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Evolution of magnetic behaviour in the graphitization process of glassy carbon

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Abstract

We have carried out DC magnetization measurements on spherical glassy carbon exposed to high temperatures and high pressures. The observed magnetic signals clearly depend on the sintering temperature. On the basis of the graphitization temperature (around 1400 °C), the behaviour can be classified into three regions: (1) paramagnetism in the no-graphitization region; (2) ferromagnetism in the near-graphitization region; (3) diamagnetic behaviour after graphitization. The magnetic transitions associated with the process of graphitization are discussed.

1. Introduction

Carbon holds a special fascination for scientists in many fields because of the great diversity of structural and electronic properties exhibited by its many forms. Graphite is a basic form of carbon; on insertion of atomic or molecular layers of a different chemical species, graphite intercalation compounds can be formed, and superconductivity can occur in such compounds [1]. It has long been recognized that the magnetic susceptibility of graphite is diamagnetic; however, recent experiments reveal that in pure highly oriented pyrolytic graphite (HOPG), ferromagnetism and superconductivity fluctuations can exist [2, 3]. Meanwhile, for the new form of carbon, C_{60}, much research work has revealed superconductivity in hole- or electron-doped C_{60} [4, 5]. Moreover, the recent discoveries of ferromagnetism in pure carbon of rhombohedral C_{60} prepared under high pressures and high temperatures, and superconductivity in graphite-related materials have triggered renewed interest in the investigation of carbon-based materials [6–8]. It is fascinating to discover how these unusual properties appear in materials containing only a light element. And these interesting experimental results have indicated that the occurrence of superconducting and ferromagnetic properties can be ascribed to structural instability; this is also supported by some theoretical studies [9, 10]. High pressure has long been recognized and used as a tool in preparing and investigating such metastable materials. In view of the above, we have carried out the synthesis of a carbon-based system under high pressures and at high temperatures, and have tried to find new physical phenomena arising

from materials of this type. In this paper, we report on some unusual physical properties of glassy carbon prepared under high pressures and at high temperatures. We have observed significant magnetic transitions appearing along with the graphitization process. It is interesting to see what happened during this evolution, which could provide evidence of the appearance of magnetic signals induced by structural instability, since the effect of disorder developed in the high-pressure high-temperature polymerization process can trigger topological defects in this covalently bonded material and cause the occurrence of unpaired spins [6]. These topological defects may still be present after graphitization, increase the hybridization of the local charge density in the graphite sheets, and therefore trigger the magnetic transition.

2. Experimental details

All of the glassy carbon used for this work was a commercial product (Alfa Aesar, 99.9%). It was in the form of powder with spherical particles, which were in the size range from 20 to 50 μm. High-pressure high-temperature treatments were carried out in a conventional cubic-anvil-type high-pressure device. The raw materials were carefully wrapped with platinum foil to avoid contamination, and were put into a BN tube. A graphite sleeve was used as an internal furnace with pyrophyllite as the pressure-transmitting medium. The treatment process was carried out at 3.0–5.0 GPa and 600–1400 °C for 5–20 min; this was followed by quenching from high temperature and release of pressure. X-ray diffraction, scanning electron microscopy (SEM), and Raman spectra were used to characterize the synthesized products. The analysis results indicate that the temperature for the transition to polycrystalline graphite is around 1400 °C. DC magnetization $M(H, T)$ measurements were performed on two magnetometers: Quantum Design MPMS5 and Oxford MagLab. In order to exclude the impurity effects, an ICP-AES method using an IRIS/AP-ICP emission spectrometer was adopted to examine the traces of impurities. The total amount of Fe, Co, Ni was found to be less than 70 ppm in the raw material examined in magnetic measurements.

3. Results and discussion

Unlike amorphous carbon, glassy carbon is believed to have the short-range order of the strained graphite layer [11]. It was found that graphitization would not occur until the heat-treatment temperature reached ∼3000 °C [12]. However, we find that this temperature can be substantially reduced, to 1400 °C, under high pressures, and the characterization of this transformation will be reported in detail elsewhere [13]. Here we restrict ourselves to reporting the results of magnetic measurements.

