Electromagnetic absorption properties of flowerlike cobalt composites at microwave frequencies

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In this work, we report the electromagnetic absorption (EMA) properties of composites consisting of micrometer-sized cobalt with flowerlike architecture synthesized by a facile hydrothermal reduction method. Compared with the conventional spherical Co-paraffin composites, the flowerlike Co-paraffin composites are favorable with respect to EMA performance in the low frequency region, ascribing interfacial polarization loss and Ohmic loss to the improvement in the impedance match.

Keywords: electromagnetic absorption, flowerlike cobalt composites, interfacial polarization loss, Ohmic loss

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1. Introduction

Hydrothermal synthesis is becoming one of the most important tools for advanced materials processing[1] due to its advantage in processing metallic soft magnetic powders with high purity, narrow particle size distribution, high crystallinity, excellent reproducibility, and especially controlled microstructure. It is well known that the properties of the products depend on their morphologies and structures. In recent years, the morphological control of metals has become a subject of much intensive research due to its importance in fundamental scientific research and potential technological applications.[2−5] In addition to one-dimensional (1D) and two-dimensional (2D) assembled structures, some effort has been devoted to self-assembling low-dimensional nanostructures into three-dimensional (3D) complex architectures, such as dendritic and flowerlike structures, by means of the hydrothermal technique.[6−12] A number of publications reported static magnetic properties of metallic soft magnetic materials with various morphologies obtained by the hydrothermal reduction method.[6−11] In contrast, relatively few investigations have been devoted to dynamic microwave magnetic properties. The authors have studied the microwave electromagnetic properties of dendritic Co composites.[13] The present work focuses on the effect of the flowerlike hierarchal structure on the electromagnetic absorption (EMA) properties of Co at microwave frequencies. In order to reveal the mechanism of electromagnetic polarizations and EMA properties, spherical Co samples are analyzed and compared with the flowerlike one.

2. Experiment

The spherical cobalt sample was synthesized via a facile hydrothermal reduction route, as described in our previous work.[13]

2.1. Synthesis of flowerlike metallic Co microstructure

All the reagents were of analytical grade and used without further purification. In a typical procedure, two identical solutions were prepared by dissolving cetyltrimethylammonium bromide (5 g) in 60 ml nhexane and 20 ml nbutanol. Then, 20 ml $CoCl_2 \cdot 6H_2O$ (1 mol/L) and 40 ml N_2H_4 (80%) aqueous solutions were added to the two solutions under sonication, respectively. After the two solutions were mixed, the PH value was adjusted to 13 by adding 20 ml NaOH (6.25 mol/L) solution under violent stirring. The resulting microemulsion solution was then transferred into a teflon-lined stainless steel autoclave for hy-

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drothermal treatment at 90 °C for 15 h. Grey powders were obtained after being naturally cooled to room temperature. The powders were also repeatedly washed with absolute alcohol and deionized water, and then dried in a vacuum furnace at 55 °C for 2 h.

2.2. Characterization

The phase identification of the product was accomplished with powder X-ray diffraction (XRD) employing a SHIMADZU XRD-7000 X-Ray diffractometer with Cu K_α source operating at a voltage of 40 kV and current of 30 mA. The size distribution and the morphology of the sample were characterized using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F). High frequency EM properties were measured using a vector network analyzer (Agilent 8720ET) operated at the transmission/reflection mode. Paraffin composites were prepared by homogeneously mixing melted paraffin with 30 vol.% flowerlike or spherical Co powders. When the paraffin solidified, the paraffin composite was pressed into a cylindrical-shape model with an inner diameter of 3.04 mm and an outer diameter of 7 mm for microwave measurement.

3. Results and discussion

Typical FE-SEM images of the as-prepared products are given in Fig. 1. Figure 1(a) shows the overall morphology of the flowerlike sample, which indicates that the majority of the particles have flowerlike superstructures. The high magnification image of a single Co flowerlike microstructure shows that the 3D architecture is constructed by a few petals radiating from the center, as shown in Figs. 1(b) and 1(c).

