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Microstructural and electromagnetic properties of MnO_2 coated nickel particles with submicron size*

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Nickel particles with submicron size are prepared by using the solvothermal method. These spheres are then coated with a layer of MnO_2 using the soft chemical method. The microstructure is characterized by x-ray diffraction, transmission electron microscopy, and scanning electron microscopy. Energy x-ray dispersive spectrometry and high-resolution images show that the granular composites have a classical core/shell structure with an MnO_2 superficial layer, no more than 10 nm in thickness. The hysteresis measurements indicate that these submicron-size Ni composite powders have small remanence and moderate coercivity. The electromagnetic properties of the powders measured by a vector network analyzer in a frequency range of 2–18 GHz are also reported in detail.

Keywords: core/shell, microstructure, submicron, electromagnetic properties
PACC: 7550, 7560J

1. Introduction

Transition-metal-based superfine particles usually display properties that make them an interesting topic in the study of ferromagnetic novel materials. When the particle size is reduced, many physical properties, such as magnetic and electric properties, will change significantly. It is known that the configurations of the atoms at the particle surface are quite different from those of the atoms in the inner part. The chemical activation becomes better with the increase of the number of surface atoms when the particle's size decreases. So far, a lot of interest has been focused on nickel-based magnetic nanometer particles.[1−11] There were also some studies of nickel particles in the micrometer range in size.[12−14] Besides these two size ranges, much interest was also attracted by magnetic particles with submicron size.[15−17] It is believed that Ni particles with submicron range in size, which is different from micrometer and nanometer dimensions, can effectively avoid the negative superparamagnetism effect of nanosized particles, and the inactivity of micro-sized ones. In addition, core/shell granular morphology is an attractive characteristic for particle composites. The coated structure can keep the superfine particles from agglomerating, and this kind of powder can be regarded as metal particles homogeneously dispersing in a dielectric matrix. The interfacial effect and the performance cooperation between the core and shell materials provide a great opportunity for application in future.

In the present work, we investigate the structural features, magnetic and electromagnetic properties of MnO_2 coated submicron size Ni spheres. A solvothermal method is employed to synthesize metal grains, followed by a soft chemical method to achieve core/shell structure.

2. Experimental methods

2.1. Preparation of Ni/MnO_2 powders

The MnO_2 coated Ni particles were prepared in two steps, core particle synthesis and superficial coating operation. The Ni spherical grains of submicron range in size were prepared by using a solvothermal method, a modified polyol process. In this way, Ni particles precipitated from nickel salt were dissolved in polyols in an autoclave. A specified amount of nickel acetate tetrahydrate acting as metal precursor

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was dissolved in 200 ml of polyol, such as ethylene glycol or trimethylene glycol, or other reductive polyols. The concentration of Ni ion was limited to 0.2 Mol/l. Then the solution was transferred into an autoclave, which was slowly heated up to a temperature under the boiling point of the polyols in an oven. 20 to 40 h later, nickel spheres formed through nucleation and growth. Size control can be achieved by adding a small amount of solution K_2PtCl_6 or $AgNO_3$ dissolved in a mixture of ethanediol and dihydroxydiethylether. The precipitated metal powders were separated from liquid by centrifugation. After being sonicated and washed several times in alcohol, water and acetone sequentially, and finally dried in argon at 50 °C, submicron Ni powders with narrow size distribution were obtained.

The as-synthesized nickel particles were coated by a thin MnO_2 layer via a chemical treatment. 2 g nickel powder was added into 100 ml of an aqueous solution of potassium permanganate at room temperature with mechanical stirring and sonication. 3 ml of 0.5 M nitric acid solution was dropped into the suspension. Manganese peroxide was produced from such an acidified aqueous solution of potassium permanganate. About 20 min later, the MnO_2 coated nickel powder was collected by centrifugation, washed in water and acetone, and dried under air for a few hours at 50 °C sequentially.

