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Structure and magnetic properties of nanoparticles trapped in a carbon matrix along with the catalytic growth of carbon nanotubes

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Abstract

The combination of magnetic materials and carbon nanotubes (CNTs) is a promising research direction with a wide range of applications such as magnetic storage and drug delivery free of toxicity. It is well known that some transition metals are mandatory for the nucleation and growth of CNTs by pyrolysis. This paper deals with a new approach where Fe–C nanostructures are developed in a carbon matrix with a random network of CNTs by the polymers pyrolysis (phenol-formaldehyde resins and polyvinyl alcohol) and ferrocene up to 900 °C in inert atmosphere. The proposed method is simple and could be a promising way to produce magnetic nanoparticles coated with carbon as well as CNTs. The characterization (TEM, Mössbauer spectroscopy) and magnetic properties of the carbon–iron system are systematically investigated.

Keywords: Magnetic nanoparticles; Carbon nanotubes; Mössbauer spectroscopy

1. Introduction

The wide range of applications due to their unusual properties has chiefly driven the growing scientific interest for the combination of magnetic materials and carbon nanotubes (CNTs). Nanosized magnetic particles along with the exceptional electronic properties and the hollow structure characteristic of CNTs could have interesting applications in various fields such as magnetic recording media, catalyst supports, and filler in epoxy matrix that could lead to nanocomposites with novel magnetic properties or magnetically guided drug delivery free of toxicity systems [1–5]. The tempting properties and applications of ferromagnetic nanoparticles encapsulated in CNTs are intensively studied because the carbon shell provides an effective barrier against oxidation ensuring a long-term stability of the metallic magnetic filler against environmental degradation [6,7]. Among inert materials up to 300 °C in air, carbon is an ideal choice due to it forms a variety of empty fullerenes such as onions and nanotubes to enclose metallic nanoclusters, as reported by many studies [8–12]. A nonmagnetic matrix such as carbon improves the magnetic stability in these nanosized particles by reducing the random flipping of the magnetic moment occurring by thermal fluctuations [13,14].

Actually, the synthesis methods used to generate nanoclusters in CNTs are: arc-discharge [15], magnetron and ion-beam co-sputtering [16], chemical vapor deposition [17], mechanical milling [18] and laser pyrolysis [19]. Less attention has been paid to catalytic pyrolysis of the carbon containing materials, in particular polymers. The advantages of this method are related to the simple processing setup combined with a large of class of carbon precursors.

This paper deals with a new approach where magnetic nanoparticle agglomerates of iron and its carbides are developing in a carbon matrix with a randomly network of carbon nanotubes (CNTs) by the pyrolysis of polymers (cross-linked phenol-formaldehyde condensation resin named novolac and

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polyvinyl alcohol) and ferrocene up to 900 °C in inert atmosphere. We present here the qualitative change in the phase composition during pyrolysis process and the magnetic properties exhibited by the carbon–iron system.

2. Experimental

Iron dissoluted in a carbon matrix was obtained by catalytic pyrolysis of polymers and ferrocene. The starting materials: novolac, resin type phenol-formaldehyde condensation (NH) as received from Romanian company Nitramonia Fagaras, cross-linked agent called hexamethylenetetramine (HMTA), polyvinyl alcohol (PVA) and ferrocene powder (Merck reagents). The weight of polymers for pyrolysis was kept constant for all compositions. A change in iron content was obtained by changing the mass percent of ferrocene. The HMTA with 10 wt.% of novolac and two amounts of ferrocene (the content of iron from ferrocene was 2.5% and 5% by weight to novolac) were dissolved in ethanol. After evaporation of alcohol, drying for 24 h at 50 °C and mincing, the pellets were formed by pressing. The same procedure was used for PVA and ferrocene. The samples were categorized as follows: NH-Fe-*x* and PVA-Fe-*x* where $x=2.5$, 5 stand for the iron content. All pellets were pyrolyzed up to 900 °C in three steps: (1) heating to 180 °C (10 °C/min) in air, 1 h soaking time to produce a large cross-linked lattice; (2) heating to 300 °C for 1 h in Ar atmosphere, 30 min soaking time which is close to initiate pyrolysis and ferrocene decomposition; (3) pyrolysis regime from 300 °C to 900 °C, at rate of 3 °C/min. At 900 °C samples were kept for 1 h and then cooled to room temperature.

