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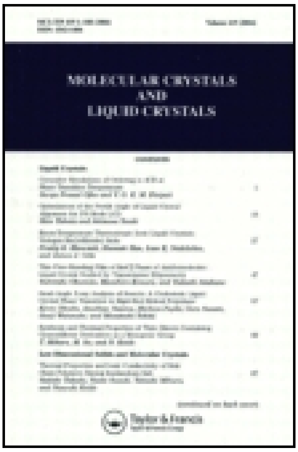

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Hirobumi Ushijima [a], Kazuhisa Murata [a], Hisashi Ueda [a] & Kenji Kawaguchi [a]

[a] National Chemical Laboratory for Industry, Tsukuba, Ibaraki, 305, Japan

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PREPARATION OF AMORPHOUSLIKE CARBONS BY PYROLYSIS OF ORGANIC COMPOUNDS AND THEIR MAGNETIC PROPERTIES

HIROBUMI USHIJIMA, KAZUHISA MURATA,* HISASHI UEDA, and
KENJI KAWAGUCHI
National Chemical Laboratory for Industry, Tsukuba, Ibaraki
305 Japan

Abstract The pyrolysis of organic compounds were carried out and the magnetic properties of the obtained carbons were investigated. Polymer-derived carbons, performed as a preliminary study, still seem to be of paramagnetic nature, although the carbons showed hysteresis even at room temperature. Next, the pyrolysis of organic monomers was tried and it is found that there are some differences in magnetic natures between monomer- and polymer-derived carbons. An amorphous-like carbon, associated with the observed magnetic properties, could have a three-dimensional network structure consisting of both sp^3- and sp^2-carbons. This is consistent with the results obtained from measurements such as scanning tunnelling microscopy, FTIR and X-ray photoelectron spectroscopy and a mechanism of the carbon formation is discussed.

INTRODUCTION

Recently there has been a growing interest in non-metallic organic magnetic materials exhibiting a spontaneous magnetization at room temperature.[1] Of these, substances pyrolyzed at a temperature of ca. 950℃ could provide suitable compounds for investigating their magnetic properties because of the many unpaired electrons in an incomplete graphite structure.[2] In this study, attempts have been made to synthesize carbon-based magnets by pyrolysis of organic polymers and/or monomers.

THE PRINCIPLE FOR PREPARATION OF PYRO-CARBONS

An amorphous carbon is a key structure. Great attention must be given to a reproducible production of the structure. The method of pyrolysis is as follows: 1) It is necessary to introduce start-

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ing materials directly into a preheated reaction tube and a short reaction time (ca.45 min) is favorable. 2)The structure of the starting materials is important.The nitrogen-containing compounds with a high ratio of hydrogen to carbon are favorable.

Preliminary Reaction - Pyrolysis of Polymers

As a preliminary study, pyrolysis of polymers was carried out at 1000℃ for 24 h under an argon stream.The field dependence of the magnetization of carbon compounds (PVC/C), prepared from commercially available poly(vinyl chloride)(PVC) premixed with activated carbon, showed hysteresis loops even at room temperature. The apparent saturation magnetization (Ms) was ca.0.27 emuG/g (1 emu = 10^3 A/m) and the coercive force(Hc) was 64 Oe(1 Oe= ca.80 A/m). However, the ESR spectra showed only the usual $\Delta m_s = \pm 1$ signal, as a Dysonian-shape without hyperfine structures, although the g-value for the $\Delta m_s = \pm 1$ signal(g = 2.0022) could suggest that the spins are ascribed to carbon. No forbidden $\Delta m_s = \pm 2$ signal was observed even at 77 K. The temperature dependenceof the magnetic susceptibility(χ), measured using a SQUID susceptometer, showed a possible linear relation between $1/\chi$ and temperature, approxi-

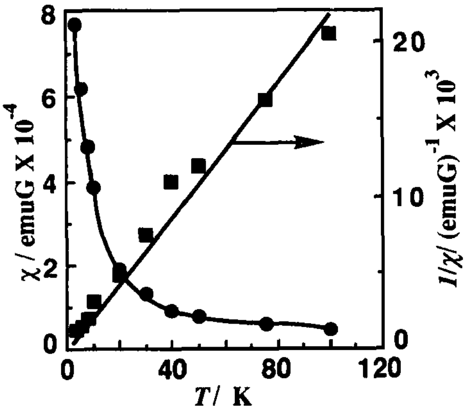

FIGURE 1 Temperature dependence of saturation magnetization of a carbon sample prepared from PVC/activated carbon.

