Magnetic ordering and interactions in iron-filled carbon foam

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Abstract

Ferromagnetically filled graphitic-carbon foams are a new class of materials characterized by an open-cell structure continuously filled with ferromagnetic crystals. Targetted design for applications requires knowledge of the magnetic ordering and the interaction between magnetic moments in the filling and those due to the spin of the delocalised π -electrons which contribute to thermal and electrical conduction in the graphitic carbon. Magnetometry together with electron spin resonance, thermoelectric, and calorimetric measurements on iron-filled carbon foam reveal ferromagnetic responses at room temperature with a transition to anti-ferromagnetic behaviour in some fraction of the filling at 130 K. This observation is consistent with the α -Fe (bcc) to γ -Fe (fcc) transition at this temperature predicted by others. Seebeck coefficient measurements revealed a behaviour typical of

unmodified graphitic carbon indicating the absence of any interaction between the magnetic moments of the filling and the conduction electrons in the graphitic carbon.

1 Introduction

Ferromagnetically filled carbon materials are multifunctional systems which can exploit controllable magnetic properties and important electromagnetic waves dissipation characteristics to be used in multiple technological applications. This class of materials frequently includes 1) graphene coated iron-filled nano-composites [1], 2) amorphous-carbon-coated iron/iron-oxide-filled composites [2-11] 3) ferromagnetically filled carbon foam [12-15], 4) ferromagnetically filled carbon nanotubes (Me@CNTs, where Me is the encapsulated metal or metal carbide) [16-28], 5) ferromagnetically filled carbon onions (Me@CNOs) [28] and 6) ferromagnetically filled CNTs-polymer composites [16, 29-35]. Typical examples of used polymers for films fabrication include (Ca-SA)/deacetylated konjac glucomannan (DKGM) [29], P(GMA-EGDMA) [34], Sodium alginate [32], P(GMA DVB) [35] and polyurethane–urea (Spandex) [16].

In typical iron-filled amorphous-carbon-coated or polymer-based composites the ferromagnetic/paramagnetic particles have been frequently coated with: 1) amorphous carbon [2-11] through the use of high intensity ultrasound for the decomposition of $\text{Fe}(\text{CO})_5$ and subsequent annealing or 2) graphene layers which have been reported to exhibit excellent microwave absorption performances [1]. Recent works have also shown that multishelled ZnO spheres could be considered possible candidates to encapsulate functional materials of interest [31].

The key advantages of ferromagnetically filled graphitic-carbon foams [12-15] relative to other, comparable systems are 1) the high-volume-fraction of the continuous ferromagnetic filling, 2) typically high saturation magnetizations comparable to those of bulk iron, and 3) the scalability of the production method, which involves fusion of Fe_3C nanocrystals encapsulated by spherical graphitic carbon shells by annealing at high temperature [12-15]. The applications of this composite material exploit the controllable ferromagnetic properties or the inherent electromagnetic absorption dissipation properties of the magnetic moments in the filling and the conduction electrons in the graphitic carbon.

The nature of the magnetic ordering and the question of whether the magnetic moments interact with those due to the spin of the π -electrons in the graphitic carbon – which contribute to thermal and electrical conduction – is therefore important if structure-property relations are to be understood and tailored design is to be achieved.

Here we address these questions in a novel investigation where we focus our attention on the magnetometry together with electron spin resonance (ESR), thermoelectric, and calorimetric measurements properties of iron-filled magnetic carbon foam.

We observe ferromagnetic hysteresis with a saturation magnetization $M_s = 180$ emu/g and a coercivity $H_s = 29$ Oe at room temperature and a reduction in magnetisation in the zero-field-cooled (ZFC) characteristic at 130 K. On the basis of the ESR and specific heat capacity measurements we conclude that this ZFC feature

is the result of a transition from ferromagnetic to antiferromagnetic ordering in some of the filling. Thermoelectric measurements indicate no interaction between the magnetic moments and the π -electron system.

2 Experimental

The iron-filled graphitic carbon foam was fabricated by using the two-stage process reported in Ref. 2-4. Self-organised Fe_3C nanocrystals encapsulated by graphitic carbon shells were firstly produced by ferrocene pyrolysis at 900 °C. Annealing was then performed in the same reactor at the temperature of 1000 °C under Ar flow.

The characterization was carried out with: a JSM-7500F 5-20 kV scanning electron microscope (SEM), an Empyrean PANalytical powder X-ray diffractometer (Cu $K\text{-}\alpha$, $\lambda = 0.154$ nm), and a 200 kV American FEI Tecnai G2F20 transmission electron microscope (TEM). Magnetisation measurements were performed with a vibrating sample magnetometer (Quantum Design). ESR measurements were performed using a JEOL JES-FA200. Differential scanning calorimetry (DSC) measurements were performed with a TA DSC 2920 in the temperature range -181 °C to 130 °C with a Sapphire reference. Seebeck measurements were performed with an MMR technologies, Inc. SB-100 Seebeck measurement system and K-20 temperature controller.

