

Microwave-absorption properties of FeCo microspheres self-assembled by Al₂O₃-coated FeCo nanocapsules

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(Received 20 April 2008; accepted 25 May 2008; published online 17 June 2008)

FeCo microspheres, self-assembled by Al₂O₃-coated FeCo nanocapsules, were prepared by means of the arc-discharge technique to investigate application in electromagnetic-wave absorption. For the FeCo microspheres, a reflection loss (RL) exceeding -20 dB was obtained in the frequency range of 10.9–15.6 GHz for an absorber thickness of 1.2–2.0 mm. An optimal RL of -30.8 dB was found at 11.4 GHz for an absorber thickness of 2.0 mm. The excellent microwave-absorption properties are a consequence of a proper electromagnetic match in the microstructure of a strong natural resonance and of the shape anisotropy. © 2008 American Institute of Physics.

[DOI: 10.1063/1.2945639]

Electromagnetic (EM) wave absorption materials have attracted much attention due to the importance of EM-interference problems. Recently, magnetic nanoparticles/nanocapsules with a magnetic core and a dielectric shell, including α -Fe/SmO,¹ α -Fe/Y₂O₃,² Fe/Fe₃B/Y₂O₃,³ Ni/C,⁴ Fe/ZnO,⁵ etc, have been studied in the gigahertz range due to their efficient complementarities between the relative permittivity and permeability. A self-assembly is an autonomous organization of components into patterns or structures without human intervention.⁶ This type of formation of ordered structures is of great interest in the area of material synthesis and device fabrication. A self-assembly may occur during the preparation of nanoproducts, in which the nanounits (such as nanoclusters and nanoparticles/nanocapsules) may form aggregates with novel structures. In addition to obtaining one- or two-dimensional assembled structures, efforts have been focused on fabricating curved structures such as spherical, tubular, and hollow structures.^{7–9} It is expected that, due to their small sizes and high surface areas, such ordered nanostructures may have potential applications as catalysts, as drug carriers and in magnetic recording. The possibility of synthesizing uniform nanospheres with diameters ranging from nano- to micro-scale sizes is desirable. Generally, there are two routes toward these ordered structures. One is the use of various template precursors, such as silica, and block copolymers in which it is usually required to remove the template after the synthesis by separate techniques, such as acid or base etching and calcination. Another route is the control of some factors to organize the components into various curved-shell structures. For example, rodlike building blocks consisting of gold and polymer blocks domains have been assembled into single-layer superstructures, including bundles, tubes, and sheets via the strong interactions between the organic polymer ends of the different rods.¹⁰ Since both routes are chemical techniques, the precursors and surfactants used are pollutants of the environment. Recently, the arc-discharge technique, as a well-known physical method to prepare

nanoparticles/nanocapsules, has been used to synthesize coral-like aggregates self-assembled by GdAl₂ nanocapsules.¹¹ In the present work, we utilized a modified arc-discharge technique,^{11,12} involving change in the hydrogen pressure, introducing an Fe–Co–Al alloy ingot as the anode and controlling the arc-discharging time, to synthesize FeCo microspheres self-assembled by Al₂O₃-coated FeCo nanocapsules.

A master alloy with nominal composition (Fe₆₀Co₄₀)₉₅Al₅ was prepared by arc melting bulk pieces of Fe, Co, and Al of 99.9 wt % purity in a high-purity argon atmosphere. In the arc-discharge process, the (Fe₆₀Co₄₀)₉₅Al₅ alloy served as the anode, while the cathode was a tungsten needle. The anode target was placed into one pit of a water-cooled copper crucible. The distance and the angle between the anode and the cathode were about 3 mm and about 60°, respectively. A mixture of Ar (16 000 Pa) and H₂ (6 000 Pa) gas was introduced into an evacuated chamber (5.0 × 10⁻³ Pa) before a voltage was applied between the cathode and the anode. During the experimental process, the current was maintained at 80 A, while the voltage was maintained at 12 V. After being passivated in 0.01 MPa argon for 24 h, the products were collected on the copper crucible in front of the target. We collected three samples—A, B, and—C after arc discharging the (Fe₆₀Co₄₀)₉₅Al₅ alloy during 1, 2, and 3 h, respectively.

