Preparation of pyrolytic magnetic carbon under magnetic field

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Abstract. We have prepared pyrolytic carbon samples from triethylamine and investigated their magnetic properties. A ferromagnetic sample was obtained from the pyrolysis products even at room temperature, with spontaneous magnetization of \(5 \times 10^{-1}\) emu/g at 300 K. The magnetization was decreased with increasing temperature up to 500 K, but increased above 550 K. After this measurement, it was found that the magnetization at 300 K was changed to \(6 \times 10^{-1}\) emu/g. Another ferromagnetic sample has been also prepared by pyrolysis under high magnetic field of 2 Tesla. The spontaneous magnetization of this field-pyrolysis sample is 1.3 emu/g, which is twice as large as that of the above-mentioned sample prepared without magnetic field. Therefore, the magnetic field may help to form a ferromagnetic structure in pyrolytic carbon.

1. Introduction

Ferromagnetic order in carbon is an attractive subject from a fundamental scientific point of view, since the spin polarization of s and p electrons suggests the existence of correlation effects between these electrons. Therefore, magnetic properties of carbon have been intensively studied theoretically and experimentally [1]. Some of the experimental studies report room-temperature ferromagnetism in carbon-based samples. They are a graphite nodule from the Canyon Diablo meteorite [2], proton irradiated graphite [3], [4], and pyrolysis products from pure organic materials [5]-[7]. The idea of proton irradiation [3] came from the magnetic properties of pyrolytic carbon made from different hydrogen-rich starting materials where the saturation magnetization increases with the hydrogen concentration in the starting material [6],[7]. So, there may be potential in the pyrolysis method to improve the ferromagnetic properties of a carbon sample, although this method had been employed in the early studies [5]-[7]. In this study, we have prepared pyrolytic carbon samples from triethylamine and improved its synthesis method.

2. Experimental Procedure

The pyrolytic carbon samples were prepared by direct pyrolysis of triethylamine, as mentioned in Ref. [8]. Triethylamine liquid was placed at an edge of a quartz tube and frozen at liquid
nitrogen temperature. The quartz tube was evacuated, and the center of the tube was heated to a desired temperature of 875-925°C. When the central temperature became stable, the chemical was melt and introduced to the heating area. The chemical vapor pressure of about 1 bar and the heating temperature were kept for 30 minutes. After the pyrolysis, the tube was evacuated again and cooled down to room temperature. Pyrolysis carbonaceous product was obtained from the inside of the tube, using a nonmagnetic hard titanium-alloy (Ti-Al-V) rod in order to avoid contamination of ferromagnetic metal impurities. A ferromagnetic sample was magnetically separated from the product. The ferromagnetic sample had no diffraction peaks of iron, iron carbides or iron oxides in the synchrotron X-ray diffraction experiments [8], even though a small amount of transition metal impurities in carbon host produces apparent diffraction peaks, especially in synchrotron X-ray diffraction experiments. It should be noted that we could never obtain a ferromagnetic sample at higher-temperature-pyrolysis than 925°C, which also suggests that the ferromagnetism is not caused by contamination of iron, iron-carbide or iron-oxide impurities. Magnetization measurements were performed by the use of a commercial SQUID magnetometer (Quantum Design MPMS). ESR spectra were recorded with an X-band spectrometer (Bruker, EMX-6/1).

3. Experimental Result and Discussion

Figure 1 shows temperature dependences of magnetization (M-T curve) at B=1 T for a ferromagnetic sample. At the first measurement, it had the spontaneous magnetization of 5 x 10⁻¹ emu/g even at 300 K, as mentioned in Ref. [8]. The magnetization decreased with increasing temperature as usual ferromagnets. It increased, however, with increasing temperature from 550 K to 700 K, and then decreased from 700 K to 800 K. The magnetization of (3 – 4) x 10⁻¹ emu/g survived even at 800 K, which indicated that the Curie temperature $T_C$ was higher than 800 K. Since the oven in the SQUID magnetometer cannot increase the measurement temperature above 800 K, $T_C$ is not determined yet and this is an important subject in the next step of this study. After the first measurement, the sample was cooled down to 300 K. And then, we found that the magnetization at $T$=300 K and $B$=1 T was increased to 6 x 10⁻¹ emu/g.

![Figure 1](image1.png)

**Figure 1.** Temperature dependences of magnetization for ferromagnetic pyrolytic carbon sample. The magnetization at room temperature increases after the measurement where temperature is increased under magnetic field.

The sample can be intrinsically changed by heating above 550 K under the application of magnetic field of $B$=1 T, since the sample was sealed in a quartz tube with vacuum during
the $M-T$ curve measurement. Another possibility of this increase of the magnetization may be a freezing effect, as observed in many disordered frustrated magnetic materials. So, ZFC and FC $M-T$ curve measurements from $T > T_C$ will also be needed to examine this possibility. The second measurement was performed at the same external condition from 300 K to 800 K at $B=1$ T. The temperature dependence of magnetization is similar to that at the first measurement - the magnetization increases from 550 K, and the magnetization at 300 K was increased after the second measurement. The third and fourth $M-T$ curves are also shown in Fig. 1. We can see that the ferromagnetic property of this pyrolytic carbon is enhanced by applying magnetic field and heating above 550 K ($=277^\circ$C).

