STRUCTURAL AND MAGNETIC PROPERTIES OF MULTIWALL CARBON NANOTUBE ARRAYS WITH INCORPORATED IRON-PHASE NANOPARTICLES

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Abstract – We have performed an experimental study of the structure, composition and magnetic properties of carbon nanotube (CNT) arrays at different catalyst source concentrations during their synthesis. Floating catalyst chemical vapor deposition was chosen for the synthesis of CNT arrays as a low-cost, simple and effective technique. Various concentrations of ferrocene/xylene solution used as a feedstock for CNT growth allowed obtaining arrays of aligned multi-wall CNTs on Si/SiO_2 substrates with different percentage content, shape and aspect ratio of catalyst inclusions being incorporated in the channels and between the shells of CNTs. In this way the nanoparticles are mostly isolated from interaction with each other, and protected from oxidation in the air atmosphere. The structure and composition of the obtained material was investigated by scanning and transmission electron microscpies, Raman, Mössbauer spectroscopies, and X-ray diffraction. Magnetic properties of CNT arrays were studied by SQUID magnetometer in parallel and perpendicular to the substrate directions at various temperatures (2-380 K). Our results show that magnetic properties of CNT-iron phases can be easily varied depending only on the initially used catalyst source concentration for CNTs synthesis.

I. INTRODUCTION

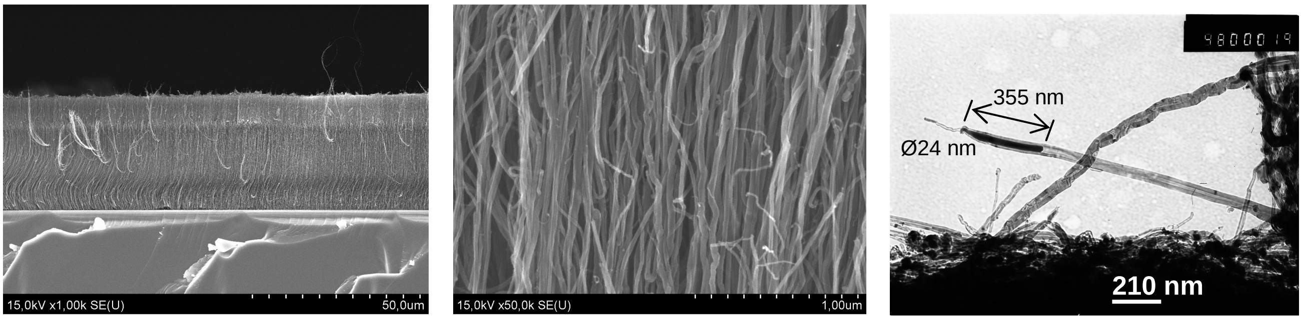
The interest of reserchers to exploring carbon nanotubes (CNTs) properties haven't subsided since their discovery. The range of their possible applications is very broad, spreading from nanoelectronics to civil engineering. Vertically aligned CNTs filled with magnetic nanoparticles are very promising as a building blocks for many nanoelectronic devices, such as nanothermometers [1], sensors for scanning force microscopy [2], ferromagnetic nanocontainers for biomedical applications [3], high density magnetic storage media [4]. Among various technological methods, floating catalyst chemical vapor deposition (CVD) is one of the most promising, since it allows creating CNT arrays over the large surface areas in controllable manner, and introducing the magnetic particles into CNTs *in situ* during their synthesis.

In this work we used three concentrations of ferrocene/xylene solution, $C_F = 0.5\%$, 1% and 10%, as a feedstock for CNT synthesis. The temperature in the reaction zone during synthesis was 1150 K, and the growth duration was 30 s. As a result, the vertically aligned CNT arrays of 50–100 μm height were obtained. In Fig. 1 the scanning (a,b) and transmission (c) electron microscopy (SEM/TEM) images of CNT arrays synthesized on Si substrate at $C_F = 10\%$ are shown. In TEM image (Fig. 1c), the elongated catalyst nanoparticle in the CNT channel is shown, and a smaller size nanoparticle is indicated by an arrow.

In our earlier study by Mössbauer spectroscopy and X-ray diffraction revealed, that these catalyst nanoparticles represent Fe_3C phase mostly [5].

II. RESULTS

Magnetic properties of the samples were studied by measuring the zero filed cooled (ZFC) and field cooled (FC) magnetizations at magnetic field of $H = 75$ Oe applied either parallel (//) or perpendicular (⊥) to the CNT axis, as a function of temperature. In Figs. 2a and b the ZFC-FC magnetization curves for the samples synthesized with $C_F = 10\%$ and $C_F = 0.5\%$ are shown, correspondingly. For both samples the ZFC-FC curves reveal the typical features of an ensemble of ferromagnetic particles with different interaction forces between them, which, in turn, depend on their concentration [6].

