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Synthesis and characterization of stable room temperature bulk ferromagnetic graphite

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Abstract

A novel and inexpensive chemical route leading to obtain macroscopic quantities of room temperature magnetic carbon is reported. This route consists of a controlled etching on the graphite structure, performed by a *redox* reaction in a closed system between graphite and CuO. X-ray diffraction suggests that this modified graphite could be represented by the coexistence of a matrix of pristine graphite and a foamy-like graphitic structure compressed along the *c*-axis. This material has a stable and strong ferromagnetic response even at room temperature where it can be attracted by any commercial magnet. At $T = 300$ K, the saturation magnetic moment, the coercive field and the remnant magnetization are 0.25 emu/g, 350 Oe and 0.04 emu/g, respectively.

Keywords: Graphite; Chemical treatment; Magnetic properties

1. Introduction

The search for macroscopic magnetic ordering phenomena in pure carbon is a very important field in the frontiers of physics, chemistry and materials science.

The production of macroscopic bulk carbon magnetic material would have immediate impact through novel applications of this material in engineering, as well as in medicine and biology as a unique biocompatible magnetic material [1].

Magnetic properties induced by defects on graphite structures, such as pores, edges of the planes and topological defects, have been theoretically predicted. The possible coexistence of sp^3 and sp^2 bonds has been also invoked to participate in those properties [1]. Some reports have proved the existence of weak ferromagnetic-like magnetization loops in highly-oriented pyrolytic graphite (HOPG) [2,3] and in a novel carbon nanofoam [4]. Other articles have showed theoretically and experimentally that the existence of ferromagnetism in pure carbon is unambiguously possible [5–7].

In this work, we report on a novel and inexpensive chemical route consisting in a controlled etching on the graphite structure to obtain macroscopic amounts of bulk ferromagnetic pure graphite. This material has a strong magnetic response even at room temperature

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where it can be attracted by any commercial magnet. This would be the experimental confirmation for the defect induced magnetism previously predicted.

2. Experimental

The chemically modified graphite here reported was produced by a vapor phase *redox* reaction in closed nitrogen atmosphere (N_2, 1 atm.) with copper oxide (CuO) (scheme shown in Fig. 1). A few grams of both powders, CuO (Merck, analytical grade) and graphite (Fluka, CAS number 7782-42-5, lot 426277/1, granularity <0.1 mm) were placed at different alumina crucibles in a sealed atmosphere, inside a tube furnace (Fig. 1)—typically 12 g of CuO and 3 g of graphite. The reaction vessel is an alumina tube. The reaction took place at 1200 °C, during 24 h. After the reaction was finished, the CuO was partially reduced to Cu(0) and, in the other container, the carbon material showed a decrease in volume −25% to 50% decrease in weight-, specially in the side closest to the CuO crucible. Two clearly different regions could be observed: (a) an upper layer, black and opaque, with amorphous aspect; (b) a lower layer, more crystalline than the original pure graphite. The material from the upper layer was the one exhibiting the magnetic behavior, detectable up to room temperature. The separation of both materials was carefully achieved with the aid of a magnet.

The reproducibility of the method and purity of the materials, with very special concern on the presence of metallic impurities, were regarded. Several samples have been prepared and all of them exhibited the magnetic behavior here described. Since the presence of any kind of ferromagnetic impurity must be avoided, we have carefully determined the chemical purity of the samples with atomic absorption spectroscopy (AAS) using a Shimadzu AA6800 spectrometer and checked these results with X-ray fluorescence analysis (XRF) and energy dispersive spectroscopy (EDS), comparing the results obtained for the pristine and the modified graphite.

We have also studied the obtained magnetic graphite samples by X-ray diffraction and scanning electron microscopy (SEM). These studies were performed using a Seifert Scintag PAD-II powder diffractometer, with CuKα radiation ($\lambda = 1.5418$ Å) and a Jeol JSM 5900LV microscope, respectively.

We have magnetically characterized our treated carbon samples by performing magnetic measurements by using a MPMS-5T quantum design magnetometer.

3. Results and discussion

This magnetic graphite was produced by the reaction of pristine graphite with controlled amounts of oxygen released from the decomposition of CuO at high temperature. This chemical attack created pores and stacking structures and increased the exposed edges of the graphene planes, producing a foamy-like graphite. The removed carbon may also recrystallize on the graphite crystallites surfaces at the same crucible, thus creating the so-called lower region. This vapor phase reaction took place in an inert gas environment. In this case both N_2 and Ar have been used with similar results, discarding the specific role of N_2 as a reagent or catalyst. The use of powder graphite as a reagent seems to be crucial because of the high reactivity to chemical attacks, due to the high exposed surface and the previous existence of defects.