The phase composition of the as-synthesized flowerlike products was characterized by XRD, as shown in Fig. 2. The characteristic peaks of the as-prepared products with flowerlike morphology have been assigned to (100), (002), (111), (200), (101), (102), (110), (220), and (103). These peaks provide evidence for the coexistence of hexagonal close-packed (hcp) and cubic closed-packed (ccp) Co in the flowerlike sample, and the grain size is estimated to be 16.0 nm by using the Scherrer formula at the main peaks. Meanwhile, the grain size of the spherical sample is estimated to be about 14.2 nm according to the XRD pattern.[13]

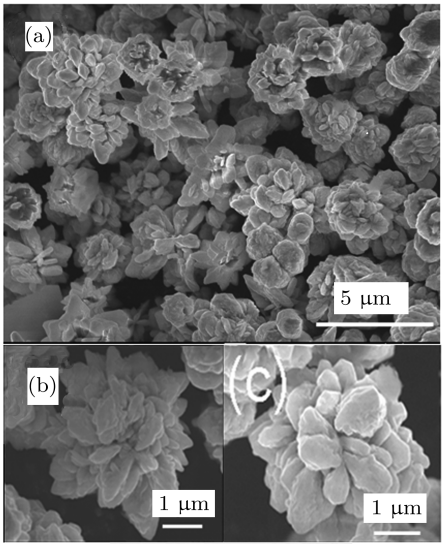


Fig. 1. FE-SEM images of the obtained samples: (a) overview of flowerlike Co superstructure, (b) and (c) local morphology of flowerlike Co superstructure.

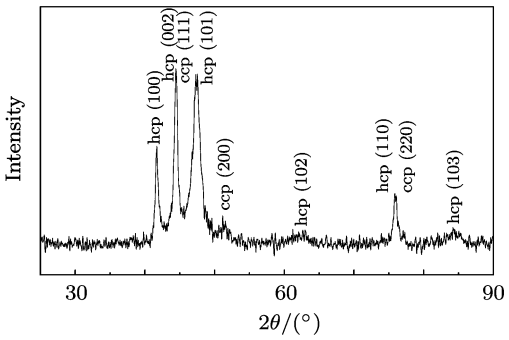


Fig. 2. X-ray powder diffraction spectrum of flowerlike samples, showing hcp and ccp phases of Co crystal.

Figure 3(a) shows the real (ε') and the imaginary (ε'') parts of the complex permittivity for the paraffin matrix composites filled with 30 vol.% flowerlike Co powder and 30 vol.% spherical Co powder in the 0.5–18 GHz range, respectively. It can be observed that ε' and ε'' of the flowerlike Co-paraffin sample experiences larger and more significant fluctuations than the spherical sample. Conventionally, the permittivity can be represented by the Debye dipolar relaxation expression with the drain current[14]

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_\mathrm{s} - \varepsilon_\infty}{1 + \mathrm{i}\omega\tau} - \mathrm{i}\frac{\gamma}{\omega}, \tag{1}$$

where ε_∞, ε_s, τ, γ, and ω are the optical dielectric constant, the stationary dielectric constant, the relaxation time, the electric conductivity, and the rotational frequency of moments, respectively. As is well known, ε' represents the polarization ability of a material. It is the interface polarization that causes the

difference in the polarization processes between our samples, which is similar to that of the published one in this field.[13] It is obvious that the interface area of a single flowerlike Co particle with a few petals is larger than that of a spherical particle of the same size. Therefore, ε' of the flowerlike case is larger than that of the spherical one ascribing to the enhancement of the interface polarization. Furthermore, a high resistivity causes a decrease in the value of ε'' according to the free electron theory.[15] From Eq. (1), it can be deduced that

$$\varepsilon''(\omega) = \frac{\omega\tau(\varepsilon_s - \varepsilon_\infty)}{1+\omega^2\tau^2} + \frac{\gamma}{\omega}. \quad (2)$$

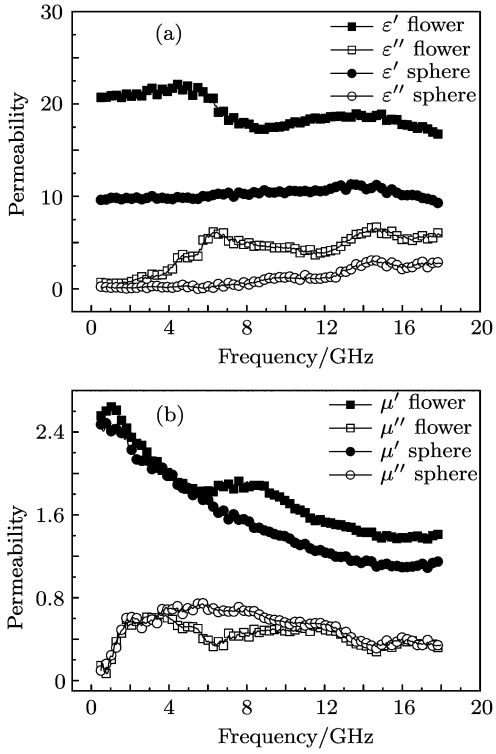


Fig. 3. Relative complex permittivity (a) and permeability (b) of flowerlike and spherical Co-paraffin composites as functions of frequency.