The samples were characterized by transmission electron microscopy (TEM) and Mössbauer spectroscopy. Philips CM120ST (Customized Microscope 120 Super Twin) was used for collecting the TEM images. The ^{57}Fe Mössbauer effect measurements at room temperature were performed in the transmission geometry using a constant acceleration type spectrometer with ^{57}Co in rhodium as source. Magnetization hysteresis loops were measured on all samples at room temperature

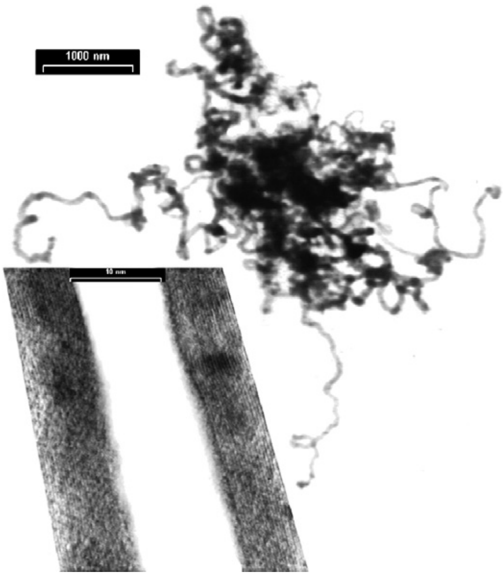

Fig. 1. TEM image showing carbon nanotubes developed from NH-Fe-5.

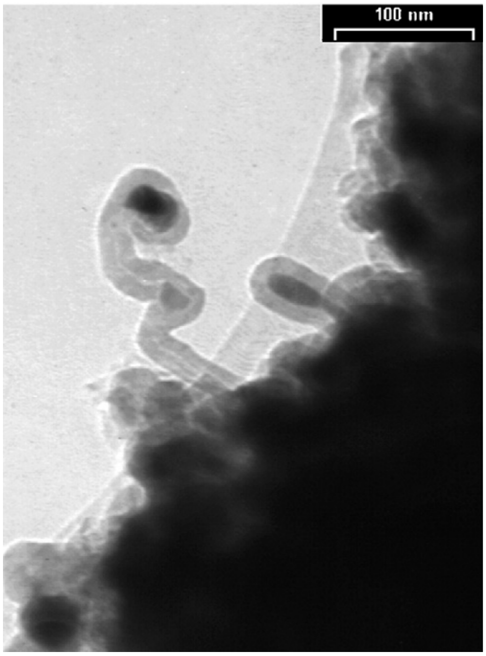

Fig. 2. TEM image showing carbon nanotubes developed from PVA-Fe-5.

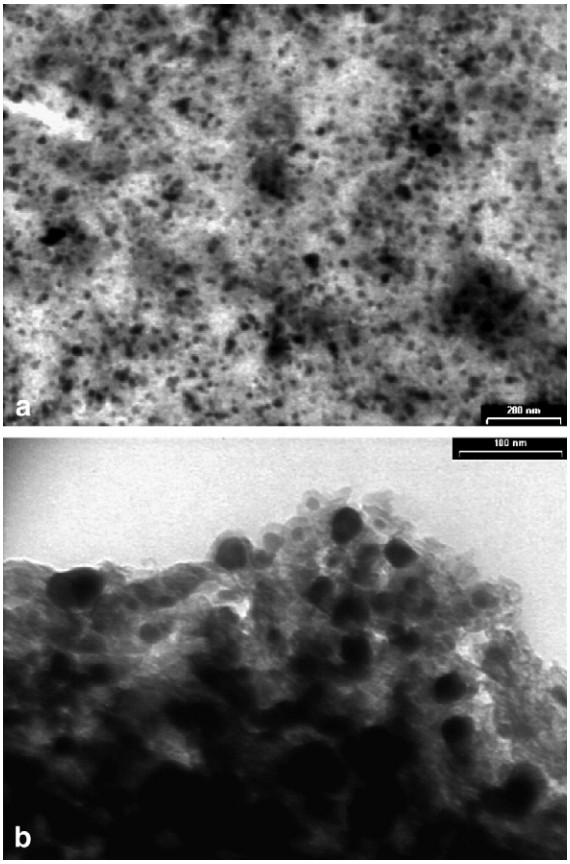

Fig. 3. TEM images of iron nanoparticles embedded in carbon matrix: (a) PVA-Fe-2.5 and (b) PVA-Fe-5.