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mately passing through the origin ($\chi = C/T$, C: Curie constant) (Figure 1). Assuming $S = 1/2$, the estimated spin density (N) is calculated as 7.5×10^{19} spins/g (Table 1). That the observed χ value obeys Curie's law could be illustrative of paramagnetism.[3]

$$c = \frac{N}{3k} S(S+1) g^2 \beta^2$$

Thus, it seems likely that a major portion of the sample is still paramagnetic, although there might be unusual high spin microregions in small portions of the sample, since an apparent hysteresis loop was observed from VSM measurements of the field dependence of the magnetization .

TABLE I Comparison of ESR and SQUID data.

	ESR[a]			SQUID	
	ΔHpp (Gauss)	g-value	Ns[b] (spins.g^{-1})	C[c] (emu.K.g^{-1})	Nc[d] (spins.g^{-1})
PVC/C	5.25	2.0022	4.9×10^{18}	4.66×10^{-5}	7.8×10^{19}

a)At room temperature. b)Curie-type spin concentration.
c)The Curie constant. d)Spin concentration.

Pyrolysis of monomers

As starting materials consistent with the principle mentioned above, aliphatic amine monomers were chosen. Typically, pyrolysis was carried out in a furnace equipped with a quartz tube. Commercially available 1,2-diaminopropane (DAP) (H/C ratio = 3.33) was separately placed in the quartz tube and heated to 950℃ under vacuum. Then, the DAP was introduced and rapidly pyrolyzed: The deposition and subsequent evacuation times at 950℃ were 45 and 30 min. After cooling the tube, the carbon product was taken out and subjected to magnetic measurements.

The results were as follows: 1)The field dependence of the magnetization(M) exhibited an apparent hysteresis at room temperature with a coercive field of 43G(Figure 2); the saturation magnetization (Ms) was found to be ca.9.2 emuG/g, almost 30 times higher than those of the polymer-derived carbons. 2)The tempera-

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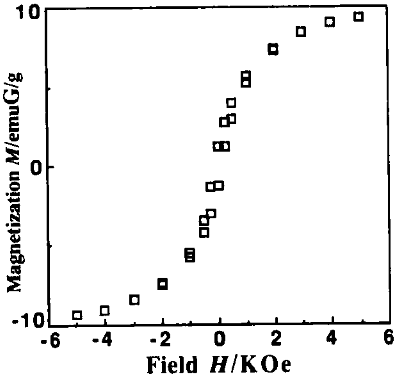

FIGURE 2 Field dependence of magnetization of carbons prepared from pyrolysis of 1,2-diaminopropane.

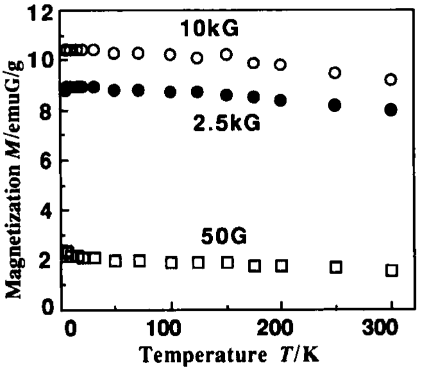

FIGURE 3 Temperature dependence of magnetization.

ture dependence of the magnetization showed a non-Curie-Weiss behavior. The Ms value slightly increased with decreasing temperature to 10.5 emuG/g (0.022 μ_B per carbon atom) at 4.3 K (Figure 3). A remnant magnetization within a field of 50 G was still retained even at 300K.3)The ESR spectra showed a broad, poorly resolved signal over the range from 1 to 6 kG, in addition to an usual $\Delta m_s = \pm 1$ signal [g = 2.0019 and ΔHpp = 8.8 G at 295 K and g=1.9724 and ΔHpp =11.3 G at 77 K]. The broad signal intensity seems to be dependent on the apparent Ms