DC magnetization measurements have been performed for all the products prepared under different pressure and temperature conditions. It seems that the variations of the synthesis conditions have important effects in determining their magnetic behaviours. Although applying high pressure can accelerate the graphitizing process and decrease the graphitization temperature, it does not affect their magnetic behaviours when only the pressure is changing (up to 6 GPa). The temperatures in the synthesis have primary effects in leading to distinct magnetic behaviours. The behaviours can be divided into three regimes in relation to the transformation temperature: the first one (the no-graphitization region) only shows paramagnetism; the second one (the near-graphitization region) reveals ferromagnetic signals; while the third one (the graphitization region) shows diamagnetic behaviour.

Figure 1 shows the magnetization hysteresis loops measured in the field range ±1.6 kOe at 10 K for glassy carbon prepared under different conditions. One is for treatment under 5 GPa at room temperature, while the other is for treatment under the same pressure but at

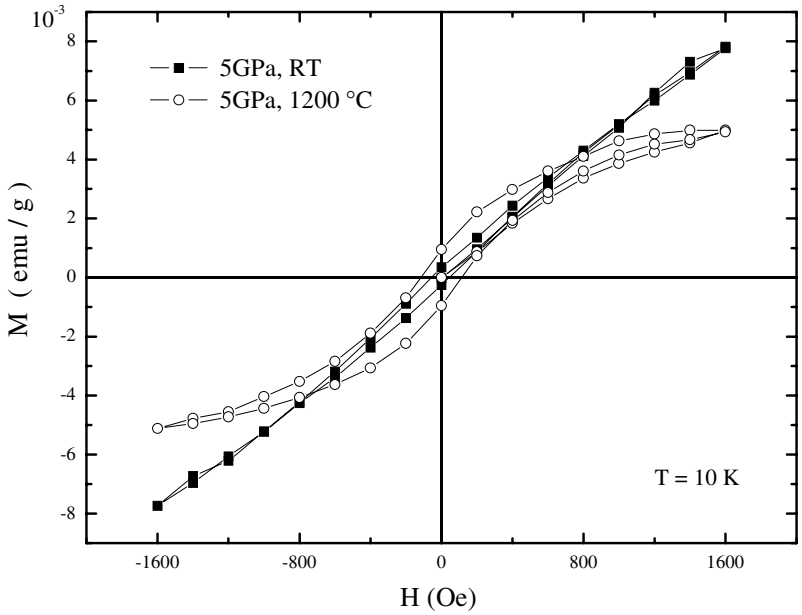

Figure 1. Magnetic moment hysteresis loops measured for samples after subtraction of the diamagnetic background signals. The samples were prepared under different synthesis conditions, as represented by the first two regions (see the text).

1200 °C (which is in the near-graphitization region). From this figure, we can clearly see the different magnetic behaviours of these two samples. The sample at room temperature only exhibits paramagnetic behaviour, while the sample at 1200 °C shows a typical ferromagnetic hysteresis loop. The appearance of paramagnetism is not surprising, since it is caused by local magnetic moments of dangling bonds, which exist extensively in amorphous carbon. With increasing synthesis temperature, the products still show paramagnetic behaviour until the temperature approaches the transition point, 1400 °C. Then a large hysteresis loop appears, as shown in figure 2 for $T = 5, 10$, and 300 K. These hysteresis loops are typical of ferromagnetic behaviours. A comparison between the results before and after (inset) the subtraction of the diamagnetic background signals is also made. Now the results presented here are not easy to understand, since it had long been thought that ferromagnetism due to interactions between p electrons is impossible. However, the discovery of a new organic material (TDAE-C_{60}) rapidly changed this view [14, 15]. The ferromagnetic state can be a result solely of the alignment of p-electron spins on the fullerene units. In view of this, the observed unusual magnetic behaviour is not too surprising, because it may be a similar case for our samples treated under high-temperature high-pressure conditions. During the graphitization process, we observed a significant shape change from spherical to polygonized [13]. We suppose these shape changes to be intimately related with the appearance of ferromagnetic behaviour. These aggregated polyhedra with the short-range order of the strained graphite layer can lead to an sp^2–sp^3 rehybridization and formation of unpaired electrons. And this pressure-induced polygonization can trigger ordered itinerant moments coming from these unpaired spins to produce itinerant ferromagnetism. Figure 6(a) shows a scanning electron topographical micrograph for the sample in the near-graphitization region. The short-range order of the strained layers can be clearly seen. The topological defect-induced ferromagnetism can also be used to explain the ferromagnetism in rhombohedral C_{60} [6].

