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Highly stable Fe–Ni alloy nanoparticles encapsulated in carbon nanotubes: Synthesis, structure and magnetic properties

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ABSTRACT

Highly stable Fe–Ni alloy nanoparticles encapsulated in carbon nanotubes have been synthesized by *in situ* catalytic decomposition of benzene over Fe–Ni alloy nanoparticles generated through procedures of sol–gel fabrication and hydrogen reduction. The phases of graphite and γ-FeNi solid solution (face centered cubic) were identified by X-ray diffraction. The results of FE-SEM and HRTEM characterization revealed that Fe–Ni nanoparticles encapsulated in carbon nanotubes are generated in large quantity. The composites are highly stable in air and show soft magnetic property, with saturation magnetization affected by the composition of Fe–Ni alloy and the temperature of benzene decomposition.

1. Introduction

From the viewpoints of fundamental as well as applied research, the studies of the structure and properties of Fe-based alloys are important. Iron is among the most abundant elements on Earth, and is probably the major alloy component for the modern industry. The Fe and Ni elements can form a solid solution in all concentrations but the interesting alloys (such as permalloy A, B and INVAR) are those of fcc phase starting at a Ni composition of 28 mol%. The major feature of the Fe–Ni alloy system is a nearly vanishing thermal expansion coefficient of the $Fe_{0.65}Ni_{0.35}$ alloy as discovered by Guillaume and Hebd in 1897, known as the Invar effect [1]. With other special properties of Fe–Ni alloys such as shape memory, soft magnetization, and martensitic bcc–fcc phase transition with increasing concentration of Ni, Fe–Ni alloys are used in aircraft engines, laser systems, bimetallic thermostats, steam turbines in power generation plants and in medical, nuclear, chemical and petrochemical industries [2,3].

Nanoparticles of transition metals have properties that are significantly different from those of the corresponding bulk materials. However, the investigations and applications of these materials are restricted because they have a great affinity to oxygen and may ignite spontaneously in air even at room temperature (RT). The studies of the nanoparticles must therefore be performed *in situ* in ultrahigh vacuum or in reducing and inert atmospheres [4]. On the other hand, Fe and its alloys (such as the Fe–Ni alloys) are soft magnetic materials that show high specific saturation magnetization, low coercivity and high Curie temperature. Nonetheless, due to their metallic characteristics and the generation of eddy currents, their applications at high frequencies are severely limited [5].

The encapsulation of metallic particles inside a carbon shell is of considerable interest because the encapsulated species can be immunized against environmental degradation [6]. The approach offers an opportunity to investigate the dimensionally confined systems [7], consequently opening a broad range of promising applications, especially in information technologies and biomedicines [8,9]. Compared to the polymer and silica shells that are widely studied, shells made of carbon exhibit much higher stability in various chemical and physical environments such as in acid or base media, and at high temperatures and pressures. It is possible to introduce metals inside the hollow part of carbon nanotubes (CNTs). The introduction of 'foreign' materials may significantly alter the conducting, electronic or mechanical behavior of CNTs. The fabricated composite materials are typically used in technologies such as magnetic data storage devices [10–12], fuel

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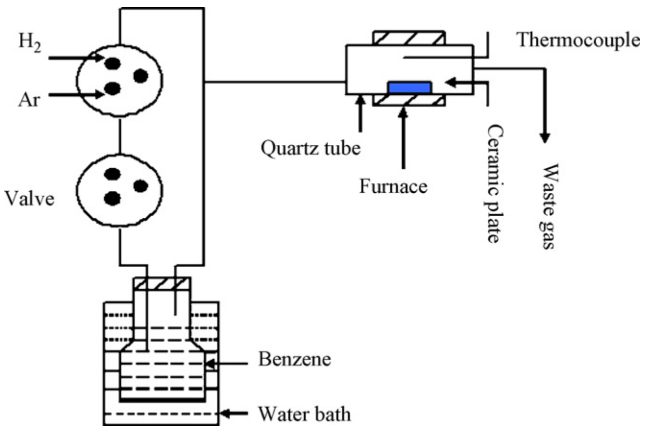

Fig. 1. Experimental setup.

cells [13,14], electromagnetic wave absorption [15,16], sensors for magnetic force microscopy [17] and human tumor therapy [18,19].