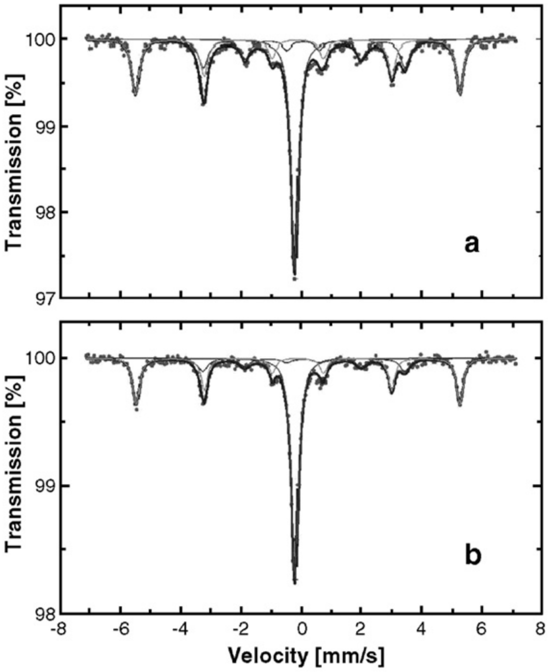

Fig. 4. Mössbauer spectra of NH-Fe-2.5 (a) and NH-Fe-5 (b).

and 77 K in the magnetic field up to 1 T using a vibrating sample magnetometer (VSM) LakeShore 7300.

3. Results and discussions

Four samples with different concentration of magnetic nanoparticle agglomerates in a carbon matrix were obtained. The presence of nanoparticles in the synthesized samples was proved by TEM analysis. The Mössbauer and magnetic moments allowed the identification of the iron nanometric phases.

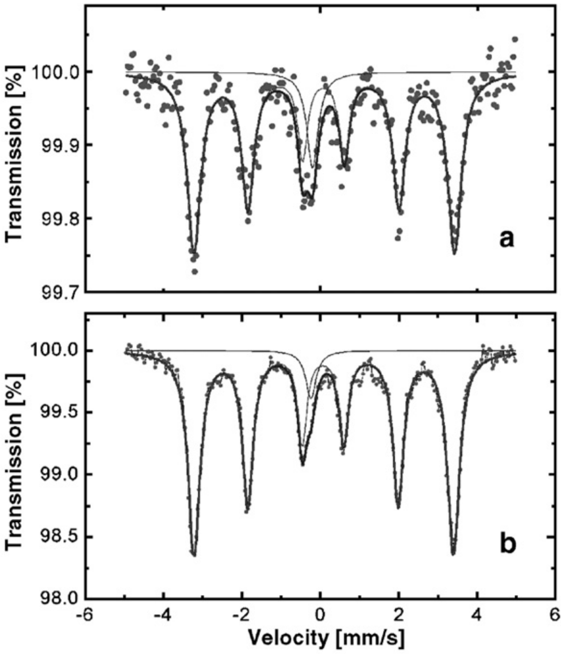

Fig. 5. Mössbauer spectra of PVA-Fe-2.5 (a) and PVA-Fe-5 (b).

Table 1
Room temperature hyperfine parameters obtained from Mössbauer spectra (δ referred to metallic iron)

Iron phase	Hyperfine parameters	2.5 wt.% Fe		5 wt.% Fe	
		NH-Fe-2.5	PVA-Fe-2.5	NH-Fe-5	PVA-Fe-5
Fe_3C (sextet I)	δ (mm s^{-1})	0.184	0.197 (5)	0.194 (1)	0.185 (17)
	H_{hf} (T)	20.79 (12)	20.57 (4)	20.72 (7)	20.47 (2)
	Relative intensity (%)	16.43	89.70	24.22	95.08
α-Fe (sextet II)	δ (mm s^{-1})	−0.009 (4)	–	−0 005 (4)	–
	H_{hf} (T)	33.20 (25)	–	33.27 (3)	–
	Relative intensity (%)	38.55	–	37.99	–
γ-Fe (single line)	δ (mm s^{-1})	−0.096 (1)	−0.085 (17)	−0.097 (1)	−0.127 (14)
	Relative intensity (%)	45.02	10.30	37.79	4.90

The specific features at nanoscale (Figs. 1 and 2) show CNTs and iron compound nanoclusters in pyrolyzed samples. It can be observed the content of CNTs is slightly lower in the case of PVA-Fe-*x* than NH-Fe-*x*. Fe(C) nanoparticles embedded in the carbon matrix are well defined in TEM images (Fig. 3a and b) for PVA-Fe precursors. The dimension of the iron species is in the range of 25–30 nm for 2.5 wt.% iron (Fig. 3a) and 30–40 nm for 5 wt.% iron content (Fig. 3b). The iron cluster density remains approximately constant even though the iron content increases in the samples. This may be explained by the aggregation of iron nanoparticles.

