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Effect of Pressure on Graphitization of Carbon. V. Electron Spin Resonance in Hard Carbon Heat-Treated under High Pressure

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By means of the electron spin resonance (ESR), the graphitization process of a hard carbon (phenolformaldehyde resin char) under a pressure of 5 kbar was investigated in relation to the results of the X-ray diffraction analysis. In the ESR measurement, there is observed only a sharp Lorentzian line having g-value of about 2.003 for the products heat-treated at relatively low temperatures. On the other hand, gradual increase in the heat treatment temperature (HTT) leads to the appearance of new 15—20 G wide line having g-value of about 2.01, overlapping on the sharp one, and its absorption intensity tends to increase further with HTT. The appearance of the broad ESR line has been found always being accompanied by an abrupt increase of the content of graphitic component deduced from the analysis of (002) diffraction profile. From further investigation of features of these ESR lines as a function of ambient temperature, the sharp one is concluded that it originates from the so-called localized spin centers, while the broad one from the delocalized. The coexistence of these two signals suggests that the turbostratic and graphitic parts have enough extent to prevent the motional mixing of these spin centers, which has also been verified by the X-ray diffraction analysis.

The graphitization process of carbons under high pressure has recently been studied by Noda and his co-workers[1-5] through an analysis of the profiles of (001) X-ray diffraction lines. In their studies,[1,2,5] every kind of carbons examined was found to be graphitized under high pressure at relatively low temperature such as 1500°C. Furthermore, it has been deduced that the graphitization process of a hard carbon under a pressure of 5 kbar is divided into three distinctive stages[5]: In the first stage, there is observed only one component, A_H, having the so-called turbostratic structure. In the second stage, the new components G'_H and G''_H seem to coexist with A_H, and the total content of G_H' and G''_H, which will hereafter be denoted by G_H, shows a gradual increase up to 20% with the increase in heat treatment temperature (HTT). At the beginning of the third stage, *i. e.*, HTT of 1400, 1500 and 1700°C for the residence time of 60, 20 and 3 min, respectively, the content of G''_H increases so abruptly as to exceed 70%, while G'_H disappears and a small amount of A_H remains still unaltered. Therefore, the sum G_H is equal to the content of G''_H in this stage, and still increases gradually with the increase in HTT towards full graphitization. The components G''_H and A_H are concluded to have the three-dimensional graphitic and turbostratic structures, respectively, but G'_H may be of intermediate structure between the turbostratic and the graphitic.

In the present work, it has been intended to study the electron spin resonance (ESR) in the hard carbons heat-treated under high pressure, making a comparison with the results of X-ray diffraction analysis performed on the same samples.

Experimental and Results

The hard carbon sample PH-7 was prepared at 700°C from phenolformaldehyde resin which was made by a conventional method using ammonium hydroxide as catalyst. Heat treatments of this sample under a quasi-hydrostatic pressure of 5 kbar were performed at various temperatures between 1100—1800°C for residence times of 3, 20 and 60 min. The temperature of heat treatment (HTT) was evaluated from the electric input power, for which the relation between temperature and input power had preliminarily been determined by using chromel-alumel thermocouple. The accuracy of the HTT determination in this way was considered to be ±50°C

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[1] T. Noda and H. Kato, *Carbon,* **3**, 289 (1965).
[2] T. Noda, K. Kamiya and M. Inagaki, This Bulletin, **41**, 485 (1968).
[3] M. Inagaki, K. Kamiya and T. Noda, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.),* **71**, 652 (1968).
[4] M. Inagaki, K. Kamiya and T. Noda, *ibid.,* **71**, 812 (1968).
[5] K. Kamiya, M. Inagaki, M. Mizutani and T. Noda, This Bulletin, **41**, 2169 (1968).

at 1500°C. Details on the sample treatment, *e. g.*, high pressure apparatus, high pressure cell arrangement and heat treatment procedures *etc.* are the same to those reported elsewhere.[3-5]

Through the heat treatment, the sample was sintered into a cylindrical block about 6 mm in length and 4 mm in diameter. An about 2 mm long piece was cut out of the central part, where the temperature gradient was hardly observed during the treatment.[4] A half of each piece was examined with ESR in this work, and another half with the X-ray diffraction analysis previously reported.[5]

The ESR work was conducted mostly at room temperature for finely-ground samples placed in vacuum. DPPH and Mn^{+2}-doped magnesia were used as primary and secondary standards, respectively, to determine the *g*-value of signals. In Fig. 1, the change of the ESR line shape with HTT is shown for the residence time of 3 min. For HTT below 1670°C, a sharp near-symmetrical line is observed around the *g*-value of 2.003. Above 1720°C, however, a new broad signal centered at $g \fallingdotseq 2.01$ turns up and develops with the increase in HTT. At 1770°C, the broad signal becomes so strong that we have to disperse the sample in solid paraffin for making clear the sharp signal (Fig. 1 d). As to the line shape and the width (w), the sharp signal is of Lorentzian type, giving $w \fallingdotseq 2$G, and the broad one considerably Dysonianized gives $w \fallingdotseq 15$ G to 20 G.

