

Preparation and Microwave Absorption Properties of Spherical Cobalt Particles

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Abstract: Spherical cobalt particles with special morphology were prepared on a large scale through a simple and low-cost liquid reduction method. The morphology, crystal structure, static magnetic properties and electromagnetic behavior of the cobalt particles were measured by SEM, XRD, VSM and vector network analyzer, respectively. The results show that saturation magnetization of the Co particles is 123 (A m²)/kg, less than that of hcp-Co single crystals, and the coercivity is 176 ×79.6 A m⁻¹, larger than that of bulk cobalt crystals. Furthermore, dual-nonlinear dielectric resonances appear at 9.8 and 15 GHz. The real part of permeability decreases with the frequency increasing, presenting an excellent frequency dispersion property. Meanwhile, the imaginary part of permeability reveals a wide resonance peak over the microwave frequency range. According to the transmit-line theory, the reflection loss (RL) was predicted through the permittivity and permeability for a given frequency and absorber thickness. A maximum reflection loss of -13.2 dB is achieved at 12.4 GHz with a thickness of 5.5 mm, and the effective absorption bandwidth (-10 dB) is 1.6 GHz, indicating the as-prepared cobalt particles have potential applications as a candidate for microwave absorption.

Key words: spherical cobalt particles; liquid reduction method; static magnetic properties; electromagnetic behavior; microwave absorption

In recent years, electromagnetic (EM) interference problems are becoming more and more serious with the development of the electronic technology^[1-6]. Thus more and more attention has been focused on the materials with superior microwave absorption. To obtain the superior microwave absorption, there are two critical problems to overcome. One is the strong attenuation as the EM-wave goes through the interior of the materials, and the other is the impedance matching between the materials and the air space, which could avoid the high reflectivity when the EM-wave is incident on the surface of the materials. Although various new materials have been investigated for microwave absorption, such as ZnO nano materials^[2,7], carbon-coated Cu nanocapsules^[8], and epoxy polyaniline composites^[9], the conventional magnetic metallic materials have irreplaceable advantages. For example, the materials have high saturation magnetization, contributing to high permeability according to Snoek's limit^[10]. Therefore, high attenuation could be achieved easily due to high magnetic

loss. Meanwhile, the materials possess high Curie temperature, so they are suitable for application at high temperature. Nevertheless, the impedance matching is still a challenge to the researchers, ascribed to the high conductivity of the magnetic metallic materials. In general, the way to solve the problem is to synthesize the magnetic metallic particles with sizes less than the skin depth.

We selected the metal cobalt as the research object because of its unique physical and chemical properties, such as catalytic properties^[11,12] and structure-dependent magnetic and electronic properties^[13]. At the same time, various morphologies of cobalt microstructures, including dendritic nanocrystals^[14], flower-like spheres^[15], sisal-like cobalt superstructures^[16] cobalt nanowires^[17,18], etc, have been fabricated by many approaches. To our best knowledge, the electromagnetic behaviors and microwave absorption have relation to the morphology of the magnetic particles. Unfortunately, the studies on the effect of the morphology of the cobalt particles on the electromagnetic

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behavior and microwave absorption are few. Thus, studies on the cobalt particles for microwave absorption are valuable academically and practically.

Herein, we reported a simple and low-cost liquid reduction method for the cobalt particles synthesis on a large scale, in which $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ acted as cobalt source, $\text{C}_4\text{H}_4\text{KNaO}_6 \cdot 4\text{H}_2\text{O}$ as a complexing agent, $\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$ as a reducing agent, NaOH as a pH-modifier, and CTAB as a morphology control agent. The EM parameters of the as-prepared cobalt particles were investigated in the microwave range of 1~18 GHz. According to transmit-line theory, the reflection loss (RL) was predicted through the permittivity and permeability for a given frequency and absorber thickness. The result reveals that the as-prepared cobalt particles have potential applications as candidate for microwave absorption.

1 Experiment

All chemicals used in the present work were of analytical grade and used as received without further purification.

Spherical cobalt particles were fabricated by a liquid reduction method. First, 2.81 g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 16.9 g $\text{C}_4\text{O}_6\text{H}_4\text{KNa} \cdot 4\text{H}_2\text{O}$ were dissolved in 100 mL de-ionized water under mechanical stirring for 30 min at 40 °C, followed by 14 g NaOH and 4 g $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$ (C_{16}TAB). In the second step, the solution was placed in a three-necked, round-bottom flask container. Then the reaction temperature, the power and the ultrasonic frequency were fixed at 90 °C, 1400 W and 40 kHz, respectively. After that, 1 mL $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (80 wt%) was quickly added to the above solution. After 15 min reaction, dark grey precipitates appeared. The precipitates were separated from the solution by placing a magnet under the container, and then washed several times with de-ionized water and absolute ethanol to remove all the residual salt. Finally, the products were obtained by drying wet precipitation in a vacuum system at 40 °C for 24 h.