The chemical impurities for different batches concentrations are shown in Table 1. The results did not indicate a significant increase of metallic impurities with respect to the original pristine graphite, enough to be responsible for the magnetic properties observed. If these impurities would have been the cause of the mag-

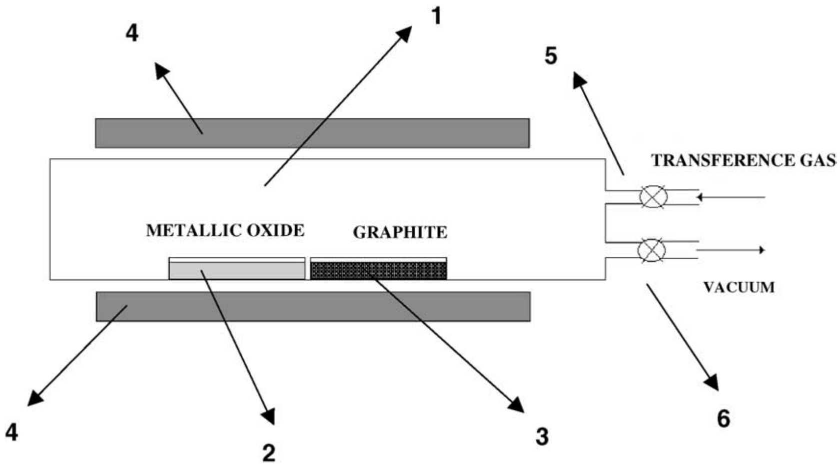

Fig. 1. Sketch of the experimental reactor. (1) Closed atmosphere, (2) CuO crucible, (3) graphite crucible, (4) tube furnace, (5) gas input, (6) vacuum.

Table 1
Concentrations of impurities (ppm for AAS and XRF; at.% for EDS–on the basis of 100% all metallic content) and saturation magnetizations at $T = 2$ K for each batch

	Fe	Co	Ni	Cu	Zn	m_s (μ_B/C atom)
AAS						
Graphite (reagent)	42(3)	0.2(1)	1.2(3)	3.0(5)	1.0(3)	
Magnetic graphite batch 1	59(3)	0.2(1)	1.2(3)	3.9(5)	1.0(3)	1.2×10^{-3}
Magnetic graphite batch 2	65(3)	0.2(1)	1.2(3)	3.1(5)	1.0(3)	1.2×10^{-3}
Magnetic graphite batch 3	68(3)	0.2(1)	1.1(3)	3.5(5)	1.0(3)	1.1×10^{-3}
XRF						
Graphite (reagent)	43(5)					
Magnetic graphite batch 1	60(5)					1.2×10^{-3}
Magnetic graphite batch 2	67(5)					1.2×10^{-3}
Magnetic graphite batch 3	66(5)					1.1×10^{-3}
EDS (at.%)						
Graphite (reagent)	89(2)	–	–	8(2)	3(1)	
Magnetic graphite batch 1	90(3)	–	–	8(2)	2(1)	
Magnetic graphite batch 2	91(3)	–	–	6(2)	3(1)	
Magnetic graphite batch 3	92(3)	–	–	6(2)	2(1)	

netic effect here reported, both graphite samples, the modified and the pristine ones, should exhibit the same magnetic behavior, which clearly is not the case. A possible explanation for the increase of the impurities concentration observed specially in iron (approximately 50%) could be the graphite evaporation and recrystallization process in the synthesis here described.

Fig. 2 shows the X-ray diffraction profile for the pristine and the modified graphite. A minor shift towards lower d-spacings is detected, in particular for the (0 0 2) and (0 0 4) reflections. In fact the peaks of the modified graphite are wider and asymmetric, suggesting less crystallinity of this specimens and/or the possible coexistence of regions with different *c*-axis values. This fact could explain the difficulty found to unambiguously determine the *c* cell parameter. In spite of this, the inset could be an evidence of the *c*-axis compression suggesting a graphite structure with defects that would have the effect to get the graphene layers closer.

