 mm and outer diameter of 7 mm. The relative complex permittivity $\epsilon_r (= \epsilon' - j\epsilon'')$ were calculated from the values of measured S -parameter (reflection: S_{11} , S_{22} and transmission: S_{12} , S_{21}). EM-wave absorption characteristics were estimated by calculation of the incident impedance Z_{in} and reflection coefficient S_{11} for various depth d from the surface of metal backed materials.

3. RESULTS AND DISCUSSION

Figure 1 shows the relation between heat treatment temperature and observed background intensity of raman scattering from the powder samples of wood-based C-C composite materials, measured under the same conditions (laser power, diameter of focused laser, grading, and acquisition time). Observed background intensity decreased with increasing heat treatment temperature. The decrease in background intensity is attributed to increase of reflection, which is due to screening by the conduction electron, of incident laser beam at the sample surface. This result suggests that the amount of conduction electron increase with increasing heat treatment temperature. This is consistent with the measurement of electric resistivity in our previous publication [6].

Figure 2 shows observed and calculated raman spectra for the wood-based C-C composite materials prepared at various temperatures. All raman spectra showed characteristic profile, which are often observed in amorphous carbonaceous materials. Roughly speaking, these spectra consisted of two intense broad bands at 1350 and 1580 cm^{-1} , which are assigned to the D and G bands of microcrystalline graphite [7].

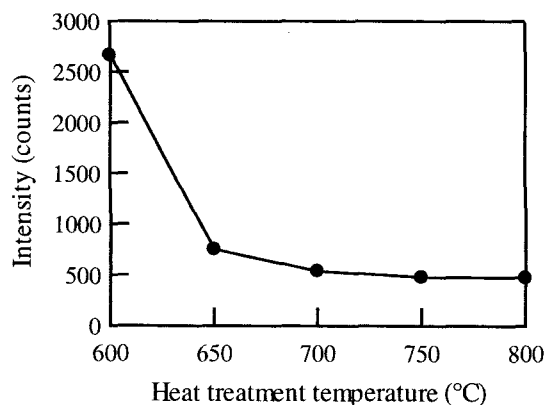


Fig. 1. Relation between heat treatment temperature and observed background intensity of raman scattering from powders of the wood-based C-C composite materials.

Raman spectra of carbon in the samples prepared in this study resolved by peak fitting using the pseudo-Voigt function which is sum of Gaussian and Lorentz as a peak profile function. However, peak fitting with two bands (D and G) did not give accurate solution.