It is easy to understand that the random current channel of flowerlike Co-paraffin composites can be formed with a relatively low volume fraction than that of spherical Co-paraffin composites. In other words, the conductivity of flowerlike Co composites is larger under the same volume fraction. Hence, according to Eq. (2), the enhanced interfacial polarization relaxation loss and Omhic loss causes the increase of the intrinsic loss of the flowerlike Co-paraffin sample. Additionally, ε' of the spherical Co-paraffin sample is around 10.0 and nearly independent of frequency. On the contrary, ε' of the flowerlike Co-paraffin sample tends to decrease with increasing frequency. The decrease with frequency is not strictly uniform, a few weak local maxima are found. For the performance of ε'', both curves exhibit the same tendency in the 0.5–18 GHz range, i.e., ε'' gradually increases from 0.58, 0.12 to 5.81, 2.86, respectively. However, the flowerlike Co sample has a significant dielectric relaxation feature as described above, and ε'' exhibits double resonance peaks around 6 GHz and 14 GHz.

Figure 3(b) shows the real (μ') and the imaginary (μ'') parts of the complex permeability for the paraffin matrix composites filled with 30 vol.% flowerlike Co powder and 30 vol.% spherical Co powder in the 0.5–18 GHz range, respectively. The μ' of flowerlike Co-paraffin composites is larger in a wide frequency range, while μ'' is lower in the range of 4–10 GHz. The same characterization of μ'' for the flowerlike and the spherical cases is that μ'' exhibits multiresonance peaks. Actually, the multi-resonance phenomenon is still a subject of debate. The most widely accepted theory may be relevant to the present observations of the non-uniform exchange resonance mode.[16] In our case, due to the small size effect of the nanocrystalline structure, the surface anisotropy and exchange energy can be evidenced. Hence, in addition to the natural resonance, the non-uniform magnetic precession may still work for our system.[13,17–19]

The dielectric loss factor and the magnetic loss factor are both plotted as a function of frequency in Fig. 4. Compared with the spherical Co-paraffin composites, the dielectric loss of the flowerlike Co-paraffin composites exhibits a significant enhancement over the whole frequency range, while the magnetic loss experiences a negligible decrease. Consequently, the dielectric loss of the dendritic case makes a greater contribution to the EMA performance compared with the spherical case.

The reflection losses (RLs) of the flowerlike and the spherical Co-paraffin composites were calculated using the transmission line theory.[20] Figure 5 shows the calculated results of the frequency dependence of RL. It can be seen that the RL value of the flowerlike Co case is larger than that of the spherical Co case for a thickness of 1 mm over a wide range of frequencies. Moreover, the EMA performance of the flowerlike Co case becomes worse in the high frequency range when the absorption thickness is increased to 1.5 mm or 2 mm. Nevertheless, the improved absorption performance can be observed at low frequencies, which is of theoretical and practical significance. Gen-

erally, the EMA performance results from the synergistic effect of the magnetic and dielectric loss. Here, the enhancement of the EMA properties for the flowerlike Co-paraffin composites in low frequencies mainly originates from the well impedance match between the composites and free air, the strong interfacial polarization relaxation loss, and the Ohmic loss.