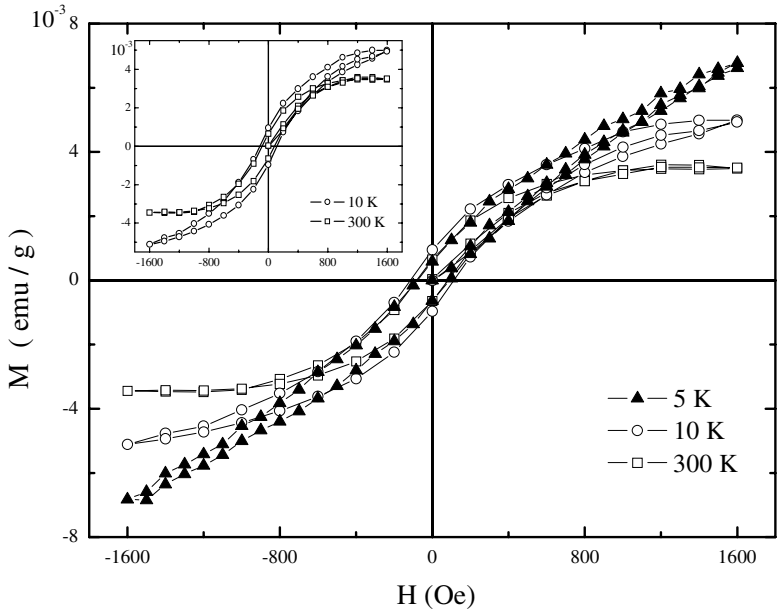

Figure 2. Magnetization loops for glassy carbon treated under 5 GPa, at 1200 °C, without subtraction of the background. The inset shows the results after subtracting the diamagnetic background data. It gives clear evidence for saturated magnetization at 300 K.

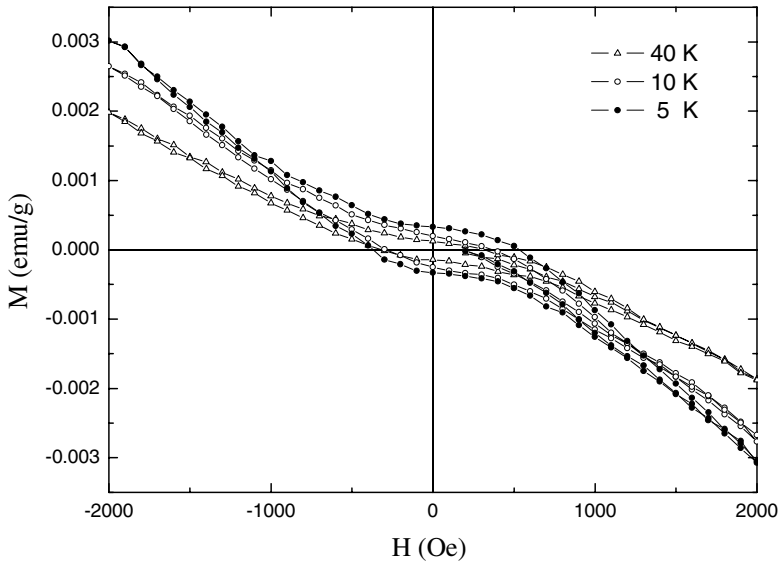

Figure 3. The diamagnetic magnetization behaviour in glassy carbon after graphitization. The diamagnetic background signals have been subtracted. Continuing to increase the temperature will cause the detected signals to become comparable to the background noise.