The phase analysis of the collected products was performed by powder x-ray diffraction (XRD) on a Rigaku D/max-2000 diffractometer at a voltage of 56 kV and a current of 182 mA with graphite monochromatized Cu K α (λ = 0.154056 nm). The morphologies of the aggregates were characterized by a SUPRA 35 field-emission scanning electron microscope (FE-SEM), with an emission voltage of 20 kV. The specimens for measuring the EM properties were prepared by uniformly mixing 40 wt % FeCo microspheres with paraffin pressing the mixture into a cylindrical shape. Then the cylinder was cut into a toroid of 7.00 mm outer diameter and 3.04 mm inner diameter. The relative permeability and permittivity values of the FeCo microspheres-paraffin sample were determined between 2 and 18 GHz using an Agilent 8722ES network analyzer.

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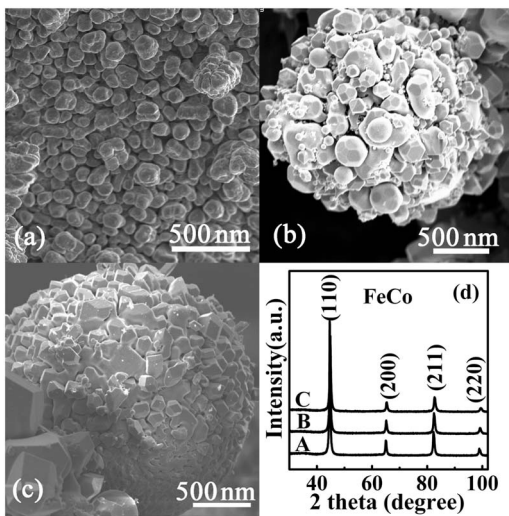


FIG. 1. FE-SEM images of the products deposited on the surface of copper crucible after different arc-discharging times. (a) 1 h, (b) 2 h, and (c) 3 h. (d) XRD patterns of samples A–C.

The SEM pictures in Figs. 1(a) and 1(c) show the morphology of the aggregates obtained after different arc-discharging times. From Fig. 1(a), it can be seen that the size of the nanocapsules, which have an irregular shape, is 60–100 nm when the arc-discharging time is 1 h. Upon increasing the arc-discharging time from 1 to 2 h, the nanocapsules self-assemble into spherulike aggregates with an average diameter of about 1.5 μm , as shown in Fig. 1(b). It can be seen in Fig. 1(b) that the spherulike aggregate consists of irregular nanocapsules with diameters varying from 50 to 150 nm, stacked together and keeping some distance. The existence of a distance between the nanocapsules can be explained by the fact that they carry remaining negative charge from the plasma which repulses them.¹³ When the arc-discharging time is increased from 2 to 3 h, the aggregates become uniform spheres with an average diameter of about 2 μm , composed of smaller aggregates of nanocapsules with an average size of about 100 nm [Fig. 1(c)]. An analysis by means of energy-dispersive spectroscopy shows the presence of the elements Fe, Co, Al, and O in all three samples. Besides the attractive force between magnetic nanocapsules, there is the remaining negative charge from the plasma that repulses them. As a result of the attractive and repulsive forces, the magnetic nanocapsules self-assemble into the spherical structure because it has the smallest surface of the possible structures in the self-assembly process and therefore the smallest surface energy. The XRD patterns confirm that the samples A–C are FeCo solid solutions. There are no oxide reflections in the XRD patterns, which should be attributed to the protective shell, which has been determined to be Al_2O_3 .¹⁴

Figure 2 shows the real part (ϵ') and the imaginary part (ϵ'') of the relative permittivity (ϵ_r) of the FeCo microsphere-paraffin sample in the 2–18 GHz range. ϵ' shows an decrease from 4.8 to 4.4 in the 2–18 GHz range, while ϵ'' is almost constant in the whole frequency range. The low ϵ'' (≈ 0.5) values of the FeCo microspheres in the 2–18 GHz interval indicate a higher electrical resistivity than other microwave-absorption materials with, e.g., $\epsilon'' = 3.7$ – 7.2 for carbon-coated Ni nanocapsules⁴ and $\epsilon'' = 2.6$ – 4.0 for carbon-coated Fe nanocapsules.¹⁵ This higher

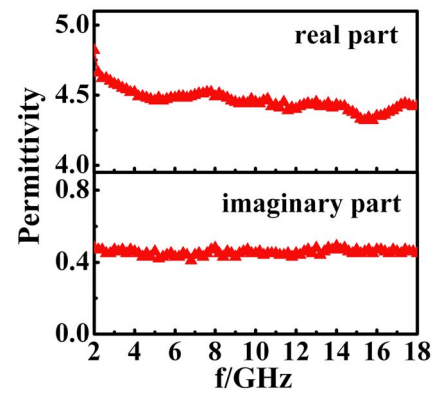


FIG. 2. (Color online) Relative permittivity ϵ_r of an FeCo microspheres-paraffin sample as a function of frequency.