The Mössbauer spectra give the relative amounts of the iron phases (Figs. 4 and 5). The spectra were fitted with two (PVA-Fe-*x*) and three (NH-Fe-*x*) subspectra: one for six-line ferromagnetic patterns and paramagnetic single line respectively. Hyperfine parameters (isomer shift, δ, hyperfine field, H_{hf} and the relative intensity (%)) based on above fitting are listed in Table 1. The first six-line pattern (sextet I) is assigned to iron carbide — Fe_3C, which in agreement with Ref. [20] has a magnetic hyperfine field 20.8(2) T. The second six-line pattern (sextet II) with the magnetic hyperfine field of 33 T is assigned

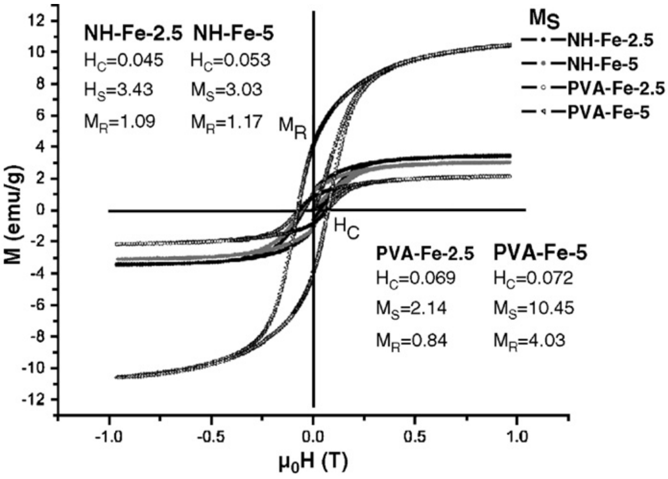

Fig. 6. Hysteresis loops for NH-Fe-x and PVA-Fe-*x* samples at 293 K.

Table 2
Magnetic parameters

293 K					77 K				
Sample	M_S (emu/g)	M_R (emu/g)	H_C (T)	$S=M_R/M_S$	Sample	M_S (emu/g)	M_R (emu/g)	H_C (T)	$S=M_R/M_S$
NH-Fe-2.5	3.43	1.09	0.0453	0.3177	NH-Fe-2.5	3.71	1.494	0.0696	0.4026
NH-Fe-5	3.03	1.17	0.053	0.3861	NH-Fe-5	3.22	1.478	0.0903	0.4590
PVA-Fe-2.5	2.14	0.84	0.0692	0.3925	PVA-Fe-2.5	2.43	1.285	0.212	0.5288
PVA-Fe-5	10.45	4.03	0.072	0.3856	PVA-Fe-5	11.73	6.188	0.2118	0.5275

to α-Fe [21]. Single line subspectrum can be assigned to the paramagnetic austenite due to its isomer shift [21–24]. NH-Fe-*x* samples (Table 1) have a large amount of paramagnetic (austenite) phase by comparison with PVA-Fe-*x*. That is a consequence of carbon precursor structures: NH samples release large amount of well-ordered graphene, which are converted in CNTs forming as a cage around of iron nanoparticle than PVA in the pyrolysis process. α-Fe phase is present in both NH-Fe-*x* samples, while for PVA-Fe-x samples α-Fe was not detected. These differences can be related with the nature of polymer and pyrolysis process. Iron atoms released from ferrocene interact either with carbon structures forming Fe_3C clusters or by diffusion processes form α-Fe clusters (ferromagnetic). Due to the pyrolysis temperature (900 °C) some clusters can appear as austenite phase (γ-Fe, paramagnetic). Therefore, depending on the polymer precursors (NH or PVA) can be obtained different ratios of α-Fe and γ-Fe phases. That means the structure of carbon material precursors influences the final structure of Fe nanoparticles.

The ferromagnetic component of NH-Fe-*x* and PVA-Fe-*x* characterized by hysteresis behavior (Fig. 6), at 293 K, depends on the iron content in the precursors as well as formed phases in the final material. The ferromagnetic nature of the nanoparticles is measured by the ratio of remanence to saturation magnetization ($S=M_R/M_S$). The saturation magnetization (M_s), coercivity (H_c) and ratio *S*, for the all samples, at 77 K and 293 K are given in Table 2. Considering the relative amount of iron in the sample, the ratio of M_S for PVA-Fe-5 to M_S for PVA-Fe-2.5 should be about twice. As it can be observed, from Table 2, the M_S is 10.45 emu/g for PVA-Fe-5 and 2.14 emu/g for PVA-Fe-2.5, respectively. In the case of NH-Fe-*x*, the values of M_S are lower ones comparatively with the M_S values for PVA-Fe-5. These results are in agreement with the increasing of the relative amount of paramagnetic component as shown in Mössbauer spectra. Taking in account the cluster size and their magnetic behavior it can be concluded they are close to the single magnetic domains.