When the preparation temperature reaches the transition point, glassy carbon will transform into polycrystalline graphite. We also examined its magnetic signals, to check whether ferromagnetism still exists, but we found that an interesting magnetic transition happens. Shown in figure 3 are magnetic moment hysteresis loops $m(H)$ measured for $T = 5$,

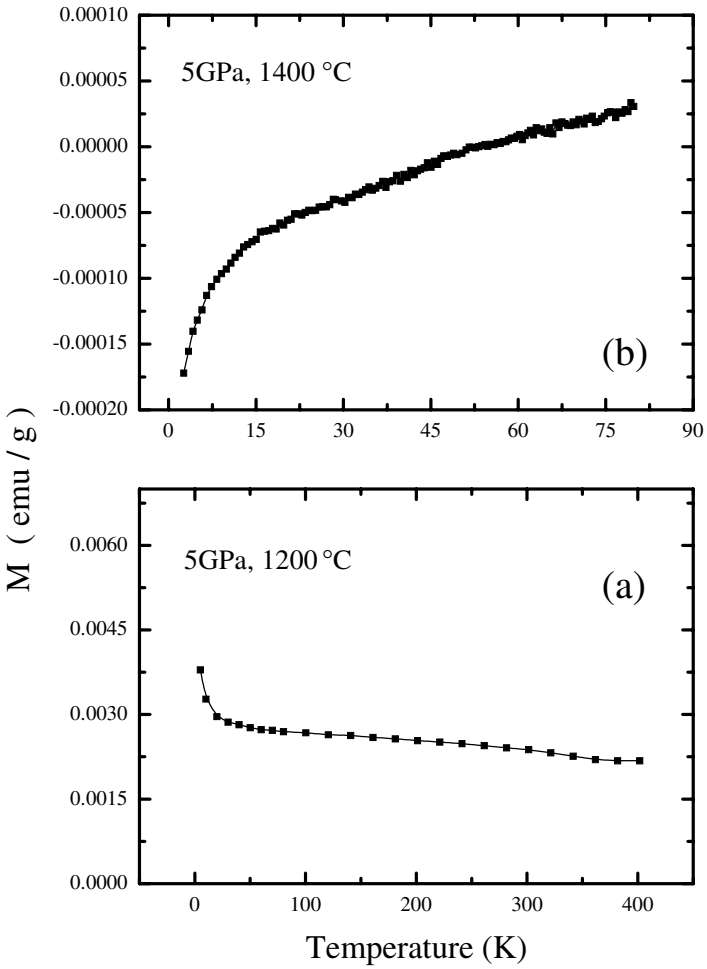

Figure 4. Temperature dependences of the magnetic moment measured for glassy carbon before (a) and after (b) graphitization in an applied magnetic field $H = 100$ Oe.

10, and 40 K. One can clearly observe the superposition of a hysteresis loop over a linear diamagnetic background ($m_0 = \chi H$, where $\chi = -1.22 \times 10^{-6}$ emu g^{-1} Oe^{-1} at $T = 10$ K). Measuring at higher temperatures will cause the detected signals to become comparable to the background noise. Our observed result has some similarities with the recent report of the existence of superconducting fluctuations in HOPG [2]. The topological disorders have played an important role in the samples. The post-transformation glassy carbon is microcrystalline graphite having warped layers with curved regions, which can present some disclinations contributing to the disorder, as shown in figure 6(b). Localization due to this disorder can occur and enhance the local charge density, and therefore trigger superconductivity. But we cannot definitely say that superconductivity exists in our sample: the observed hysteresis loop is rather small as compared with loops for typical superconducting behaviour. In order to avoid ambiguity as regards the hysteresis loop data presented here, we would rather use the term 'diamagnetic' instead of 'superconducting' in describing our observation. Since both the ferromagnetism and diamagnetism in this material can be ascribed to structural instability,