electrical resistivity may be due to the protective Al_2O_3 shells at the surface of the FeCo nanocapsules. Also, a single Al_2O_3 -coated FeCo nanocapsule is a heterogeneous system, in which interfacial polarization is important and the associated relaxation will give rise to significant loss. In general, a high electrical resistivity and a proper dielectric loss are favorable for improving the microwave absorption.

Figure 3 shows the real part (μ') and the imaginary part (μ'') of the relative permeability (μ_r) of the FeCo microsphere-paraffin sample. μ' decreases from 1.27 to 0.95 in the 2–18 GHz range. Meanwhile, μ'' increases from 0.05 to 0.19 at 2–4.2 GHz and then decreases at higher frequencies. The maximum value of μ'' at 4.2 GHz implies that a natural resonance occurs in the present FeCo microspheres. In comparison with Fe nanowires (5.6 GHz),¹⁶ the magnetic resonance of FeCo microspheres has shifted to a smaller frequency, probably due to the smaller shape anisotropy of microspheres. For the FeCo alloy, it can be estimated that the natural-resonance frequency will be located at a much lower frequency around several tens of megahertz. In particles with small size, especially of nanometer dimensions, this frequency may be remarkably large due to the large surface-anisotropy field which is determined by the size effect.^{15,17,18}

The reflection loss (RL) curves were derived from the relative permeability and permittivity for a given frequency and absorber thickness, by means of the following equations:^{2,3}

$$Z_{\text{in}} = Z_0(\mu_r/\epsilon_r)^{1/2} \tanh[j(2\pi f d/c)(\mu_r\epsilon_r)^{1/2}], \quad (1)$$

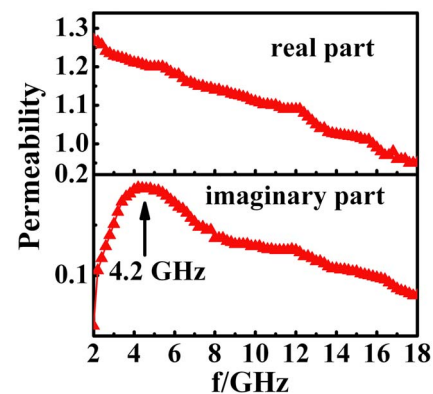


FIG. 3. (Color online) Relative permeability μ_r of an FeCo microspheres-paraffin sample as a function of frequency.

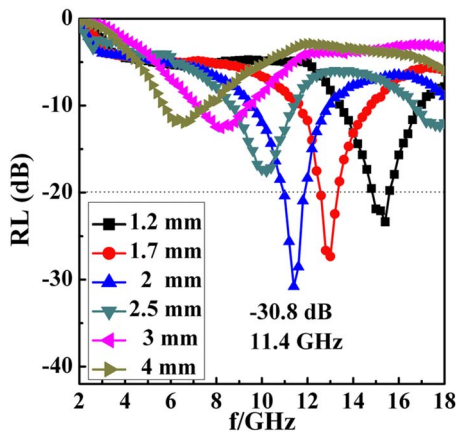


FIG. 4. (Color online) Frequency dependence of the RL of paraffin containing 40 wt % FeCo microspheres, for layers of different thicknesses.

$$RL = 20 \log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right|, \quad (2)$$

where f is the frequency of the EM wave, d is the thickness of the absorber, c is the velocity of light, Z_0 is the impedance of free space, and Z_{in} is the input impedance of the absorber. According to Eqs. (1) and (2), an RL value of -20 dB corresponds to 99% EM-wave absorption and thus $RL < -20$ dB can be considered as an adequate EM-absorption criterion.