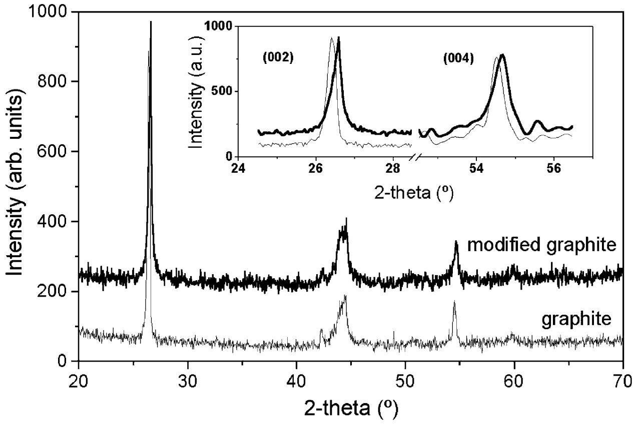

Fig. 2. X-ray diffraction profiles of pristine and modified graphite. The inset shows the details of the (0 0 2) and (0 0 4) reflections regions (smoothing has been applied to the (0 0 4) region, for clarity).

SEM micrographs have given enough evidences about the topological changes occurring at the

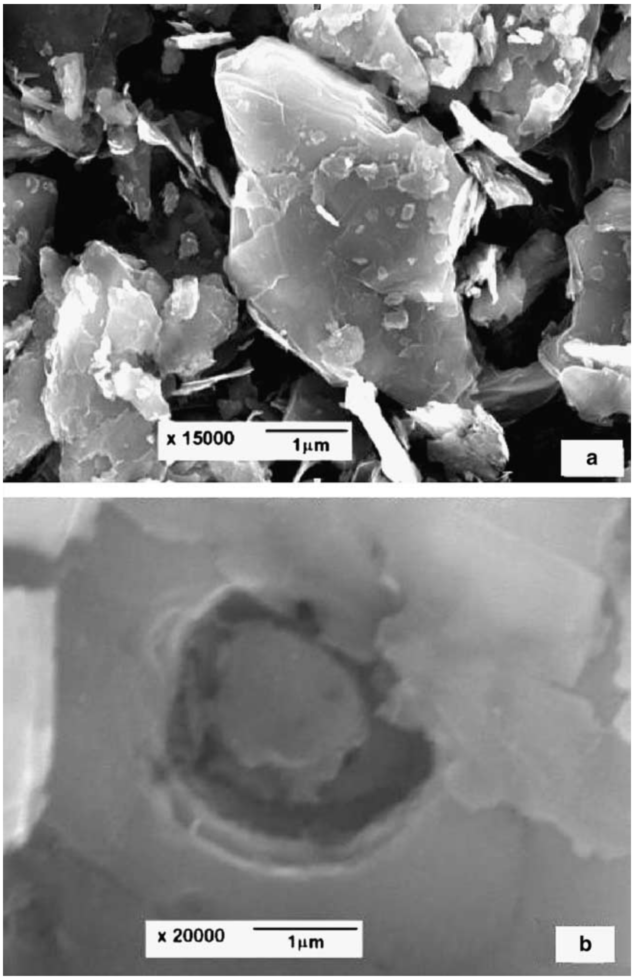

Fig. 3. SEM images of the morphology of (a) the graphite used as reagent; (b) one pore in the modified graphite, 1 µm diameter—the propagation of the pore along the lamellar structure can be seen.

micro-structural scale. Fig. 3a and b show micrographs from the pristine graphite powder used as reagent and the processed material, respectively. Fig. 3b shows a graphite grain after chemical attack, exhibiting a pore. The pores exhibit a large dispersion of sizes with diameters ranging from a few nanometers to approximately 1 μm.

In Fig. 4 we show the zero-field cooled (ZFC) magnetization vs. temperature for an external magnetic field $H = 1000$ Oe. The inset shows χT vs. T for two measurements for the same specimen, where magnetic transitions at 110 and 320 K can be seen, as well as the stability of the material after 6 months.