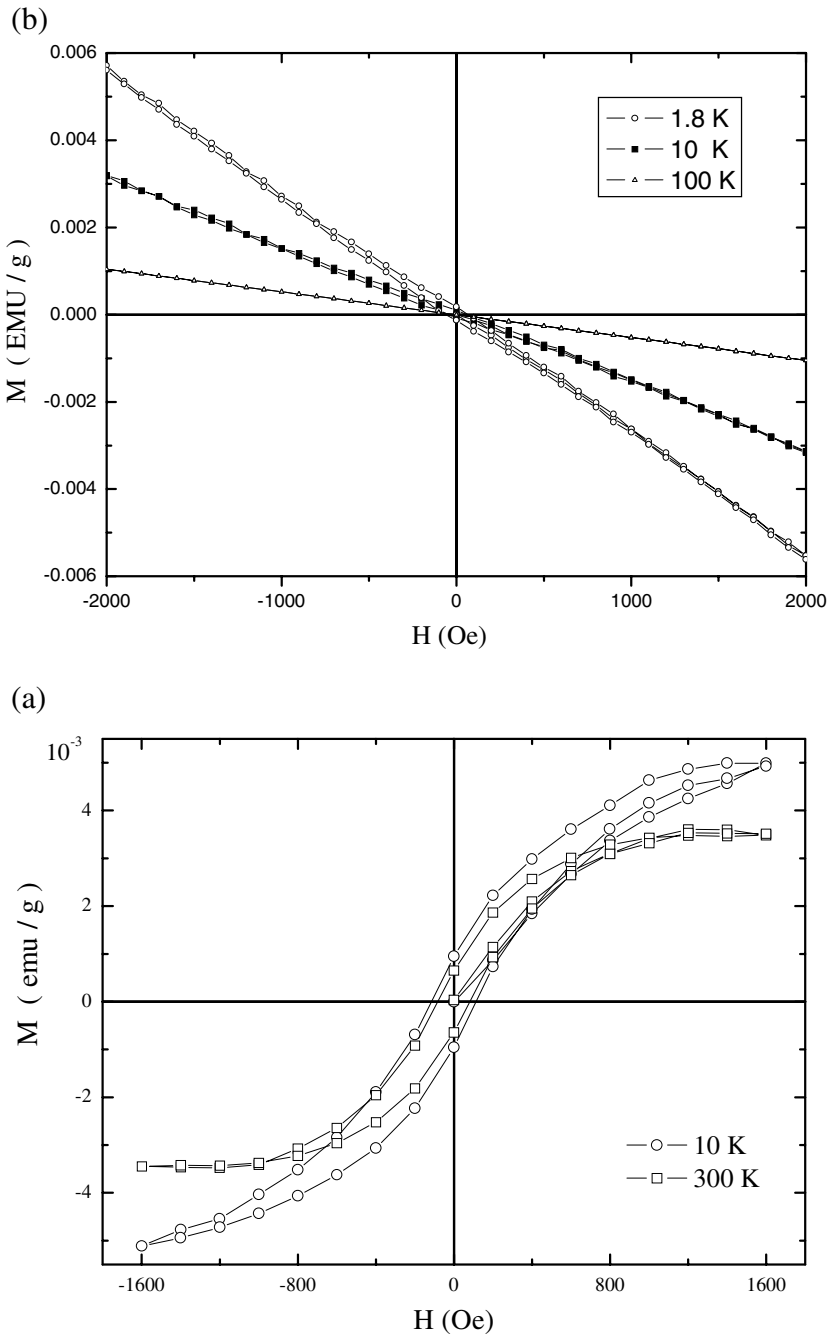

Figure 5. Magnetic moment hysteresis loops for the samples re-examined after two months. All the diamagnetic background signals have been subtracted. (a) The same sample as in figure 2. (b) The same sample as in figure 3.

during the process of graphitization they could possibly coexist. Figure 4 shows the temperature dependence of the magnetic moment $m(T)$ for an applied field $H = 100$ Oe. That shown in figure 4(a) is for the sample in the near-graphitizing region; note the upturn around 50 K—