In the past decade, various techniques for encapsulating metals, alloys, metal oxides and chlorides in multi-walled or single-walled CNTs have been developed [20–22]. Herein, we report the encapsulation of Fe–Ni nanoparticles in CNTs by *in situ* catalytic decomposition of benzene in an Ar atmosphere at a temperature within the 430–600 °C range over freshly prepared FeNi alloy nanoparticles. The structure and magnetic properties of the composites (i.e. Fe–Ni alloy nanoparticles encapsulated in CNTs) were studied in detail.

2. Experimental

Two steps were used to synthesize the composites: (i) the preparation of Fe–Ni alloy nanoparticles and (ii) the simultaneous synthesis of CNTs and encapsulation of Fe–Ni nanoparticles. The experimental setup is shown in Fig. 1.

All the reagents were of analytical grade and used as received. To prepare the Fe–Ni nanoparticles, 0.03 mol $FeCl_2{\cdot}4H_2O$, quantitative amount of $NiCl_2{\cdot}6H_2O$ (Fe:Ni atomic ratios = 1:3, 2:2, and 3:1) and 0.045 mol citric acid monohydrate were dissolved in 250 mL absolute ethanol (while stirring at 60 °C for 6 h). The as-obtained mixture was kept at 80 °C for several hours, and then heated to 150 °C for the generation of a xerogel. Subsequently, the xerogel was heated in air at 500 °C for 4 h for the generation of the iron-nickel oxide (i.e. Fe_2O_3/NiO powder). To obtain the composites of FeNi alloy and CNTs in large quantity, a quartz tube reactor (6 cm in inner diameter and 75 cm in length), equipped with temperature and gas-flow controls was utilized. The iron-nickel oxide powder (30 mg, spread on a ceramic plate) was placed inside the reactor, and reduced to the iron-nickel nanoparticles with H_2 at 500 °C for 4 h. The FeNi alloys obtained with Fe:Ni atomic ratios equal to 1:3, 2:2, and 3:1 are denoted hereafter as FeNi13, FeNi22, and FeNi31, respectively. Then benzene (kept in a three-necked flask maintained at 70 °C in a water bath) was carried into the reactor in an argon flow. The decomposition of benzene was conducted *in situ* over the freshly prepared FeNi alloy nanoparticles at 500 °C for 6 h, and after cooling to RT, the as-prepared composites (black in color) were collected (denoted hereinafter as FeNi13@C, FeNi22@C, and FeNi31@C, respectively). The samples were examined at RT on an X-ray powder diffractometer (XRD) for phase identification using CuK_α radiation (Model D/Max-RA, Rigaku, Japan). Samples morphology was examined with a high resolution transmission electron microscope (HRTEM, model JEOL-2010, Japan) operated at an accelerating voltage of 200 kV, and a field-emission scanning electron microscope (FE-SEM model 1530VP, LEO, Germany; equipped with a JEOL JFC-1600 auto fine-coater) operated at an accelerating voltage of 5 kV. The resistivity (ρ) of the samples was measured at RT by standard direct-current four-probe technique using a Model-6000 physical property measurement system (PPMS). The magnetic properties of samples were measured at 300 K over a Quantum Design MPMS SQUID magnetometer (Quantum Design MPMS-XL, U.S.A.). The square samples (long 4.5 mm, width 3.5 mm, thickness 0.5 mm) were fabricated for measuring static state hysteresis loop. The complex permeability μ of a composite sample which contained 30 wt% of FeNi13@C (pressed into a ring with outer diameter of 7 mm and inner diameter of 3 mm with paraffin being binder matrix), was measured using an Agilent PNA E8363B (USA) network analyzer in the frequency range of 2 to 18 GHz. Thermoanalysis was carried out on a thermal analysis system (PerkinElmer TGA7 series) with ca. 5.0 mg of sample heated in air at a rate of 10 °C min^{-1}.