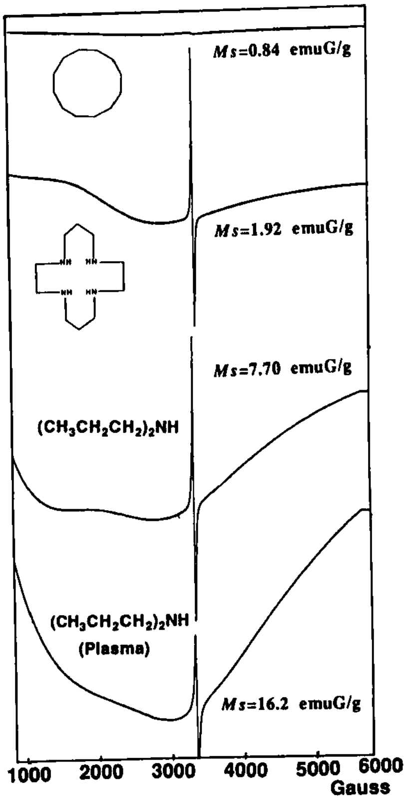

FIGURE 4 ESR spectra at room temperature of carbon samples baked at 950℃.

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values (Figure 4) and decreasing temperature resulted in a decrease in the intensity. 4)The reproducibility of the magnetic data was extremely good. 5)The observed Ms values at room temperature were dependent on the structure of the various nitrogen-containing starting materials: The order was 1,2-diaminopropane (9.2 emuG/g)>di-n-propylamine(7.77)> diethylamine (6.69)>n-butylamine (5.19) > n-propyl-amine (4.29)> triethylamine(2.63) > di-n-butylamine(2.60) >1,5,8,12-tetraazadodecane(1.92). 6)When the carbon prepared from di-n-propylamine was plasma-treated#, the Ms value was dependent on both plasma power and treatment time; A maximum Ms value was obtained when the plasma power was 120 W (Figure 6,○) and the time was 10 min. As mentioned above, the Ms values seem to be related to the amorphous carbon content. Other magnetic natures of plasma-treated sample were analogous to those of the untreated, except that the intensity of a broad, poorly resolved ESR signal over the range from 1000 to 6000 was much stronger than that of the untreated.

Ferromagnetic impurities in these carbon samples were examined using fluorescent X-ray spectroscopy. The carbon from 1,2-diaminopropane contained Fe of about 0.05~0.1wt% and Ni of 0.005 wt% with no Co metal: These impurities, if Fe_3O_4 = 90 emuG/g, correspond to 0.09 emuG/g, which can account for ca.0.9% of the observed Ms values. However, 1)there were no serious differences in the impurity contents among the samples examined, regardless of the preparation conditions (starting materials, temperature, reaction time and atmosphere). 2)In another study, magnetic properties of Fe/activated carbon powder were examined[4]: It was confirmed that ferromagnetism by Fe metal could be observed only when Fe concentration exceeds 6~8%.The magnetism of Fe/activated carbon samples where the Fe concentration was below 6%, was qual-

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The radio frequency (R.F.) plasma treatment conditions were as follows: air pressure: ca.66 Pa, plasma power: 30 ~195 W (13.56 MHz), reaction time: 5~60 min.

itatively identical to that of pure activated carbon. Taking these results into consideration, it seems likely that the observed magnetic properties of the carbons could mainly come from an amorphous carbon structure.

A Plausible Carbon Structure

As described above, a three-dimentional amorphous structure, which could consist of a mixture of sp^3- and sp^2-carbons, is a key for us. In fact, there was no distinct crystalline phase, as shown by powder X-ray diffraction, laser-Raman spectroscopy, transmission electron microscopy and electron diffraction analyses of the obtained carbons. In the XPS spectra, there were small differences in the C1s binding energy and full width at half maximum (FWHM) between amine-derived carbons and commercially available graphite (Figure 5), being consistent with the presence of an amorphous, disordered structure.