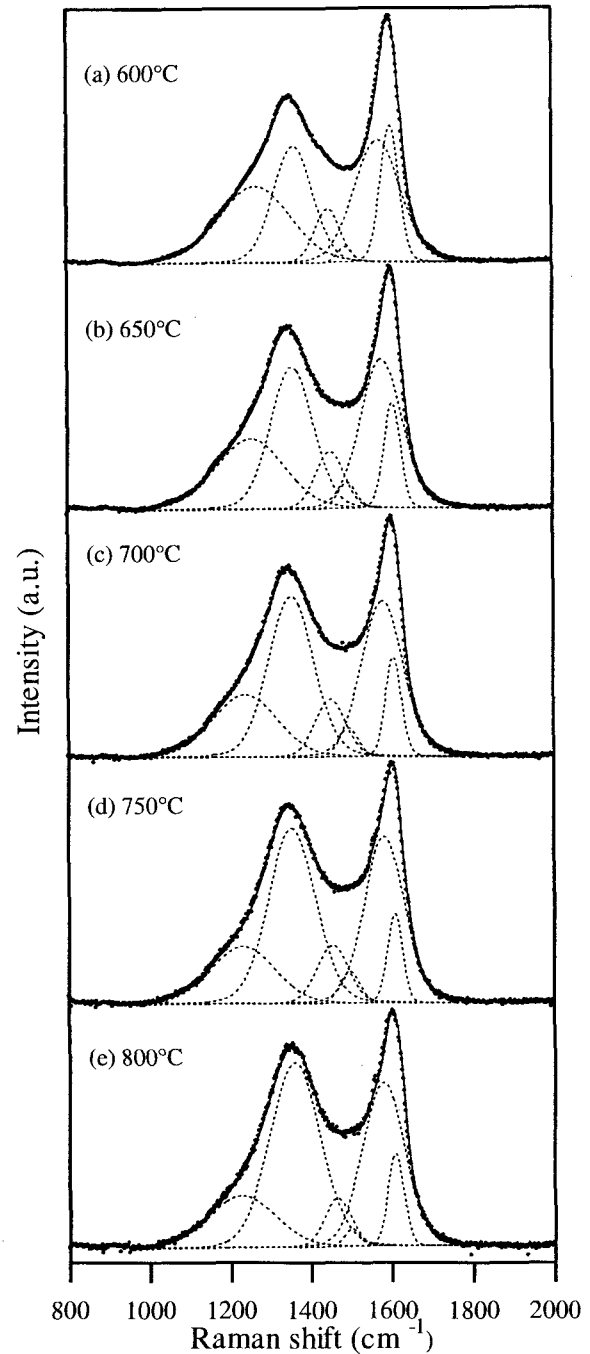


Fig. 2. Raman spectra for the wood-based C-C composite materials obtained by heat treatment at various temperatures. Experimental values are denoted by closed circles. Solid line shows total calculated spectra which are obtained by combining six peaks (broken line).

Table 1 Values of raman shift for various samples and assignment.

Raman shift (cm^{-1})						Assignment
600°C	650°C	700°C	750°C	800°C	Graphite	
1268	1254	1238	1231	1226	–	Benzene nucleus?
1363	1357	1353	1353	1358	1360	D
1448	1451	1450	1454	1465	–	Adsorbed molecule?
1492	1494	1495	1497	1500	–	O ² ?
1578	1579	1579	1582	1578	1583	G
1602	1605	1606	1608	1608	–	Benzene nucleus?

To account for the observed raman spectra with minimum error, six bands were required. The raman shift of these six bands are 1220 ~ 70, 1360, 1450, 1490, 1580 and 1605 cm^{-1} . The values of raman shift for the samples prepared at various temperatures and assignment are summarized in Table 1.

The band at 1580 cm^{-1} can be assigned to the E_{2g} mode, which is the vibration of carbon with hexagonal symmetry in two-dimensional graphite layer. The band at 1360 cm^{-1} can be assigned to be the A_g mode excited by the decline of symmetry at the edge of the two-dimensional graphite layer. Wave number of raman shift for these two raman bands had no dependence on heat treatment temperature.

It is possible that the band at 1220 ~ 70 and 1606 cm^{-1} are due to the mixture of various polycyclic aromatic compounds. The band at 1220 ~ 70 cm^{-1} , which is often observed in raman spectra for poorly crystallized carbon materials such as mesophase pitch, seems to be related the stretching vibration of C = C double bond in benzene nucleus. Raman shift of this band shifted to lower wave number with increasing heat treatment temperature. This shift suggests that the progress of condensation polymerization between components which included in mixture of various polycyclic aromatic compounds.

The band at 1605 cm^{-1} may be attributed to the breathing mode of benzene nucleus. The bands at 1450 and 1490 cm^{-1} could not identify as the raman band of carbon-related compound. The value of raman shift such as 1490 cm^{-1} is close to that of gaseous oxygen molecule. Thus, these bands may be due to the adsorbed gaseous molecules. However, details of these bands are not clarified at the present stage.