3 Results and Discussion

The morphology of the powder extracted from the reactor is detailed in Fig.1.

Figure 1: Photograph (A) and SEM micrographs (B,C) of iron-filled graphitic carbon foam.

The SEM micrographs in Fig.1B,C show an interconnected network. The mass contrast observed in backscattered electron SEM images revealed a high volume fraction of the heavier iron, Fig.Supp.1.

The XRD data in Fig.2 shows the progressive disappearance of Fe_3C features as a consequence of annealing.

Figure 2: XRD analyses of the iron-filled graphitic carbon foam showing structural variation as a consequence of annealing for (A) 2h and (B) 35h.

The intense diffraction peak observed at $2\theta \approx 45$ degrees is that of the 110 reflection of α -Fe. The TEM micrograph in Fig.Supp.2 is that of a typical iron/graphitic-carbon interface. Raman spectroscopy revealed the G and D peaks with a sp^3 -rich arrangement, in agreement with ref. 13-15 (Fig.Supp.3).

On the Raman spectrum shown in Fig.Supp.3 two bands could be detected at approximately $\sim 1300\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$. The first band (D band) is associated to the disordered induced scattering produced by imperfections or loss of hexagonal symmetry in the carbon structure and or presence of sp^3 -defects. The second band (G band) can instead be assigned to the Raman active $2E_{2g}$ mode which is generally observed in graphite like materials [43-45]. These observations are in agreement with those reported in ref. [13-15].

The room temperature variation of magnetization with applied magnetic field, Fig.3A, revealed ferromagnetic hysteresis with saturation magnetisation $M_s = 180\text{ emu/g}$, comparable to that of bulk iron (220 emu/g), and a coercivity $H_c = 29\text{ Oe}$. However, the ZFC characteristic shows a depletion of magnetization greater than the trend at approximately 130 K, Fig.3B.

ESR analyses through 130 K revealed further evidence for a transition in magnetic ordering below 130 K, Fig.4. The broad differential absorptions typical of ferromagnetic systems have minor superimposed features with g-factor values of 1.99 (attributable to the π -electron contribution [36,37]).

Figure 3: Magnetization versus (A) applied magnetic field strength at room temperature, and (B) temperature with no applied field (ZFC).

However, at a temperature less than 130 K there is also a significant narrow feature with a g-value of 4.16. This observation is compatible with the presence of magnetic contributions from both γ -Fe (fcc) and α -Fe (bcc) at temperatures below 130 K [36-38]. The diminution of the ZFC magnetisation at 130 K also suggests that the γ -Fe is in the antiferromagnetic state [21,24].

Figure 4: ESR spectra at (A) 300 K, (B) 130 K and (C) 77 K.

DSC measurements show a decline in specific heat capacity in the temperature range at approximately 130 K; this is further evidence for a significant structural transition at low temperature, Fig.5. The temperature dependence of the Seebeck coefficient, S , (Fig.6) is of the smoothly varying form generally observed in unmodified carbon nanotube networks, which comprises semiconductor- and metal-like terms,

$$S = AT + (B|\lambda|/T + C)\exp(-\lambda/T) \quad (1)$$

where A , B , and C are constants and λ is the band-gap temperature of the semiconductor-like component [39]. The fitting of the data in Fig.6 to Equation 1 was achieved with A : $0.0257 \mu\text{V}/\text{K}^2$, B : $-0.0041 \mu\text{V}/\text{K}$, C : $-20 \mu\text{V}/\text{K}$, λ : 536 K ; the sign and magnitude of these values are comparable with those extracted from carbon nanotube networks [39,40].

There are no large peaks associated with the Kondo effect in Fig.6 [41,42]; meaning there is no interaction of the magnetic moments of the filling with the spin of the conduction π -electrons in the graphitic carbon.

Figure 5: Specific heat capacity versus temperature obtained from the DSC measurement.

Figure 6: Variation of the Seebeck coefficient with the temperature. The solid line is the fit to Equation (1) with the values of parameters given in the text.

4 Conclusion

In conclusion, iron-filled graphitic carbon foam exhibits ferromagnetic ordering at room temperature and both ferromagnetic and antiferromagnetic ordering at temperatures below 130 K. There is no significant interaction between the magnetic moments in the iron and those due to the spin of π -electrons in the graphitic carbon.

Acknowledgements

We acknowledge the NSFC 11404227.

Data Availability

Additional characterization analyses can be found in the electronic supplementary information (ESI).

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