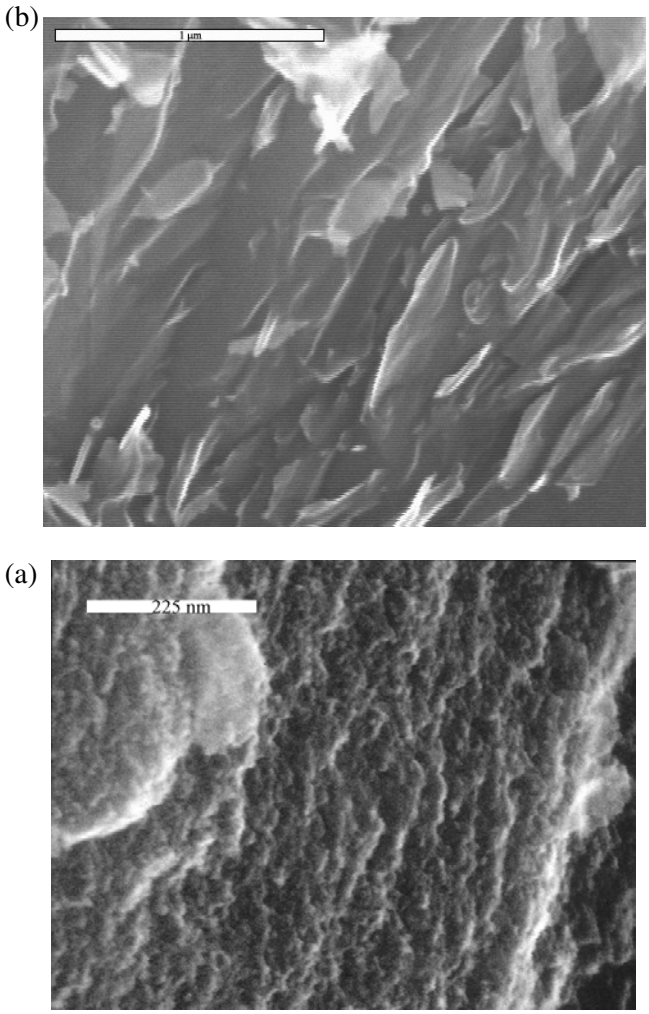

Figure 6. Scanning electron topographical micrographs of (a) a sample treated under 5 GPa, at 1200 °C, (b) a sample treated under 5 GPa, at 1400 °C.

this can be attributed to the coupling of the paramagnetism of common amorphous carbon with some ferromagnetic clusters formed by defects as discussed above. For figure 4(b), the sample is polycrystalline graphite transformed from glassy carbon. Although x-ray diffraction and Raman spectra have not shown any sign of amorphous carbon, we cannot exclude the possibility of magnetic effects caused by them. The turning point seems to be at $T = 20$ K, but the magnetization reaches zero around 50 K. This may indicate the existence of some untransformed glassy carbon.

Even after two months, reproducible results were still obtained from all of the samples, as shown in figure 5. However, a large change in the magnetic response that occurred for the graphitizing sample can been seen in figure 5(b)—after subtraction of the diamagnetic background signal ($m_0 = \chi H$, where $\chi = -3.17 \times 10^{-6}$ emu g^{-1} Oe^{-1} at $T = 10$ K). The diamagnetic background signal dominates while the diamagnetic response of our sample is rather weak now. This may be caused by the release of the weak coupling in the pressed

powder sample. As regards impurities in our samples, all of our samples were wrapped in Pt foil to avoid external contamination before each separate high-temperature high-pressure run, and Pt is a non-magnetic element with a susceptibility of 2.6×10^{-4}. The continuous magnetic response changes depend only on the different synthesis conditions, and it is difficult to account for the observed behaviour change from ferromagnetic to diamagnetic during the graphitization process in terms of impurities and the weakening of the diamagnetic behaviour due to the time ageing effect. The ferromagnetism and the diamagnetism appear to be intrinsic properties of samples, and the mechanism responsible for the unusual phenomena shown here may be structural instability during the graphitization process.

So far we have investigated the magnetic response in glassy carbon synthesized at different temperatures and pressures. The observed continuous occurrence of paramagnetism, ferromagnetism, and diamagnetism, in accord with three regions distinguished in relation to the graphitization temperature, is seen to be reasonable if we take it into account that the structural changes have a great impact on this magnetic behaviour evolution. The dangling bonds in the amorphous state are responsible for paramagnetism, and itinerant spins may form in the polygonized glassy carbon; after graphitization, the local disclinations can enhance the local charge density. Here we made some speculations regarding the experimental results; further studies are necessary to verify these hypotheses.

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