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Crystalline Control of Bincho Charcoal by using Catalytic Graphitization and Electromagnetic Wave Absorption Characteristics of Derived Carbon

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Effects of carbon crystallinity derived from Fe-loaded Bincho charcoal (Fe-BC) on relative complex permittivity have been studied as a function of the heat treatment temperature of Fe-BC. Formation of turbostratic carbon was clearly observed in X-ray diffraction patterns for the Fe-BC samples heat-treated above 700°C. Relative complex permittivity of various Fe-BC dispersed in paraffin (Fe-BC-P) was measured by using the S-parameter method. Relative complex permittivity of Fe-BC-P was increased with increasing the heat treatment temperature of Fe-BC.

Electromagnetic wave absorption of the Fe-BC-P were dependent on crystallinity and volume fraction of the Fe-BC in paraffin. By using our proposal function, relative complex permittivity of various Fe-BC-P compounds was found to be estimable. In combination with no-reflection curve and our proposed function curve, we can estimate optimum volume fraction and matching thickness of Fe-BC-P composites designed for wave absorbers at 5 GHz. The observed absorption characteristics of Fe-BC-P were sufficiently consistent with the designed ones on the basis of above calculations.

Key words: Charcoal, Composite, X-ray diffraction, Permittivity, Electromagnetic Wave Absorption

1. INTRODUCTION

Developments of electromagnetic wave absorbers are required to reduce the electromagnetic interference with electric devices such as wireless LAN (Local Area Network) and ETC (Electronic Toll Collection).Carbon composites hybridized with rubber are widely used for electromagnetic wave absorbers for higher frequency (GHz)[1]. Absorption characteristics are usually controlled by the type of carbon source and the carbon content in rubber [2-4]. However, there are few studies to control the absorption characteristics of carbon composites by changing the crystallinity of carbon sources.

In this study, we investigated the effects of crystallinity of carbon source derived from Fe-loaded Bincho charcoals (Fe-BC) on their permittivity and microwave absorption characteristics. The crystallinity of carbon could be controlled by the heat treatment procedures of Fe-BC [5, 6]. By revealing a relationship between the crystallinity and permittivity of carbon sources, it is possible to make non-empirical estimation of absorption characteristics of the carbon composites.

2. EXPERIMENTAL

Fe-loaded Bincho charcoals (Fe-BC) were prepared by using following procedure. Commercial Bincho charcoal (average diameter: 1.0 mm) was impregnated with an aqueous solution of $Fe(NO_3)_3$ (1.0 mol dm^{-3}) at room temperature for 24 hours. That charcoal was filtrated, and naturally dried at room temperature for 1 week. After that, the charcoal was thermally dried at 110°C for 1 hour and heated at temperature range of 500 - 900°C for 1 hour in N_2 gas flow (0.3 dm^{-3} min).

The various Fe-BC were characterized by an X-ray diffraction (XRD) technique using Cu $K\alpha$ radiation (RIGAKU RINT-2500). The precise d-spacings of carbon matrix were determined by using Si powder as an internal standard. The amount of iron content in the Fe-BC was determined by X-ray fluorescence analysis (XRF) (RIGAKU ZSX100s). The real density was measured by the helium displacement method (QUANTACHROME Ultra Pycnometer).

Fe-BC were ground and sieved to a size of 32-63 μm. After that the Fe-BC powders were dispersed in paraffin (melting point 70-72°C, relative complex permittivity ε_r^*=2.2) with different Fe-BC contents of 10 vol%, 16 vol% and 23 vol%. The Fe-BC composites with paraffin (Fe-BC-P) were molded into a cylindrical shape with outer and inner diameters of 7.0 mm and 3.0 mm, respectively. Both of relative complex permeability and permittivity of Fe-BC-P were evaluated by the S-parameter method in frequency range from 1 to 10 GHz by using a network analyzer (HEWLETT PACKARD HP8720D).

3. RESULT AND DISCUSSION

3.1 Characterization of Fe-BC

XRD patterns pure and Fe-loaded Bincho Charcoals obtained at different heat treatment temperatures were shown in Fig. 1. It is clearly observed that impregnated Fe into Bincho Charcoal was crystallized to Fe_3O_4 for the sample (Fe-BC500) after heat-treated at 500°C. On the other hand the Fe-BC samples (Fe-BC700 and

Fe-BC900) heat-treated at 700°C and 900°C contained metallic iron of both α-Fe and γ-Fe phases. Obtained iron phases and iron content are summarized in Table I.