Also, evidence for the amorphous structure, being closely

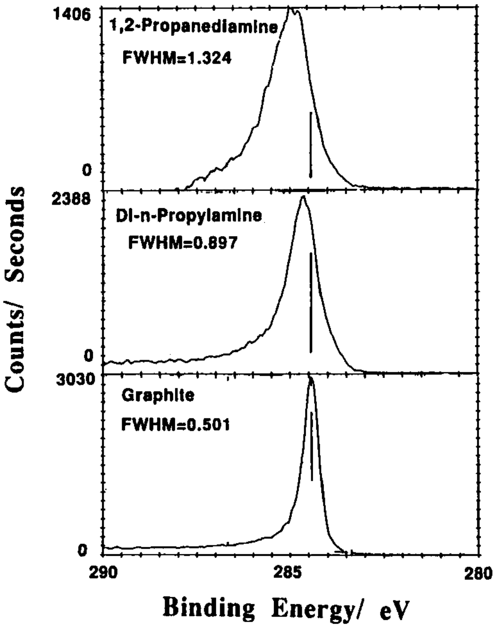

FIGURE 5 XPS spectra of carbon 1s band.

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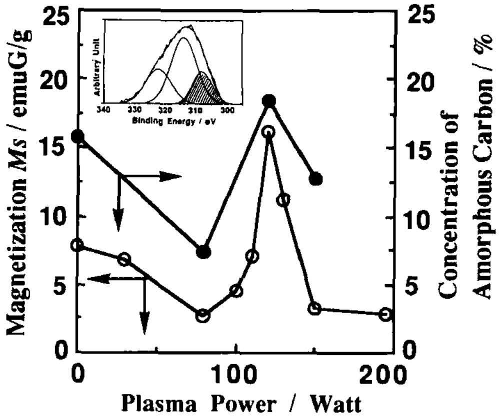

FIGURE 6 Plasma power dependence of 1)the Ms value at room temp.(○) and 2) amorphous carbon content (●) of the carbon material. Inset:An example of analysis of C1s energy loss spectra.

related to the magnetic properties, could come from XPS spectra of plasma-treated and -untreated carbon surfaces. In fact, there were some differences in the carbon 1s energy loss region at 295 to 335 eV, which was divided into respective spectra of three kinds of carbons such as amorphous-like, graphite and diamond, although there was little difference in the C1s binding energy.[5] As shown in Figure 6(●), the amorphous-like carbon concentration could be changed by plasma treatment and attained a maximum at 120W, in good accordance with the maximum magnetic property of plasma-treated carbons (Figure 6,○) (See previous section).

The following experimental results are consistent with the presences of sp^2- and/or sp^3-type carbons. 1) GC-MS analysis of hexane-soluble products, prepared from di-n-propylamine by CVD method, showed the presence of a series of aromatics with aromatic nitrile and/or heterocyclic compounds, indicating that aromatization and/or heterocyclization could occur. 2)The electrical conductivity of a carbon film prepared from 1,2-diaminopropane was 417 S/cm at room temperature and 377 at 4.3K, lower for stan-

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dard graphite of sp^2-carbon only. 3)Scanning tunnelling microscopy (STM) and atomic force microscopy(AFM) observations of the carbon film demonstrate an irregular array of carbon atoms of benzenoid rings relative to graphite. 4)The FT-IR-ATR spectra of the carbon film, exhibited integrated bands at 2850- to 3000 cm^{-1} and a number of bands from 1350 to 1750 cm^{-1}, and bands at 850- to 1100 cm^{-1}: These are associated with the combined absorptions of C-H stretches and C-H in-plane and out-of-plane bends of sp^3- carbons (-CH$_2$-) and/or of sp^2-carbons (=CH-)[6].