2.2. Microstructural and magnetic characterization of the composite particles

Phase analysis was performed by a PANalytical X' pert PRO MPD x-ray powder diffraction (XRD) with filtered Co K_α radiation of wavelength $\lambda = 0.178901$ nm. The morphological characteristics were determined by using a Hitachi S-3500N scanning electron microscope (SEM) and a JEOL JEM-2011 transmission electronic microscope (TEM) with a nanoprobe attachment for energy dispersive x-ray spectrometry (EDS). In order to benefit the investigation of magnetic properties, the powders were mechanically compacted into a cylindrical shape with c.a. 2 mm in diameter and 4 mm in thickness. The hysteresis loops of powders were measured by using a Lakeshore 7410 vibrating sample magnetometer (VSM) at room temperature in an applied field with a maximum of 10 KOe (1 Oe=80 A/m). The electromagnetic properties were studied by an Agilent 8722ES vector network analyzer (VNA) in a frequency range of 2–18 GHz. Testing samples were prepared into toroids in three steps. Firstly, Ni/MnO_2 composite powders were mixed with paraffin wax (60 wt. % Ni/MnO_2 powder), then the mixtures were compacted. Finally the as-compacts were cut into a toroidal shape with 7.00 mm in outer diameter, 3.00 mm in inner diameter and 2 mm in thickness.

3. Experimental results and discussion

3.1. Microstructural characteristics of the composite particles

The as-synthesized powders obtained by using this method are composed of spherical particles with diameters mainly in the submicron range. The particle sizes are quite well distributed. As shown in Fig.1, the average diameter is about 300 nm. Additionally these powders exhibit perfect dispersibility. The nickel spheres are of a face-centered cubic crystalline structure as evidenced by the XRD pattern with narrow diffraction peaks shown in Fig.2. There exist a few impurity peaks as arrowed beside the Ni (111) peak and (220) peak. The TEM morphology of the coated Ni particles in Fig.3(a) reveals that the Ni particles are homogeneously coated by a superficial layer of MnO_2. This characteristic is also confirmed from the EDS analysis of fringe (Fig.3(b)) and central (Fig.3(c)) regions of composite particles. The concentrations of manganese and oxygen elements in the fringe region are higher than those in the central part. However, the distribution of Ni particles is the other way around. This characteristic of element concentrations is consistent with the Ni/MnO_2 core/shell structural feature. The inset of Fig.3(b) shows electron diffraction rings of the composite particles. It exhibits only the polycrystalline diffraction pattern of Ni particles. The above discussion can be further confirmed by the HRTEM image shown in Fig.4. The MnO_2 layer is revealed to be of an amorphous phase. It is obvious that the central region of the particle exhibits a clear crystal lattice. From the lattice distance measurement and simple calculation, the (111) face of nickel is marked as shown in Fig.4. The interface between the Ni core and the MnO_2 layer can be seen clearly. The thickness of the MnO_2 layer is estimated to be less than 10 nm.

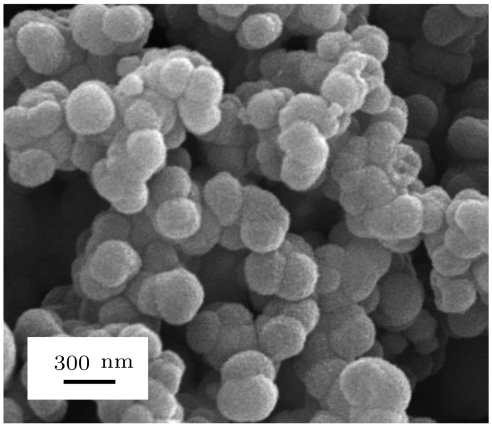


Fig.1. SEM image of Ni powder prepared by using the solvothermal method.

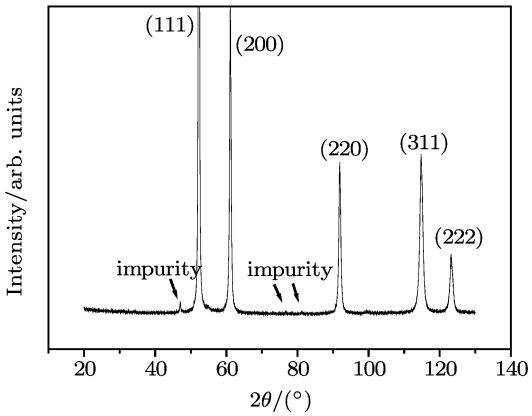


Fig.2. XRD pattern for Ni powder.

