COMPOSITES BASED ON NANOSIZED HIGHLY EXFOLIATED GRAPHITE

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Abstract

Composites of highly exfoliated graphite (HEG) with iron, cobalt, nickel, manganese and their several compounds have been prepared and studied by X-ray and neutron diffraction. Metal phases that are not observed for the bulk metals at room temperature were found in the prepared composites. The HEG-Co composite contained two phases: one of them was thermodynamically stable hexagonal phase and the other was a cubic phase, which is observed in bulk Co-samples only at ≥ 693 K. For the HEG-Mn composite, even three high-temperature phases were registered. It is suggested that phase transition temperature should be fallen significantly due to the low size of the composite components and their interaction. Magnetic properties of the composites are roughly identical to their bulk counterparts.

1 Introduction

Carbon materials are often used in composites, and with development of new kinds of nano-carbon materials it becomes interesting to use them as building blocks in nanocomposites. Composites of carbon nanotubes were widely studied during the last decade. Since recently, single- and multilayer graphenes received considerable attention [1-3] and were explored in various kinds of composites where second component is a polymer, a non-metal or a metal or their compounds, other carbon moiety (nanotube, fullerene, sphere etc.). Potential applications of such composites range from catalysis and energy storage to sensing, biotechnology and pollutant removals. Several excellent reviews on the topic have appeared in high-impact journals [4-8].

The majority of graphene nanocomposites including metal counterparts contain noble metals (Pt, Pd, Ru, Rh, Ir, Au, Ag), although there are some reports on Cu, Sn, Co, Ni, Fe, Ge – graphene hybrids [4-8]. The reported metal compounds deposited on graphene sheets include oxides, hydroxides, sulfides, selenides, nitride, inorganic salt and clay [4-8]. Graphene nanosheets decorated with magnetic nanoparticles such as Fe, Co, Ni, Fe_3O_4, etc. are studied for such diverse applications as batteries, targeted drug delivery, magnetic resonance imaging, removal of organic pollutants and metal ions etc [9-11]. Moreover, it was shown that charge

transfer, electronic and magnetic interactions between graphene nanoplatelets and semiconductor or magnetic materials can lead to new interesting properties [11].

Graphene supports used in nanocomposites are most often prepared through liquid-phase synthesis employing graphite oxide route. We have developed a new type of HEG, which is composed of <10 layers on average and can, therefore, be considered as a multilayered graphene [12-13]. This material is produced by rapid heating of fluorinated graphite intercalation compounds $C_2F \bullet xR$ (R = ClF_3, BrF_3) to 800ºC (the regime of «thermal shock»), and its higher exfoliation degree is due to increased volume of gaseous products coming from both intercalated molecules and C_2F matrix decomposition. In this work we have prepared and investigated HEG-based magnetic composites.

2 Materials and testing methods

We have synthesized eight composite samples HEG-Mn, HEG-Co, HEG-Fe, HEG-Ni, HEG-Fe_3O_4, HEG-$FeCl_3$, HEG-$CoCl_2$, HEG-$Ni(HCO_2)_2$. Composites with transition metal salts were prepared by adsorption of the dissolved salt on the HEG surface. By tuning the salt concentration it is possible to obtain composites with various salt contents. Composites with transition metals are prepared by heating the precursors in hydrogen at 350 ^{0}C.

Magnetic measurements were performed by using a commercial SQUID magnetometer (MPMS-5XL, Quantum Design, USA) at the Institute of Metal Physics.

Neutron powder diffraction experiments were carried out with D-2 diffractometer (IVV-2M reactor, Russia), with neutron wavelength λ=1.803 Å. We used the Rietveld program Fullprof for our analysis of neutron diffraction data.

3 Results and discussion

Figs.1 and 2 show neutron-diffraction patterns of HEG and HEG-Fe_3O_4 composite, correspondingly.
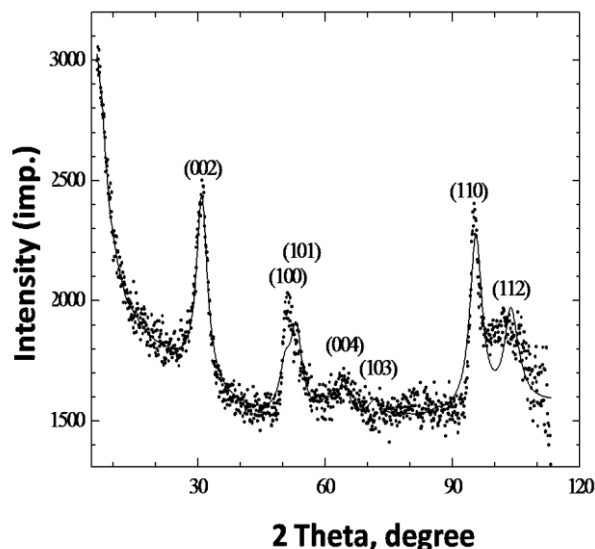
**Figure 1.** Observed (symbols) and calculated (line) neutron diffraction pattern of HEG.
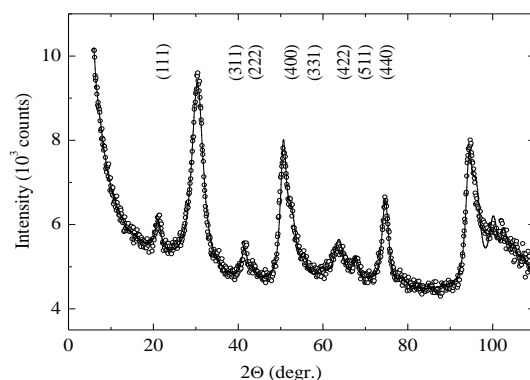
Figure 2. Observed (symbols) and calculated (line) neutron diffraction pattern of HEG-Fe$_3$O$_4$.