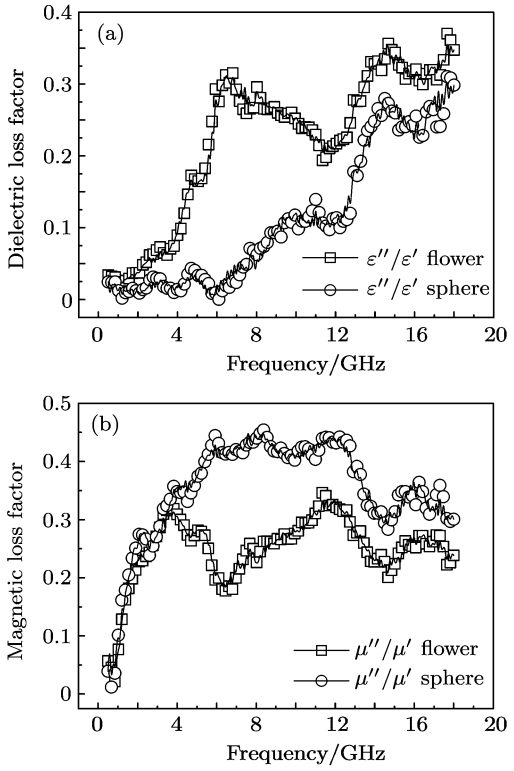


Fig. 4. Dielectric loss factor (a) and magnetic loss factor (b) of paraffin matrix composites containing 30 vol.% flowerlike and spherical Co powders as functions of frequency.

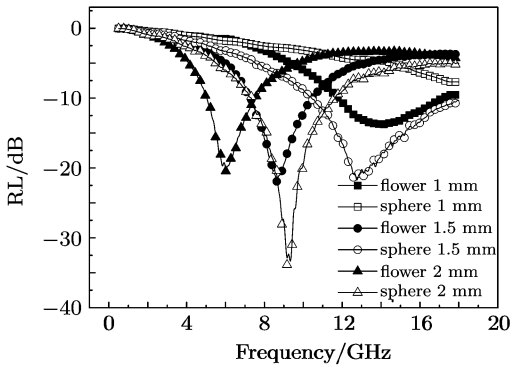


Fig. 5. Frequency dependence of RL for paraffin matrix composites containing 30 vol.% flowerlike and spherical Co with thichnesses of 1 mm, 1.5 mm, and 2 mm.

4. Conclusion

In conclusion, flowerlike and spherical Co microstructures have been synthesized by using the facile hydrothermal reduction route. A significant dielectric polarization relaxation can be found in the flowerlike Co-paraffin composites. Compared with the conventional spherical case, the flowerlike Co case is favorable to the EMA performance in the low frequency range, which is mainly ascribed to the well impedance match between the composites and free air, the strong interfacial polarization relaxation loss, and the Ohmic loss.

References

[1] Byrappa K and Adschiri T 2007 *Prog. Cryst. Grow. Ch.* **53** 117
[2] Whitesides G M and Grzybowski B 2002 *Science* **295** 2418
[3] Wang Z L, Dai Z and Sun S 2002 *Adv. Mater.* **12** 1944
[4] Wen F S, Qiao L, Zhou D, Zuo W L, Yi H B and Li F S 2008 *Chin. Phys.* B **17** 2263
[5] Yan J F, You T G, Zhang Z Y, Tian J X, Yun J N and Zhao W 2011 *Chin. Phys.* B **20** 048102
[6] Liu X M, Gao W L, Miao S B and Ji B M 2008 *J. Phys. Chem. Solids* **69** 2665
[7] An Z G, Zhang J J and Pan S L 2010 *Mater. Chem. Phys.* **123** 795
[8] Li H, Jin Z, Song H Y and Liao S 2010 *J. Magn. Magn. Mater.* **322** 30
[9] Wang R H, Jiang J S and Hu M 2009 *Mater. Res. Bull.* **44** 1468
[10] Liu X M and Fu S Y 2007 *J. Cryst. Growth* **306** 428
[11] Wang Y, Zhu Q S and Zhang H G 2007 *Mater. Res. Bull.* **42** 1450
[12] Li Q and Du W M 2009 *Rare Metal Mat. Eng.* **38** 2080
[13] Liu T, Zhou P H, Xie J L and Deng L J 2010 *J. Appl. Phys.* **110** 033918
[14] Li H R 1990 *Introduction to Diectric Physics* (Chengdu: University of Electronic Science and Technology of China Press) p. 176
[15] Ramo S, Whinnery J R and Duzer T V 1984 *Fields and Waves in Communication Electronics* (New York: Wiley)
[16] Aharoni A 1991 *J. Appl. Phys.* **69** 7762
[17] Zhang Q, Li C F, Chen Y N, Han Z, Wang H, Wang Z J, Geng D Y, Liu W and Zhang Z D 2010 *Appl. Phys. Lett.* **97** 133115
[18] Zhou P H, Zhang L and Deng L J 2010 *Appl. Phys. Lett.* **93** 112510
[19] Deng L J, Zhou P H, Xie J L and Zhang L 2007 *J. Appl. Phys.* **101** 103916
[20] Naito Y and Suetake K 1971 *IEEE Trans. Microwave Theory Tech.* **19** 65