Figure 3 shows relations between heat treatment temperature and relative integrated intensities of the six raman bands. Relative integrated intensities were calculated from the parameters obtained by peak fitting of observed raman spectra. It is shown that the intensity of D band (closed circle) increase with increasing heat treatment temperature, however, the intensity of G band (closed square) shows no change. Intensities of two bands (closed and open upper triangles), which assigned as the band associated with polycyclic aromatic compounds, decreased with increasing heat treatment

temperature. From the results mentioned above, we can conclude that most of the structural change at the temperature range between 600°C and 800°C is promotion of incomplete disordered two-dimensional graphite layer from benzene nucleus in various polycyclic aromatic compounds and the growth of two-dimensional graphite layer with hexagonal symmetry hardly occurs. It is possible that the increase of electroconductive two-dimensional graphite layer with decrease of insulating aromatic compounds brings drastic change in electrical resistivity.

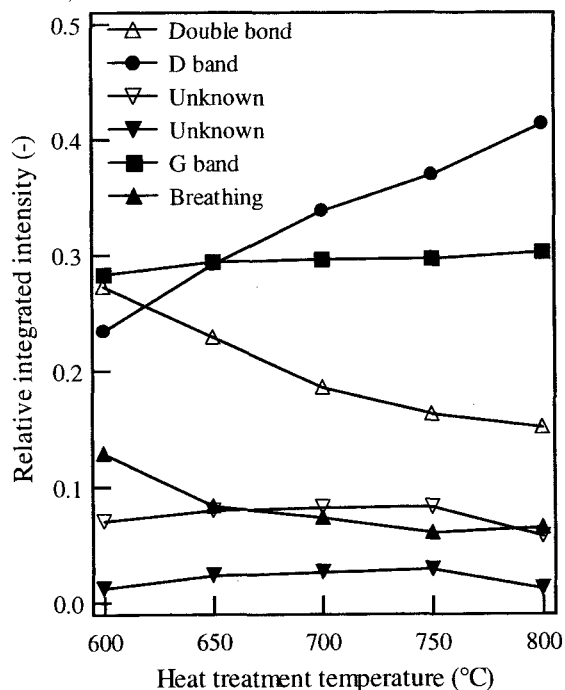


Fig. 3. Relations between heat treatment temperature and relative integrated intensities of the six raman bands calculated from the parameters obtained by peak fitting of observed raman spectra.

The intensities of two unidentified bands (closed and open down triangles) showed no dependence on heat treatment temperature.

4. CONCLUSIONS

Short-range correlated structure, which could not detect by X-ray diffraction, of the wood-based C-C composite materials prepared at relatively low temperature range between 600°C and 800°C is investigated by raman spectroscopy. Structural change of these materials was discussed as a function of heat treatment temperature.

Possible model of structural change and the relation with electrical properties are described as follows.

The electroconductive incomplete disordered two-dimensional graphite layer is promoted from benzene nucleus in various insulating polycyclic aromatic compounds and the enhancement of electroconductive region causes drastic change in electrical resistivity.

The behavior of two unknown bands observed in measured raman spectra suggests adsorb of specific gaseous molecules. It shows possibility of new application of wood-based C-C composite materials (woodceramics) as the useful functional porous materials.

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References

- [1] T.Okabe, "Woodceramics", Uchida Roukakuho Co. Ltd. (1996) *in Japanese*.
- [2] T.Okabe and K.Saito, *J. porous mater.*, **2**, 223-228 (1996).
- [3] K.Kakishita, T.Suda and H.Irisawa, *Trans. Mater. Res. Soc. Japan*, **25**, 705-708 (2000).
- [4] K.Shibata, Abstract of 11th symposium of MRS-J., p.36 (1999) *in Japanese*.
- [5] M. Miki, T. Kikuchi, M. Nakamura, K. Hatakeyama, and J. Takada, *Trans. Mater. Res. Soc. Japan*, **26**, 867-870 (2001).
- [6] T. Kikuchi, M. Miki, M. Nakamura, K. Hatakeyama, M. Nakanishi, and J. Takada, *Proc. 10th International Ceramics Congress, Part-D*, Ed. By P. Vincenzini, 523-530 (2003).
- [7] F. Tuinstra, and J. L. Koenig, *J. Chem. Phys.*, **35**, 1126-1130 (1970).

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