Indices mark reflections of Fe$_3$O$_4$ phase.

Carbon atoms occupy $2b$:(0, 0, 0) and $2c$:(0.333, 0.667, 0.25) positions in the hexagonal lattice (space group P 6$_3$/mmc) with parameters a = 2.463(3) Å and c = 6.860(7) Å. Iron oxide crystallizes in a spinel structure (s. gr. Fd3m) with lattice parameter a=8.441(6) Å, where iron ions occupy positions $8a$:(0.125, 0.125, 0.125) and $16d$:(0.5, 0.5, 0.5), and oxygen ions are located at the site $32e$:(0.244, 0.244, 0.244). Also, the sample contains the third phase, which is the metallic iron with Fe atoms at position $1a$:(0, 0, 0) (s. gr. Im3m, a=2.866(6) Å).

The most interesting result obtained with HEG-metal composites is the existence of metal phases at room temperature that are observed for the bulk metals only at high temperatures. For example, in case of the HEG-Co composite at 293 K, along with the thermodynamically stable hexagonal phase, we have revealed a high-temperature cubic phase, which is observed in bulk Co samples only at ≥ 693 K. For the HEG-Mn composite, even three high-temperature phases were found at 293 K. These results directly indicate that the temperature of structural phase transitions in metals significantly lowers with particle size decrease.

Magnetization values, type of magnetic ordering and temperature of the transition to the paramagnetic state were determined from field and temperature dependencies of the magnetization. Fig. 3 shows such dependencies for HEG-Fe composite.
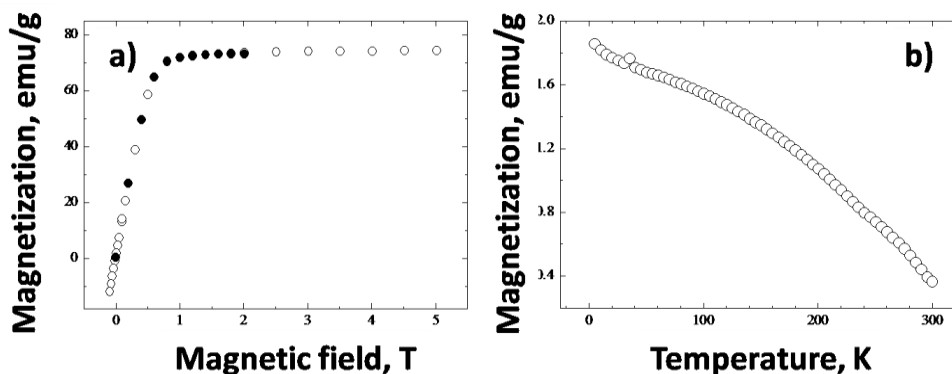
Figure 3. a) Field-dependence of the magnetization for HEG-Fe composite at 5K.
b) Temperature dependence of the magnetization for HEG-Fe.

The field dependence points on a ferromagnetic structure of the iron nanoparticles in this composite. Magnetization value is roughly equal to that of a bulk iron. Magnetization decreases slowly with temperature increasing. By extrapolating this dependence with help of Brillouin dependence, the Curie temperature was found to be about 1000 K that is approximately the same as for bulk iron. Similar curves for HEG-Co and HEG-Ni composites point on ferromagnetic-like ordering in these samples. The HEG-Mn composite demonstrated field and temperature dependencies of the magnetization typical for antiferromagnets. The dependencies for HEG-Fe_3O_4 show spontaneous magnetization, so it is possible to suggest a ferrimagnetic structure of this sample similar to that at bulk iron oxide.

3 Conclusions

Our study on the composites of HEG with transition metals has shown that at 293 K the composites contain metallic phases which are usually stable only at higher temperatures in bulk metals. This fact points on the strong influence of the size effect originating from both small size of the metal particles stabilized on the high surface area HEG support and their interaction with nanocrystalline carbon layers of HEG. The HEG-metal and HEG-Fe_3O_4 composites possess magnetic properties similar to those of the corresponding bulk samples.

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