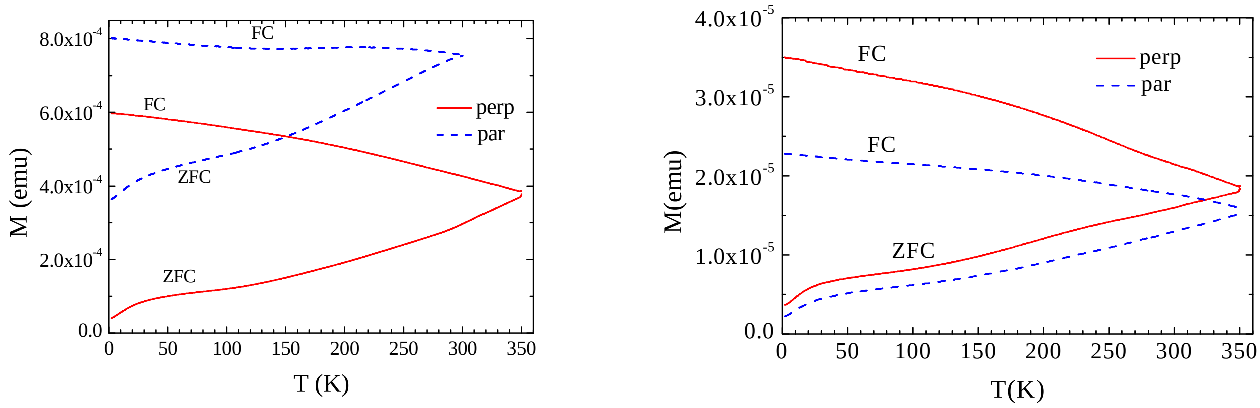


a) b) c)

Figure 1 – SEM (a,b) and TEM (c) images of aligned CNT arrays for C_F = 10%.

In Fig. 2a, it is clearly seen that the curves only coincide at the highest measured temperature (300K for the parallel and 350K for the perpendicular orientation). Therefore, the blocking temperature (T_B) is above these values. The behavior of the ZCF curve for C_F =10% is identical for both parallel and perpendicular field orientations, and its increase with temperature indicates the strong dipolar coupling between particles. The behavior of the FC curve, on the contrary, depends on the magnetic field orientation. For parallel orientation, a horizontal FC curve indicates strong demagnetizing effect, while for the perpendicular orientation FC curve decreases with temperature. This behavior indicates strong coupling of nanoparticles along the CNT axis (mainly situated inside CNT) and less coupling between particles belonging to different CNT. It is reasonable to associate the observed effect with the influence of CNTs on the magnetic coupling in different directions.

In Fig. 2b, the behavior of ZFC and FC curves is identical for both orientations which is explained by much lower concentration of nanoparticles in the C_F = 10% sample.

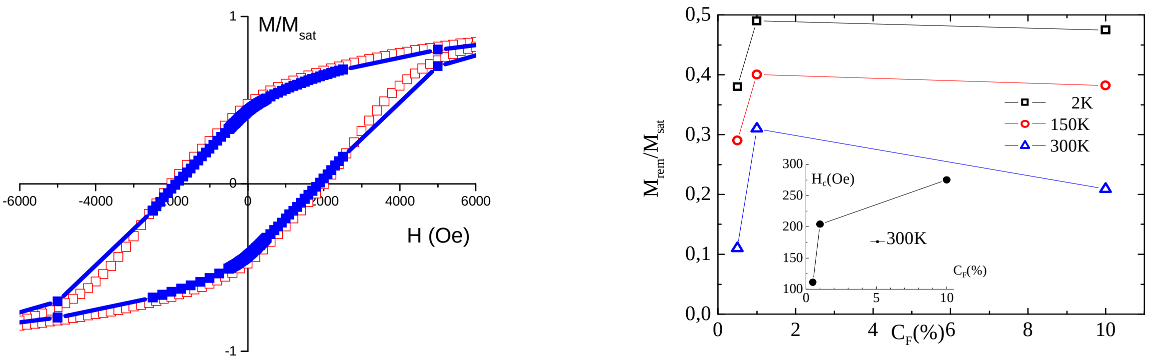


a) b)

Figure 2 – ZFC-FC curves as a function of temperature for perpendicular (solid lines) and parallel (dashed lines) orientation of the magnetic field of 75 Oe: (a) C_F=10%; (b) C_F=0.5%.

Next, magnetic hysteresis loops, $M(H)$, were measured using a Superconducting Quantum Interference Device (SQUID) magnetometer The magnetic field was varied in the range –8T…+8T and was also applied both in parallel and perpendicular to the CNT axis directions.

The $M(H)$ curves recorded for the C_F = 10% sample at 2K and different orientations of the magnetic field, are presented in Fig. 3a. Both curves are very similar to each other what corresponds to the almost isotropic behavior. In Fig. 3b the squareness (M_{rem}/M_{sat}) versus C_F at different temperatures and H_c versus C_F at 300K (in the inset) are plotted. Analysis of these data indicates that for C_F =10% the squareness at 300K becomes much lower than for the C_F =1% sample, while at other temperatures it almost does not change between C_F =1% and 10%; and for C_F = 0.5% it is always the smallest. This indicates that the sample synthesized at C_F = 0.5% is more isotropic and consist of small scattered non-interacting nanoparticles, which is in agreement with the results of ZFC-FC. The decrease of squareness as temperature goes down could be caused by thermal fluctuations. The coercive field value extracted from $M(H)$ curves measured at room temperature appeared to increase with C_F.



a) b)

Figure 3 – (a) $M(H)$ curves measured at T=2 K for CNT arrays obtained at C_F=10%. Magnetic field was applied in parallel (filled squares) and perpendicular (hollow squares) to CNT axis. (b) Squareness vs. C_F at different temperatures. Inset: Coercivity vs. C_F at T = 300K. Data refer to the perpendicular magnetic field.

III. Conclusions

In conclusion, the magnetic properties of CNT array with the iron phases nanoparticles obtained by the floating catalyst CVD have been studied. The main ferromagnetic phases were determined (Fe_3C). The overall content of magnetic phase, as well as the particle size can be easily controlled by changing C_F during synthesis. All the hysteresis loops measured on different samples were symmetric. Both the squareness and coercivity dependences on the C_F indicates the smallest inter particle interactions for the C_F = 0.5% sample with the lowest nanoparticles content and diameters.

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