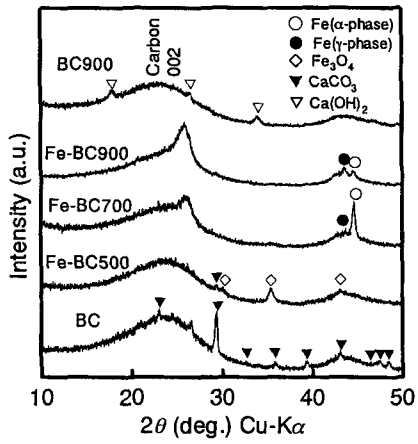

Fig. 1 XRD patterns of pure and Fe-loaded Bincho charcoals obtained at different heat treatment temperatures. BC is commercial pure Bincho charcoal without heat treatment. Fe-BC500, Fe-BC700 and Fe-BC900 are Fe-loaded Bincho charcoals heat-treated at 500°C, 700°C and 900°C, respectively. BC900 is pure Bincho charcoal heat-treated at 900°C.

Pure BC without Fe-impregnation had amorphous carbon structure even after the heat treatment at 900°C. However the carbon matrix of Fe-BC was partly crystallized to turbostratic carbon after the heat treatment above 700°C. All XRD patterns had one intense but broad diffraction line at about 2θ=25.4°, which was assigned to (*002*) diffraction line of amorphous carbon. While the (*002*) line of turbostratic carbon appeared at about 2θ=26° for the samples of Fe-BC700 and Fe-BC900, and its intensity was increased with increasing heat treatment temperature. Presence of Fe-metal seemed to produce the catalytic graphitization of BC even at relatively low temperature. After the correction of XRD intensity by atomic scattering factor, Lorenz-polarization factor and absorption coefficient, (*002*) diffraction peaks of both amorphous and turbostratic carbon were deconvoluted with each other by the least squared fitting with Pearson type VII functions. The crystalline size of carbon matrix along the *c* axis, L_c, was determined by using the Sherrer formula [7]. Structural parameters of d_{002}-spacing and L_c for each carbon component are summarized in Table II.

Table I Characteristics of Bincho charcoals used for electromagnetic wave absorption measurements.

Sample name	Impregnation solution	Heat-treatment temperature (°C)	Supported compounds	Metal content (mass%)
BC		Commercial		
Fe-BC500		500	Fe_3O_4	1.6
Fe-BC700	$Fe(NO_3)_3$	700	α-Fe, γ-Fe	1.8
Fe-BC900		900	α-Fe, γ-Fe	0.9
BC900	–	900	–	–

Table II Structural parameters determined by powder X-ray diffraction profiles. (A) and (T) in this table indicate amorphous component and turbostratic component, respectively.

Sample name	d_{002} (nm)	L_c (nm)
BC	0.349	1.2
Fe-BC500	0.347	1.2
Fe-BC700	(A) 0.350	1.1
	(T) 0.341	6.5
Fe-BC900	(A) 0.350	1.1
	(T) 0.342	5.4
BC900	0.349	1.2

Crystallinity of carbon matrix of Fe-BC was gradually changed from amorphous carbon at 500°C to turabostratic one at 700°C. But the structural parameters of both amorphous and turabostartic carbon were similar and seemed to be independent of heat treatment temperature. Only the relative intensity of turabostratic to amorphous component was increased with increasing heat treatment temperature. The iron content for Fe-BC samples was at most 1.8 mass%. A very small amount of iron was supported to carbon. Therefore, the iron loading was considerably effective to promote crystallization Bincho Charcoals of carbon matrix.

3.2 Calculation of the permeability and permittivity

Permeability and permittivity of Fe-BC-P composites with different Fe-BC volume fractions to paraffin were evaluated to measure the reflection and transmission coefficients by using a network analyzer, which is known to be S-parameter method. The relative complex permeability μ_r^* and permittivity ε_r^*, described in following equation (1) and (2), respectively, were calculated by Nicolson-Ross method [8].

$$\varepsilon_r^* = \varepsilon'_r - j\varepsilon_r'' \quad (1)$$

$$\mu_r^* = \mu_r' - j\mu_r'' \quad (2)$$

where μ_r' and μ_r'' are real and imaginary parts of μ_r^*, respectively, and ε_r' and ε_r'' are real and imaginary parts of ε_r^*, respectively. Increase in the crystallinity of carbon matrix enhanced the real and imaginary parts of relative complex permittivity as mentioned later. On the other hand, the measured permeability of all Fe-BC-P was very small. As a result, iron had only a function as catalyst to promote the crystallization of carbon matrix and no contribution to magnetic loss permeability.