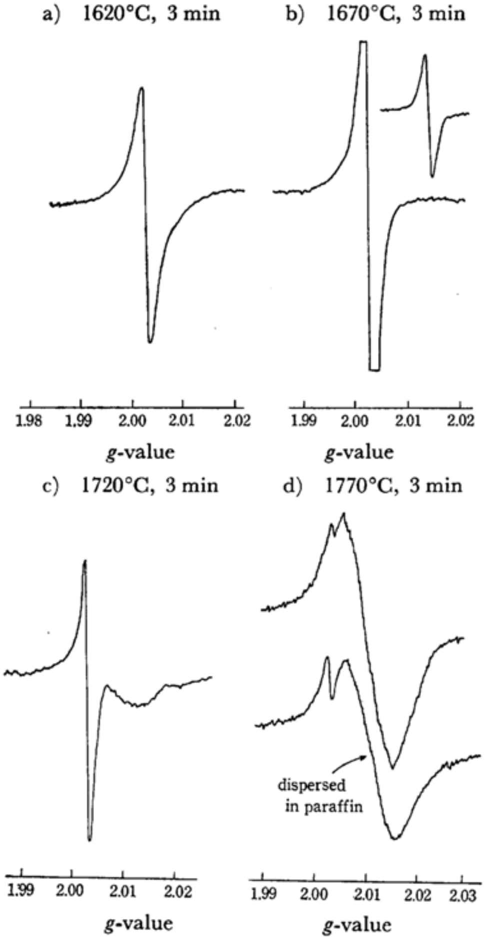

Fig. 1. Change of the line shape of ESR signal of the hard carbon, heat-treated under 5 kbar for 3 min, with HTT.

The critical temperature at which the broad signal appears is strongly dependent on the residence time; *e. g.*, about 1500°C for 20 min, and 1400°C for 60 min. It is noticeable that such critical temperatures are coincident with those at which the content of the component G_H shows an abrupt increase. As shown in Fig. 2, a beautiful correspondence between the results of ESR and X-ray analyses, where the *g*-value and the content of G_H are plotted both as functions of HTT, and the critical points are marked by arrows.

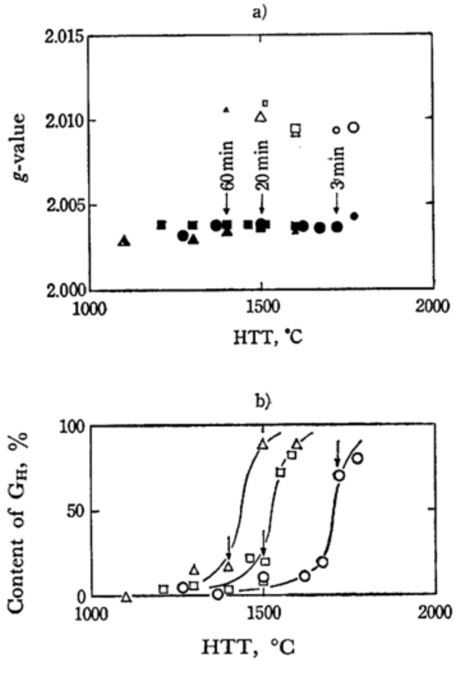

Fig. 2. a) Changes of *g*-values of ESR signals with HTT.

Localized spin	Delocalized spin	
●	○	3 min
■	□	20 min
▲	△	60 min

b) Change of content of the component G_H with HTT.[5]

○ 3 min □ 20 min △ 60 min

In order to obtain further information on the nature of the spin the absorption intensity, line width and *g*-value as functions of ambient temperature were investigated on two typical samples, say A and B, poorly and highly graphitized, respectively. Sample A heat-treated under 5 kbar at 1370°C for 3 min does not contain the component G_H at all, while for sample B subjected to the same pressure at 1500°C for 60 min the content of G_H amounts to 89%. Ambient temperature was precisely controlled, during the ESR measurement, by suitable ventilation of cold and warm nitrogen gases into the cavity.