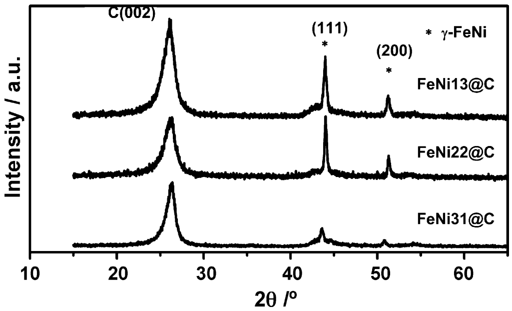

Fig. 2. XRD patterns of composites obtained at 500 °C.

3. Results and discussion

3.1. Structure and morphology of as-prepared composites

In this study, 30 mg of the iron-nickel oxide powder (containing ca. 22.99, 22.26 and 21.62 mg of FeNi13, FeNi22, and FeNi31, respectively) was used and about 0.517, 0.379, and 0.592 g of as-prepared composites of FeNi13@C, FeNi22@C, and FeNi31@C were obtained at 500 °C in each run, respectively.

The XRD patterns of the composites obtained over FeNi13, FeNi22, and FeNi31 at 500 °C are shown in Fig. 2. A reflection at 26.22° can be attributed to (0 0 2) plane of hexagonal graphite (JCPDS Card File No. 41-1487, lattice parameters a = 2.470 Å and c = 6.756 Å), denoting the formation of graphitic species. Reflections at 43.92° and 51.22° can be indexed, respectively, to (1 1 1) and (2 0 0) planes of fcc γ-FeNi alloy (JCPDS Card File No. 47-1417, lattice parameter a = 3.597 Å). There is no XRD signal assignable to pure Fe and Ni metals. These results suggest that the as-prepared composites are composed of graphite and Fe–Ni alloy nanoparticles. Using the Scherrer formula with deal consideration to the FWHM (full width at half maximum) of the (1 1 1) peak of Fe–Ni alloy, the average grain size of Fe–Ni alloy is estimated to be 18.7, 27.9, and 13.9 nm for FeNi13@C, FeNi22@C, and FeNi31@C, respectively.

Representative FE-SEM images of as-prepared composites obtained at 500 °C are shown in Fig. 3. It can be observed that composites of one-dimensional nanostructure with irregular morphology are formed. There is no direct relationship between the

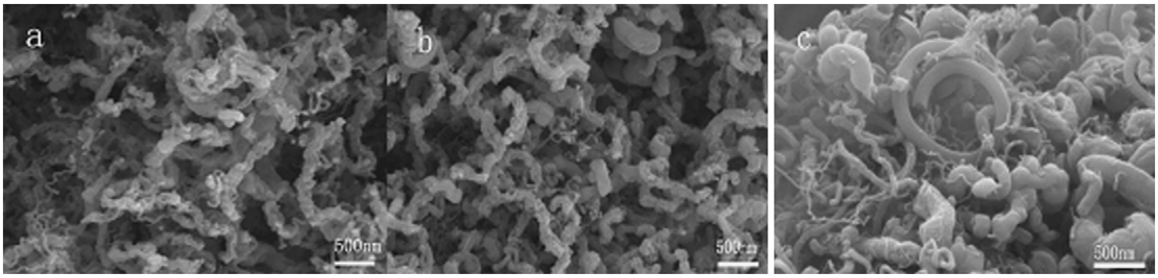

Fig. 3. FE-SEM images of as-prepared composites: (a) FeNi13@C, (b) FeNi22@C, and (c) FeNi31@C.