Although the possibility of the freezing effect is not examined yet due to the high temperature limit of the SQUID magnetometer oven, this enhancement by ‘annealing under magnetic field’ motivated us to improve the synthesis method for a ferromagnetic carbon sample. From the above-mentioned experimental result, we expected that the application of magnetic field ‘during pyrolysis’ would increase the magnetization of ferromagnetic carbon. The generation of magnetic field is, however, difficult at the pyrolysis temperature of around 900$^\circ$C. The permanent magnets in a magnetic circuit are demagnetized at the high temperature. Also, coolant is usually needed for electromagnets. An air-core non-superconducting electromagnet needs cooling water due to its resistive heating, and a superconductive electromagnet should be kept below its superconducting critical temperature. Therefore, the magnet should be set out of the high temperature area. So, we employed a superconductive electromagnet with a large internal diameter of 150 mm$^\phi$, and constructed a new electric furnace which can be put in the superconducting magnet. The electric furnace has vacuum-thermal-isolation and cooling-water jackets, as shown in Fig. 2 (a). The schematic view and picture of the electric furnace and the superconducting magnet are also shown in Fig. 2 (b). The internal temperature ($T_{in}$) of the furnace can be increased up to around 900$^\circ$C. The vacuum-thermal-isolation jacket works well at $T_{in} <500^\circ$C. When $T_{in}$ increases above 500$^\circ$C, heat flows through the vacuum jacket due to radiation and the cooling water removes the heat. Therefore, outside surface of the furnace can be kept at room temperature, which enables us to put it in the superconducting magnet.

So, we have tried to prepare pyrolytic carbon by the use of the new furnace and the superconducting magnet. The preparation procedure is almost the same as mentioned before, except for the fact that the magnetic field is applied during pyrolysis.

Figure 3 shows the magnetization curve of a ferromagnetic carbon sample pyrolyzed at

![Figure 3. Magnetization curve at 300 K for the ferromagnetic carbon sample pyrolyzed in the magnetic field of 2 Tesla.](image)

![Figure 4. ESR spectra for the ferromagnetic carbon samples pyrolyzed in the magnetic fields of 0 and 2 Tesla.](image)
$T_p=900^\circ$C and $B=2$ T. The spontaneous magnetization of this field-pyrolysis sample is 1.3 emu/g, which is twice as large as that of the above-mentioned sample prepared without magnetic field. Although the sample is the mixture of ferromagnetic and nonmagnetic carbons due to the synthesis method, the magnetic moment per a carbon atom can roughly be estimated to be $\sim 10^{-3}$ $\mu_B$ by multiplying the magnetization of $\sim 1$ emu/g, the atomic weight of 12 g/mol and $1/5585$ $\mu_B$·mol/emu·f.u. So a part of carbon atoms seems to have dangling bonds and contribute the ferromagnetism. In order to determine the magnetic structure, the crystal structure of the ferromagnetic component should be determined as the first of all. According to the previous synchrotron X-ray diffraction experiments, there still remain possibilities of IGD, graphite-like and diamond-like carbon structures for the ferromagnetic sample. So, we are going to perform the synchrotron X-ray diffraction experiments for the ferromagnetic sample in this field-pyrolysis study and to examine which crystal structure is the main cause of the ferromagnetism.

The ESR spectra of the ferromagnetic carbon samples prepared at $B=0$ and 2 T are also shown in Fig. 4. There is a sharp peak around 3490 G in the spectrum for the sample prepared without magnetic field. This indicates there remain paramagnetic radical spins in the normal-pyrolysis sample, although it is ferromagnetic. Whereas, no peak is observed in the spectrum for the sample pyrolyzed in $B=2$ T. Therefore, the amount of paramagnetic spins in the field-pyrolysis sample is much lesser than that of the normal-pyrolysis sample. The magnetic field may help to form a ferromagnetic structure in pyrolytic carbon, make ferromagnetic interactions between radical spins, and then decrease the number of paramagnetic free radical spins.

4. Summary

We have investigated magnetic properties of pyrolytic carbon samples from triethylamine. A ferromagnetic sample was obtained from the pyrolysis products even at 300 K, with spontaneous magnetization of $5 \times 10^{-1}$ emu/g. The magnetization was decreased with increasing temperature up to 500 K, but increased above 550 K. After this measurement, it was found that the magnetization at 300 K was changed to $6 \times 10^{-1}$ emu/g.

From this enhancement, we expected that the application of magnetic field ‘during pyrolysis’ would enhance the ferromagnetism. We constructed a new electric furnace which can be put in the superconducting magnet with a large internal diameter of 150 mm. Another ferromagnetic sample was prepared by the use of this furnace under magnetic field of 2 Tesla. The spontaneous magnetization of this field-pyrolysis sample became 1.3 emu/g. Also, ESR experiments show that the amount of paramagnetic spins in the field-pyrolysis sample is much lesser than that of the normal-pyrolysis sample. The magnetic field during pyrolysis may help to form a ferromagnetic structure in pyrolytic carbon.

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