The experimental results for these samples are shown together in Fig. 3: Sample A exhibits only the sharp signal. Its relative intensity is found to obey the Curie law, showing an excellent linearity when plotted against $1/T$ (reciprocal temperature in $°K^{-1}$), whereas the line width ($\fallingdotseq$2G) and the *g*-value ($\fallingdotseq$2.003) are almost independent of temperature in the range from 140°K to 300°K. Such characters are in agreement with those of localized spin centers which have generally been found for various chars on the way of carbonization.⁶⁾ On the other hand, behaviors of the broad signal solely displayed by sample B are much different from the above; *viz.*, the line width as well as the *g*-value decrease with the increase of ambient temperature, while the absorption intensity shows a slightly increasing tendency. Undoubtedly, these trends are associated with the delocalized nature of spins, and hence may conform with the Pauli-McClure type paramagnetism⁷⁾ of conduction electrons in graphite which has practically been justified by Wagoner⁸⁾ (for single crystal) and further by Singer and Wagoner⁹⁾ (for polycrystal).

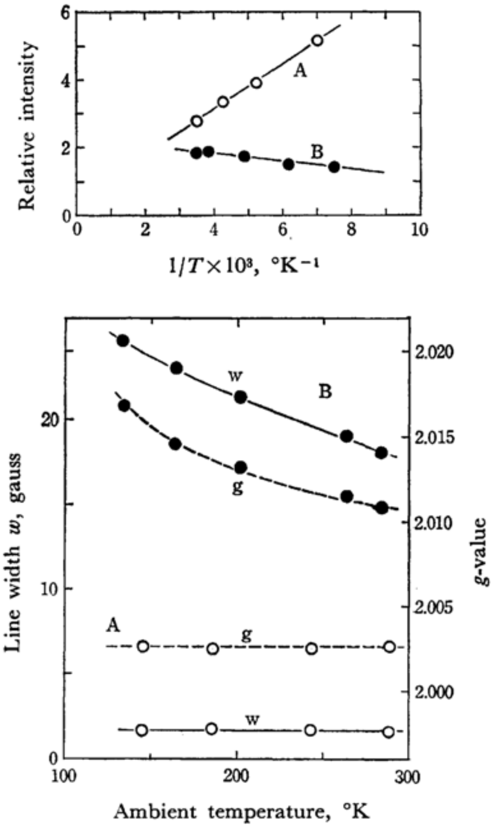

Fig. 3. Dependences of relative intensity, line width and *g*-value of two kinds of signals on ambient temperature (T).
○ Sample A ● Sample B

Discussion

As shown in Fig. 2, the critical points on HTT axis, at which the broad ESR signal of delocalized nature turns up, coincide with those where the abrupt increase of component G_H is observed in the X-ray analysis. On this basis, we can conclude that the conduction carriers can take part in ESR just through the agency of the three-dimensional graphitic structure. On the other hand, the free spin species giving rise to the sharp signal are mostly distributed, may be bound with some structural defects, in the turbostratic media. However, for the second-stage product in which the content of graphitic part (the component G''_H) is far below 20%, the broad signal due to conduction carriers has not yet been detected. In this sense, the ESR analysis as a tool for detecting the structural change in carbons is likely less sensitive than the well-arranged X-ray diffraction analysis.

Another fact to be remarked in this work is that for some not-fully graphitized sample, there are simultaneously observed two kinds of absorption lines which are due to the localized and delocalized spin centers, respectively. This makes a sharp contrast to the past observations¹⁰,¹¹⁾; *i. e.*, for usually-treated carbons, one can obtain an ESR line which exhibits intermediate nature between fully localized and delocalized spins as a result of the so-called motional narrowing. Therefore, in our specimens the both structures responsible for such two lines, the turbostratic and the graphitic, have enough extent to prevent such a motional mixing of these spins. This may corresponds to that in the X-ray diffraction either of the turbostratic or of the graphitic portions has enough extent to produce the coherent scattering of X-ray.

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6) For instance, S. Mrozowski, "Proceedings of the Fourth Conference on Carbon," Pergamon Press, London (1960), p. 217.

7) J. McClure and Y. Yafet, "Proceedings of the Fifth Conference on Carbon," Vol. I" Pergamon Press, (1962), p. 22.

8) G. Wagoner, *Phys. Rev.*, **118**, 647 (1960).

9) L. S. Singer and G. Wagoner, "Proceedings of the Fifth Conference on Carbon," Vol. II, Pergamon Press, London (1963), p. 65.

10) K. Antonowitz, *J. Chem. Phys.*, **36**, 2046 (1962).

11) Y. Yokozawa, *ibid.*, **37**, 204 (1962).

Several years ago, Honda *et al.*⁽¹²⁾ found double-fold ESR lines for some chars prepared in usual way from phenolformaldehyde resin and its derivatives. However, the broad component observed in their study has the same *g*-value as the sharp one. Therefore it might originate from other mechanism than that outlined in the present work. They did not mention the correspondence between the ESR and X-ray diffraction data.

The authors are indebted to Dr. T. Noda of Mie University for his encouragement and valuable discussions.

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12) H. Honda, T. Toyoda, Seventh Carbon Conference, held at Cleveland, in 1965.