The RL values of the FeCo microspheres-paraffin sample as a function of frequency for various layer thicknesses are shown in Fig. 4. It can be seen that an optimal RL of -30.8 dB is reached at 11.4 GHz for a layer thickness of 2.0 mm, while, the absorption exceeding -20 dB is obtained in the 10.9–15.6 GHz range for absorber thicknesses from 1.2 to 2.0 mm. Compared with ZnO-coated Fe nanocapsules and carbon-coated Ni nanocapsules, the thickness of FeCo microsphere absorber decreased by about 30%–50% in the same frequency region.^{4,5} The dielectric Al_2O_3 shell is responsible for increasing the dielectric losses in the FeCo nanocapsules. As a magnetically inactive layer, it causes a demagnetizing field and prevents the magnetic interaction between the magnetic components, which leads to increased magnetic losses in the FeCo nanocapsules. The core/shell structure of the FeCo nanocapsules with Al_2O_3 shells and ferromagnetic FeCo cores is apparently favorable for the

EM-absorption properties by reducing the magnetic coupling, by the large surface anisotropy of the nanocapsules, and by realizing EM match in the nanoscaled geometry. The special structure of the FeCo microspheres may additionally contribute to the excellent absorption properties.

In conclusion, self-assembled FeCo microspheres consisting of Al_2O_3 -coated FeCo nanocapsules have been synthesized by a modified arc-discharge technique, involving changing the hydrogen pressure, introducing a Fe-Co-Al alloy as the anode, and controlling the arc-discharging time. The FeCo microspheres exhibit excellent EM properties. It is found that RL exceeds -20 dB from 10.9 to 15.6 GHz for absorber thicknesses between 1.2 and 2.0 mm. The optimal value of RL is -30.8 dB at 11.4 GHz for a layer 2.0 mm layer. Microspheres consisting of Al_2O_3 -coated FeCo nanocapsules may be attractive for use as absorbers of EM waves

This work has been supported by the National Natural Science Foundation of China under Grant No. 50331030.

- ¹S. Sugimoto, T. Maeda, D. Book, T. Kagotani, K. Inomata, M. Homma, H. Ota, Y. Houjou, and R. Sato, *J. Alloys Compd.* **330**, 301 (2002).
- ²J. R. Liu, M. Itoh, and K. Machida, *Chem. Lett.* **32**, 394 (2003).
- ³J. R. Liu, M. Itoh, and K. Machida, *Appl. Phys. Lett.* **83**, 4017 (2003).
- ⁴X. F. Zhang, X. L. Dong, H. Huang, Y. Y. Liu, W. N. Wang, X. G. Zhu, B. Lv, J. P. Lei, and C. G. Lee, *Appl. Phys. Lett.* **89**, 053115 (2006).
- ⁵X. G. Liu, D. Y. Geng, H. Meng, P. J. Shang, and Z. D. Zhang, *Appl. Phys. Lett.* **92**, 173117 (2008).
- ⁶G. M. Whitesides and B. Grzybowski, *Science* **295**, 2418 (2002).
- ⁷Y. L. Hou, H. Kondoh, and T. Ohta, *Chem. Mater.* **17**, 3994 (2005).
- ⁸P. Yang, *Nature (London)* **425**, 243 (2003).
- ⁹A. R. Urbach, J. C. Love, M. G. Prentiss, and G. M. Whitesides, *J. Am. Chem. Soc.* **125**, 12704 (2003).
- ¹⁰S. Park, J. H. Lim, S. W. Chung, and C. A. Mirkin, *Science* **303**, 348 (2004).
- ¹¹S. Ma, D. Y. Geng, W. S. Zhang, W. Liu, X. L. Ma, and Z. D. Zhang, *Nanotechnology* **17**, 5406 (2006).
- ¹²Z. D. Zhang, *J. Mater. Sci. Technol.* **23**, 1 (2007).
- ¹³S. O. Cho, E. J. Lee, H. M. Lee, J. G. Kim, and Y. J. Kim, *Adv. Mater. (Weinheim, Ger.)* **18**, 60 (2006).
- ¹⁴X. G. Liu, D. Y. Geng, H. Meng, B. Li, Q. Zhang, D. J. Kang, and Z. D. Zhang, *J. Phys. D: Appl. Phys.* (submitted).
- ¹⁵X. F. Zhang, X. L. Dong, H. Huang, Y. Y. Liu, B. Lv, J. P. Lei, and C. J. Choi, *J. Phys. D: Appl. Phys.* **40**, 5383 (2007).
- ¹⁶J. R. Liu, M. Itoh, M. Terada, T. Horikawa, and K. Machida, *Appl. Phys. Lett.* **91**, 093101 (2007).
- ¹⁷D. A. Dimitrov, and G. M. Wysin, *Phys. Rev. B* **51**, 11947 (1995).
- ¹⁸F. Bødker, S. Mørup, and S. Linderøth, *Phys. Rev. Lett.* **72**, 282 (1994).