4. Conclusions

The catalytic assisted pyrolysis proved to be an appropriate method to prepare Fe and Fe–C nanostructures embedded in carbon matrix. The iron resulted from ferrocene decomposition are clustering by diffusion processes and reactions in the solid state. The presence of iron in pyrolyzed system leads to carbon structures similar with nanotubes, in our case MWNTs. The magnetic properties of iron-based bulk materials could be highly enhanced if particles are in nanometer range. This method could be useful for large-scale applications where metal-carbon with high CNTs content is need.

References

[1] T. Mühl, M. Ritschel, R. Kozhuharova, D. Elefant, A. Graff, A. Leonhardt, I. Mönch, C.M. Schneider, St. Groudeva-Zotova, Highlights 27 (2002).

[2] J. Qiu, Y. Li, Y. Wang, Y. An, Z. Zhao, Y. Zhou, W. Li, Fuel Processing Technology 86 (2004) 267.

[3] M. Leonowicz, M. Woźniak, Y.M. Shulga, V.E. Muradyan, Z. Liu, H.A. Davies, W. Kaszuwara, J. Grabski, Materials Letters 60 (2006) 442.

[4] X.X. Zhang, G.H Wen, S. Huang, L. Dai, R. Gao, L. Wang, Journal of Magnetism and Magnetic Materials 231 (2001) L9.

[5] D. Zilli, C. Chiliotte, M.M. Escobar, V. Bekeris, G.R. Rubiolo, A.L. Cukierman, S. Goyanes, Polymer 46 (2005) 6090.

[6] B.H. Liu, J. Ding, Z.Y. Zhong, Z.L. Dong, T. White, J.Y. Lin, Chemical Physics Letters 358 (2002) 96.

[7] H. Song, X. Chen, Chemical Physics Letters 374 (2003) 400.

[8] Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, S. Yamamuro, K. Wakoh, K. Sumiyama, K. Suzuki, A. Kasuya, Y. Nishina, Journal of Applied Physics 75 (1994) 134.

[9] P.J.F. Harris, S.C. Tsang, Chemical Physics Letters 293 (1998) 53.

[10] D. Babonneau, T. Cabioch, A. Naudon, J.C. Girard, M.F. Denanot, Surface Science 409 (1998) 358.

[11] S. Tomita, M. Hikita, M. Fujii, S. Hayashi, K. Yamamoto, Chemical Physics Letters 316 (2000) 361.

[12] C.H. Liang, G.W. Meng, L.D. Zhang, N.F. Shen, X.Y. Zhang, Journal of Crystal Growth 218 (2000) 136.

[13] J. Hery, J. Scott, S. Majetich, Physical Review B 52 (1995) 12564.

[14] V.P. Dravid, J.J. Host, M.H. Teng, B.E.J. Hwang, D. Lynn Johnson, T.O. Mason, J.R. Weertman, Nature 374 (1995) 602.

[15] F. Yu, J.N. Wang, Z.M. Sheng, L.F. Su, Carbon 43 (2005) 3018.

[16] T. Hayashi, S. Hirono, M. Tomita, S. Umemura, Nature 381 (1996) 772.

[17] M. Chhowalla, K.B.K. Teo, C. Ducati, N.L. Rupesinghe, G.A.J. Amaratunga, A.C. Ferrari, et al., Journal of Applied Physics 90 (2001) 5308.

[18] L. Daroczi, D.L. Beke, G. Posgay, M. Kis-Varga, Nanostructured Materials 6 (1995) 981.

[19] B. David, N. Pizúrová, O. Schneeweiss, P. Bezdièka, R. Alexandrescu, I. Morjan, A. Crunteanu, I. Voicu, Journal of Magnetism and Magnetic Materials 290–291 (2005) 179.

[20] V.I. Goldanskii, Chemical Applications of Mössbauer Spectroscopy, Academic Press, New York, 1968.

[21] E.D. Cabanillas, J. Desimoni, G. Punte, R.C. Mercader, Materials Science and Engineering A 276 (2000) 133.

[22] A. Aydin, E. Guller, H. Aktas, H. Gungunes, Bulletin of Materials Science 25 (2002) 350.

[23] S. Iwama, T. Fukaya, K. Tanaka, K. Ohshita, Y. Sakai, NanoStructured Materials 12 (1999) 241.

[24] A. Mijovilovich, A. Gonçalves Vieira, R. Paniago, H.D. Pfannes, B. Mendonça Gonzalez, Materials Science and Engineering A 283 (2000) 65.