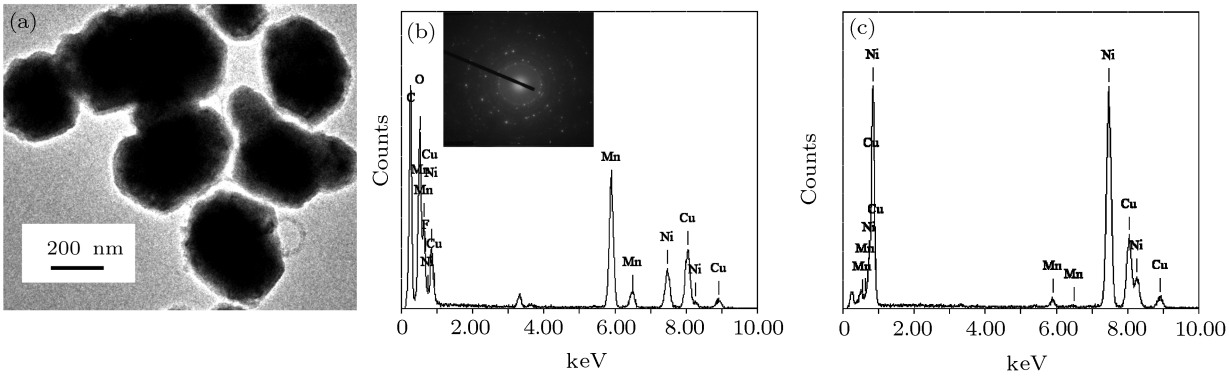


Fig.3. Core/shell structural characteristic of the Ni/MnO_2 powder. Figure 3(a) shows a TEM image of MnO_2 coated Ni particles, (b) and (c) indicate the EDS analyses of fringe and central regions of the composite particle respectively. The inset of (b) exhibits the electron diffraction of composite particles. (The copper and carbon element spectra in (b) and (c) are from the carbon microgrid.)

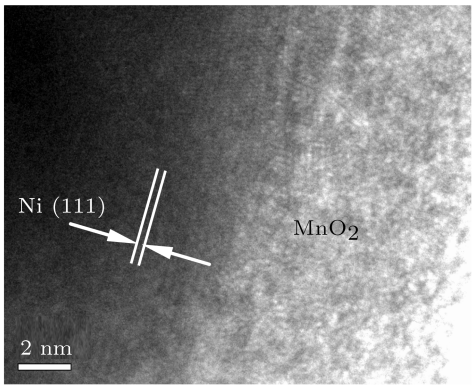


Fig.4. HRTEM image of the fringe of a MnO_2 coated Ni particle.

3.2. Magnetic and electromagnetic properties of the Ni/MnO_2 composite powders

The hysteresis loop of the as-prepared core/shell structural Ni/MnO_2 powders is shown in Fig.5, from which we can find that the composite powders have a small remanence, a moderate coercive field (about 120 Oe), and a desirable initial susceptibility as indicated in the inset. The ferromagnetic property of these as-synthesized powders is different from that of bulk nickel. We may attribute these magnetic characteristics to the small particle effect and interfacial interaction between core and shell. Meanwhile, with respect to magnetism, such Ni particles with submicron size are not as prone to having superparamagnetism as

nanoparticle metal-based materials. Nevertheless, the saturation magnetization of the as-prepared Ni/MnO_2 powders is lower than that of bulk nickel. This can be attributed to the MnO_2 composition fraction, nonmagnetic impurities such as carbonyl and oxygen compounds in the as-synthesized Ni particles.

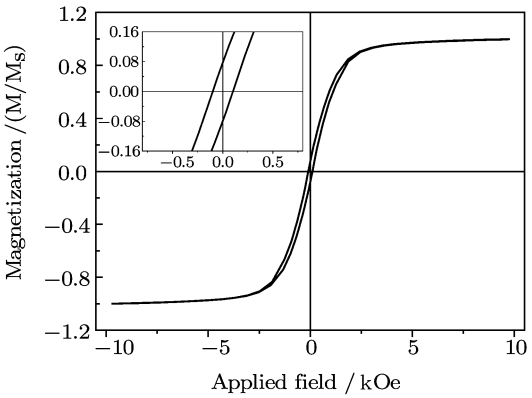


Fig.5. Hysteresis loop of the as-synthesized Ni/MnO_2 powder at room temperature. The inset shows an enlargement of the central part of the loop.