3.3 Design of Electromagnetic wave absorber and absorption characteristics

According to the calculation results by Nicolson-Ross method, Fe-BC-P composites were considered to be dielectric loss material without magnetic loss. The complex permeability of them should be fixed to μ_r'=1 and μ_r''=0. Therefore the complex permittivity calculated by Baker-Jarvis method [9] was more reliable used to design electromagnetic wave absorber.

In the case of dielectric loss material, the input impedance for metal-terminated absorber Z^* is

$$Z^* = Z_0 \frac{1}{\sqrt{\varepsilon_r^*}} \tanh\left(j\frac{2\pi}{c} f \cdot d\sqrt{\varepsilon_r^*} \right) \quad (3)$$

where Z_0, c, d and f are the characteristic impedance of a vacuum, light velocity, thickness of specimen and frequency, respectively. The reflection coefficient Γ^* is expressed as a following equation.

$$\Gamma^* = \frac{Z^* - Z_0}{Z^* + Z_0} \quad (4)$$

When the reflection coefficient is theoretically zero, $\Gamma^*=0$, this condition is called perfect matching or no-reflection. The perfect matching condition of $Z^*=Z_0$ in Eq. (3) gives,

$$1 = \frac{1}{\sqrt{\varepsilon_r^*}} \tanh\left(j\frac{2\pi}{c} f \cdot d\sqrt{\varepsilon_r^*} \right) \quad (5)$$

If the value of $f \cdot d$ in Eq. (5) is assigned, ε_r^* are calculated for the perfect matching condition. The relationship between the imaginary and real parts of complex permittivity satisfying the perfect matching condition as function of the $f \cdot d$ values is called no-reflection curve.

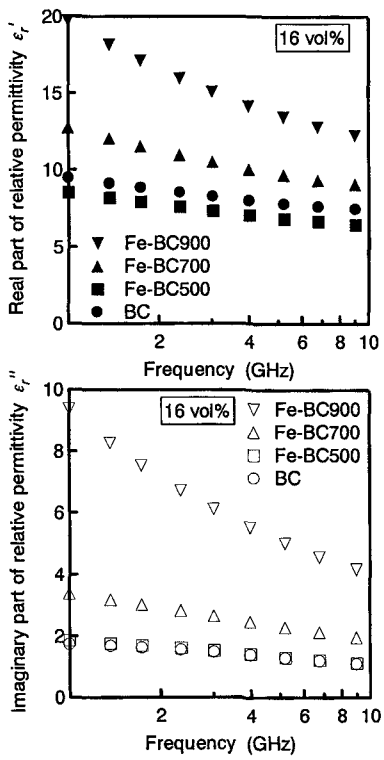

Fig. 2 Relative complex permittivity of the molded samples, 16 vol% content in paraffin

Fig. 2 shows dependencies of relative complex permittivity on frequency of the Fe-BC in paraffin. Both real and imaginary parts of relative complex permittivity were increased with increasing the heat treatment temperature. It was found that the relative complex permittivity was clearly influenced by the crystallinity of Fe-BC. Moreover, with increasing the volume fraction, relative complex permittivity was increased. It is considered that conductivity of Fe-BC composites was increased with increasing the Fe-BC volume fraction.

Dependencies of relative complex permittivity of Fe-BC-P composites on both frequency and volume fraction were considered. We proposed here the following model equations.

$$\varepsilon_r' = a_1 + a_2 \cdot v + a_3 \cdot v^{a_4} \cdot f^{a_5} \quad (6)$$

$$\varepsilon_r'' = b_1 + b_2 \cdot v + b_3 \cdot v^{b_4} \cdot f^{b_5} \quad (7)$$

where a_1 to a_5 and b_1 to b_5 are fitting parameters, v is volume fraction of Fe-BC in paraffin, and d is thickness of molded sample. To combine the no-reflection curve with our model equations, the values of v and d for perfect matching can be estimated.