Fig. 5 exhibits the hysteresis cycle for the m vs. H curve at 300 K. The diamagnetic background of the specimen at $T = 2$ K, obtained in fields up to 50 kOe is shown in the inset. A saturation magnetization of 0.58 emu/g is obtained after subtracting this background—equivalent to 1.2×10^{-3} μ_B per carbon atom ($1\ \mu_B = 9.27 \times 10^{-21}$ erg/G). Assuming that $g = 2$ and $S = 1/2$ for the defects, this value of magnetization would lead to an approximate defect concentration of 1250 ppm. At 300 K the saturation magnetic moment was 0.25 emu/g. To justify these values through the role of magnetic impurities by assuming that all these impurities behave as bulk ferromagnetic material—which most probably would not be the case, it would be required about 2600 ppm of Fe. Since this value is much higher than the one determined as the total content of Fe in the studied samples, this justification could be ruled out. The coercive field observed at 300 K was $H_c = 350$ Oe, and the remnant magnetization was 0.04 emu/g, which corresponded to 16% of the saturation magnetic moment at 300 K. It is noteworthy that this room temperature ferromagnetic behavior of our treated carbon samples has also been verified through magnetic force microscopy experiments. This work and a more complete magnetic characterization of the complex behavior of this material, including a discussion of the nature of the magnetic transition temperatures observed has been recently published [8].

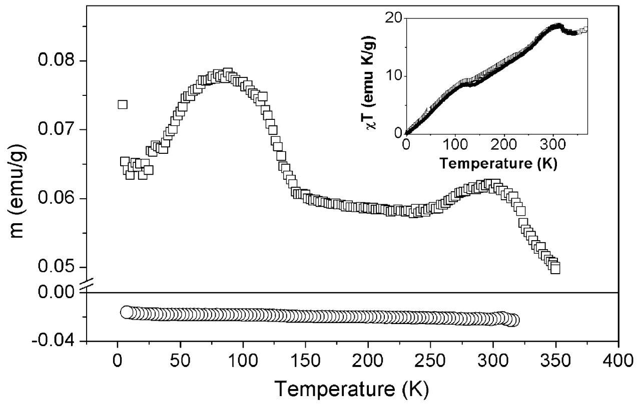

Fig. 4. Zero-field cooled (ZFC) magnetization vs. temperature curve, for an external magnetic field $H = 1000$ Oe (open squares); the curve with open circles shows the magnetic behavior of the pristine graphite powder used as reagent. The inset shows χT vs. T for two measurements for the same specimen (closed symbols $t = 0$, open symbols $t = 6$ months). Specimen mass: 0.4 mg.

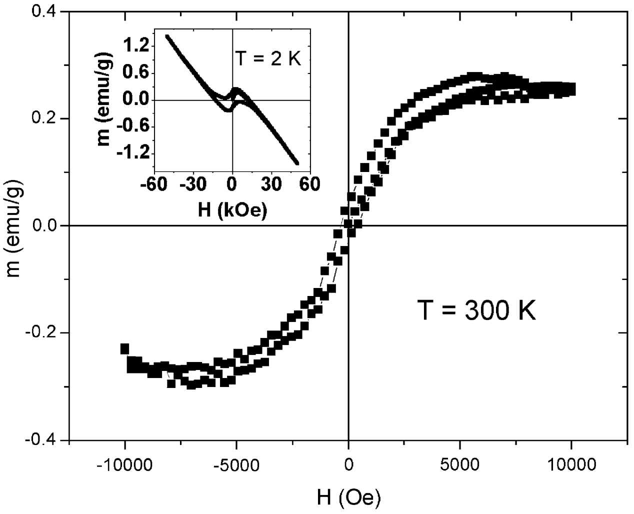

Fig. 5. Hysteresis curves, m vs. H, for the magnetic graphite material, for $T = 300$ K. The inset shows the m vs. H curve at $T = 2$ K, where the diamagnetic contribution can be seen. Specimen mass: 0.4 mg.

4. Conclusions

We have found a simple and inexpensive chemical route, based on a vapor phase reaction, to obtain bulk ferromagnetic graphite. According to theoretical studies [9], defects in the honeycomb structure of graphite could develop spontaneous magnetization due to the rise of a sharp asymmetric peak in the density of states at the Fermi level, which is required for a system of itinerant electrons to show ferromagnetism. The magnetic behavior here reported would be associated to microstructural features observed in the attacked sample that produce an inhomogeneous material with enhanced magnetism. The sp^3 and sp^2 bonds could also play an important role. The decrease in the d-spacings of the ($00l$) reflections, could be explained through the existence of tetrahedral carbon atoms located at the graphene sheets, producing a foamy carbon material [10]. More work has to be done in the future on this material to better understand the arising magnetism.

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