The electromagnetic properties of the powder samples are demonstrated by the complex permittivity and permeability in a frequency range of 2–18 GHz as shown in Fig.6. The real (ε'_r) and imaginary (ε''_r) components of relative complex permittivity, which are in correlation to electric energy storage and dielectric loss respectively, are plotted with respect to frequency. In this entire frequency range, the Ni/MnO_2 powder samples have a stable and lower permittivity. Based on the free electron theory, the electric conductivity σ is proportional to the imaginary components ε''_r as shown in the expression $\sigma = 2\pi f \varepsilon_0 \varepsilon''_r$, where ε_0 is the dielectric constant of vacuum and f is the frequency of the electromagnetic field applied. Apparently, the small imaginary part (ε''_r) implies a well coated state of nickel particles by an insulative layer of MnO_2, which brings a rather high resistivity. the small real part (ε'_r) can partially result from the small size effect of nickel particles, because of weak space charge polarization.[18] The lower ε'_r is of benefit to an impedance match between the material and free space. These Ni/MnO_2 powders are two-phase electromagnetic materials. According to the theoretical analysis of interface polarization,[19] both ε'_r and ε''_r are functions of the metal volume fraction q in the total powder volume comprising the metal spheres' volume and the dielectric material volume. Herein q is the volume fraction of Ni metal spheres in the total volume of core/shell powder. It is feasible to obtain a preferable complex permittivity through the adjustment of the q value by modulating the metal core particle size or shell thickness of the assembly core/shell powder.

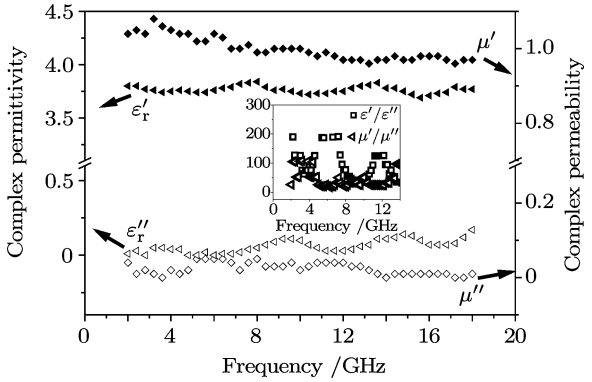


Fig.6. Relative complex permittivity and permeability in a frequency range of 2–18 GHz. The inset shows the change of inverses of dielectric and magnetic loss tangent with frequency.

The complex permeability of the powders is represented by real (μ') and imaginary (μ'') part spectra with frequencies ranging from 2 to 18 GHz. μ' and μ'' reflect the magnetic energy storage and magnetic loss respectively. Though the complex permeability is low, which may be mainly ascribed to low magnetization, it is interesting that the real part (μ') reveals a very slight decline (from 1.05 to 0.97) with frequency increasing. A sufficient coating of the MnO_2 layer prevents the eddy current from occurring among submicron nickel particles. This can account for the stable real part of complex permeability[4] to a certain extent. To demonstrate the electromagnetic property of the Ni/MnO_2 powders further, the inverses of dielectric and magnetic loss tangent are shown in the inset of Fig.6. Based on the rule of general impedance matching, $(\varepsilon'/\varepsilon'') = (\mu'/\mu'')$, it is favourable for sufficient incidence of electromagnetic wave into materials, if the values of $\varepsilon'_r/\varepsilon''_r$ and μ'/μ'' are approximately equal. The ratios of $\varepsilon'_r/\varepsilon''_r$ and μ'/μ'' of the Ni/MnO_2 powders measured are basically matched in a frequency range of 2–14 GHz as shown in the inset. In fact, such Ni/MnO_2 powders should have a more suitable electromagnetic matching in the frequency range, if ε''_r is moderately promoted. It is possible to achieve this aim by tailoring the core size, composition, and shell thickness, owing to the advantageous core/shell structure of the powders.

4. Conclusion

MnO_2 coated Ni particles with submicron size are prepared by combining a solvothermal method and a soft chemical treatment. The Ni/MnO_2 powders display a ferromagnetic property with small remanence and moderate coercivity. As for electromagnetic properties, they have a rather small and stable permittivity in a frequency range of 2–18 GHz. These powders also have a very stable real component of complex permeability. The well coated feature of the submicron Ni/MnO_2 particles contributes to these electromagnetic characteristics. In the frequency range mentioned above, Ni/MnO_2 powders exhibit desirable electromagnetic matching, which can be improved through the structural modulation, such as changing core size or shell thickness. This kind of Ni/MnO_2 powder with structural modulability can be a compelling candidate and become an advanced magnetic material in the field of electromagnetic applications.

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