On the mechanism of the pyro-carbon deposition

Although it is still not clear how these carbons compounds are formed under the conditions of temperature as high as 900-1000℃, radicals such as atomic hydrogen and methyl generated in situ from the amine compounds seems to play an important role in a predominant formation of amorphous-like carbons over graphite formation[7]. In fact, we have reported that the Ms value at room temperature is dependent on the hydrogen/carbon (H/C) ratio of starting materials such as pyrene, tricyclohexylmethanol, cyclododecane, 1,4,8,11-tetraazacyclotetradecane, 1,5,8,12-tetraazadodecane. This is true for aliphatic amines,as shown in Figure 7,

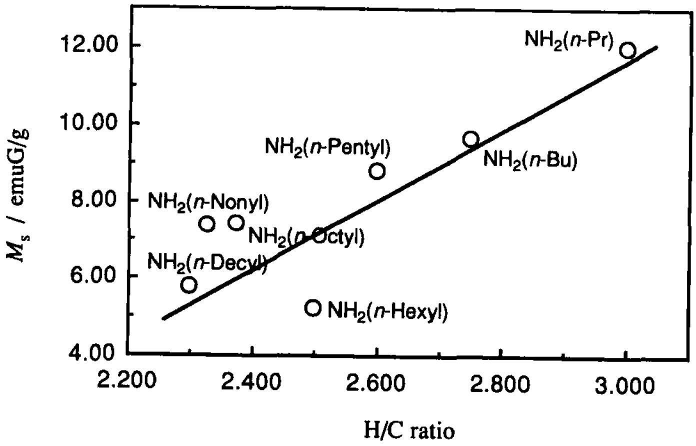

FIGURE 7 Correlation between Ms values of carbons and H/C ratio of starting amines.

where all samples were pyrolyzed at 880℃ for 60 min. Also, the Ms value is dependent on the structure of butylamine isomers (Figure 8) and branched isomers are favorable. Thus, if radicals

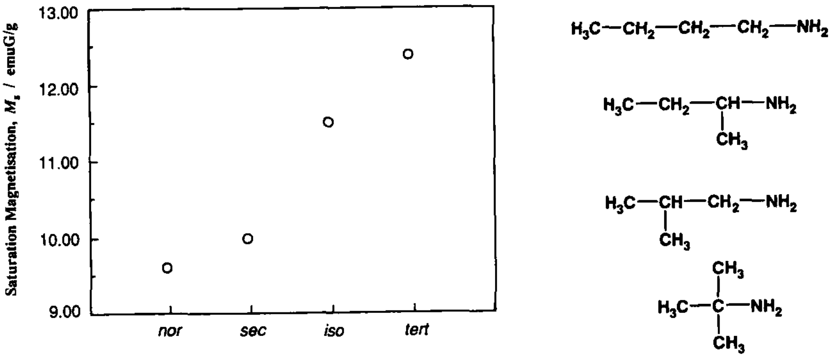

FIGURE 8 Relationship between saturation magnetization and isomerism of butylamines.

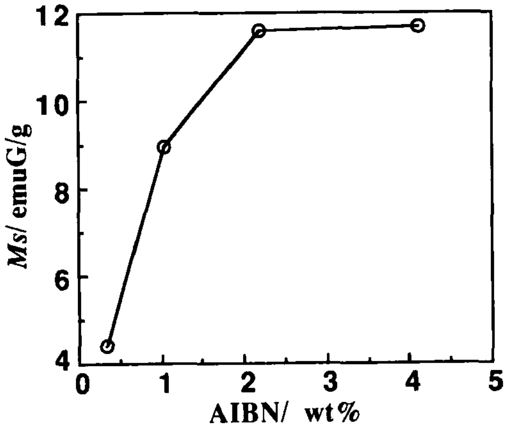

FIGURE 9 Effect of AIBN on Ms of carbon prepared at 900℃ from 1,2-diaminopropane.

are important, addition of radical source such as 2,2'-azobis(isobutyronitrile) (AIBN) to the pyrolysis reaction should be effective for the predominant formation of amorphous structure, leading to an enhancement of the Ms values. As shown in Figure 9, where pyrolysis of 1,2-diaminopropane was carried out at 900℃, the Ms

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values increased with the increase in the AIBN concentration. Further study is in progress to elucidate a role of radical species in the amorphous carbon formation.

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