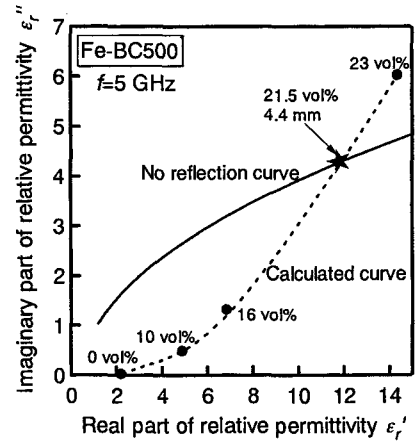

Fig. 3 Typical no-reflection and calculated curves derived from the model equations for the Fe-BC500 samples at the matching frequency of 5 GHz. Optimum volume fraction of 21.5%, and thickness of 4.4 mm are determined from the cross point between two curves.

Fig. 3 shows typical no-reflection and calculated curves derived from the model equations for the Fe-BC500-P samples at the matching frequency of 5 GHz. Optimum volume fraction v of 21.5% and matching thickness d of 4.4 mm were determined from the cross point between two curves. The value of v and d for other Fe-BC samples with different heat treatment temperature are summarized in Table III. The matching thickness of all samples was almost the same within a narrow range between 4.2 to 4.4 mm. This is probably because the volume fraction of the Fe-BC in paraffin was decreased monotonically with increasing the heat treatment temperature of Fe-BC and thus the relative complex permittivity of Fe-BC-P composites was nearly unchanged for all heat treatment temperatures.

Table III Calculated volume fraction and thickness of Fe-BC-P composites designed for electromagnetic wave absorber at 5 GHz.

Sample name	Volume fraction (%)	Thickness (mm)
BC	22.0	4.3
Fe-BC500	21.5	4.4
Fe-BC700	19.5	4.2
Fe-BC900	15.0	4.2

The electromagnetic wave spectrum was theoretically calculated by using following equation.

$$S = 20\log|\Gamma^*| \tag{8}$$

where S is reflection loss. Solid line in Fig. 4 shows a typical absorption spectrum calculated from model specimen having the optimum volume fraction and the thickness in Table III. S = -20 dB means that 99% of incident electromagnetic wave was absorbed. To confirm the accuracy of this calculated spectrum, we have actually prepared the Fe-BC500-P composite with v = 21.5% and d = 4.4 mm and measured the absorption spectrum by means of the metal-terminated Fe-BC500-P. The circle points in Fig. 4 were measured on spectrum of Fe-BC500-P. It was clearly suggested that the measured absorption spectrum was well consistent with the calculated one.

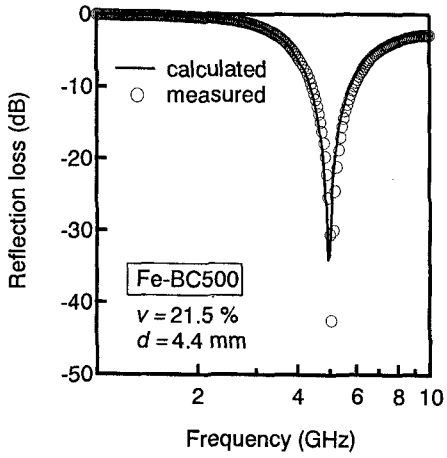

Fig. 4 Frequency dependence of reflection loss of Fe-BC500-P

4. CONCLUSION

Carbon crystallinity of commercial obtained BC with amorphous structure was improved to turbostratic structure after the Fe-impregnation and subsequent heat treatment above 700°C. The relative complex permittivity ε_r^* of carbon matrix of Fe-BC became larger with increasing the heat treatment temperature; BC, Fe-BC500, Fe-BC700, and Fe-BC900 in order. Both the crystallinity and the relative complex permittivity of Fe-BC were controlled by heat treatment temperature.

Dependencies of relative complex permittivity on frequency and volume fraction of the Fe-BC in paraffin were analyzed by using Eq. (6) and (7). The observed absorption characteristics were sufficiently consistent with the designed ones. Our model equations are very useful in design of absorption characteristics of Fe-BC-P composites.

We successfully obtain non-empirical estimation of the optimum volume fraction of Fe-BC in paraffin and the thickness of Fe-BC-P for the electromagnetic wave absorbers in GHz bands.

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