The morphology of the sample was observed by scanning electron microscope (SEM) (QUANTA600). The phase was examined by X-ray diffraction (XRD) at 50 kV and 30 mA using Mo $K\alpha$ radiation ($\lambda=0.07093$ nm) on a Bruker D8 X-ray diffractometer. The static magnetic property of the sample was measured using a Lake Shore 7304 vibrating sample magnetometer (VSM).

The EM parameters of the composites containing cobalt particles and paraffin were measured on a vector network analyzer (VNA) in transmission/reflection mode. The spherical cobalt particles were uniformly dispersed in paraffin wax of 50 wt%. Then the composites were pressed into an O-ring VNA specimen (outer diameter 7 mm, inner diameter 3 mm and thickness 2 mm). The electromagnetic parameters were measured on an HP8575E network analyzer. The reflection loss of the as-prepared products

was predicted according to the transmit-line theory.

2 Results and Discussion

Fig.1 shows the morphology of the quasi spherical cobalt particles and Fig.1b is the magnified image taken from a selected section in Fig.1a. The size of quasi spherical cobalt particles is mostly in microscale. It is clearly seen that a microsphere is composed of nanoflakes. As shown in Fig.2 EDS spectrum demonstrates the presence of cobalt without other impurities, indicating that the as-prepared products are pure cobalt particles.

Fig.3 is the X-ray diffraction (XRD) pattern of the cobalt particles at room temperature. It demonstrates that the crystal structure of the cobalt particles is a mixture of fcc (face-centered cubic) and hcp (hexagonal closed packed) structure. It can be well indexed with the reflection of fcc and hcp structure. As shown in Fig.3, the peaks located at $2\theta = 19.957^\circ$, 23.086° , 32.878° , 38.759° and 40.556° ,

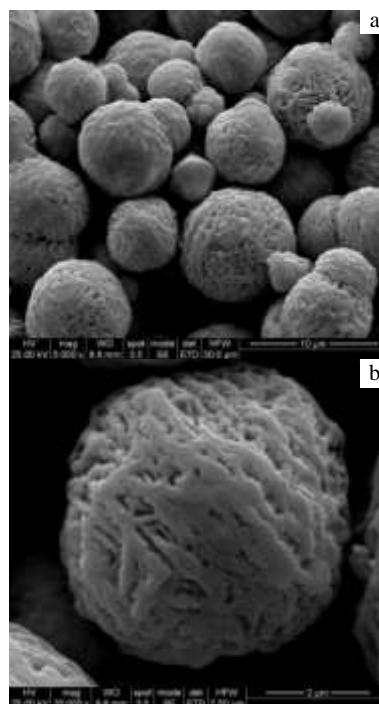


Fig.1 Morphology (a) of the cobalt particles and its magnification (b)

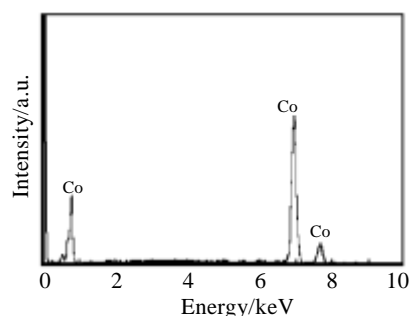


Fig.2 EDS spectrum of the cobalt particles

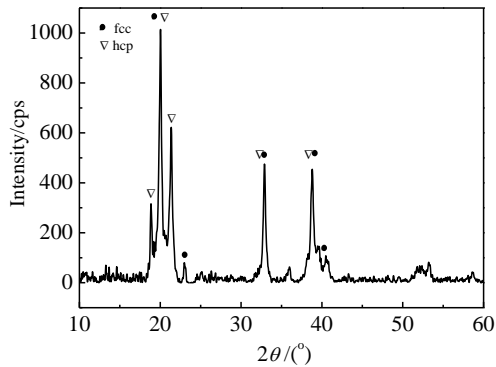


Fig.3 XRD pattern of the cobalt particles

correspond to the (111), (200), (220), (311) and (222) planes of fcc-Co, respectively (space group: Fm3m (225); JCPDS card: 15-0806, $a=0.3545$ nm). The peaks located at $2\theta = 18.856^\circ$, 20.193° , 21.402° , 32.911° and 38.865° , are well indexed to the (100), (002), (101), (110) and (112) planes of hcp-Co, respectively (space group: P63/mmc (194); JCPDS card: 05-0727, $a=0.2503$ nm, $c=0.4061$ nm).

Fig.4 shows the hysteresis loops of the cobalt particles measured at room temperature. We can see from the figure that the saturation magnetization value M_s of the cobalt particles is $123 \text{ (A m}^2\text{)/kg}$. The coercivity value H_c for the samples is $176 \times 79.6 \text{ A m}^{-1}$. The saturation magnetization of the cobalt particles at room temperature is decreased compared to that of bulk cobalt ($168 \text{ (A m}^2\text{)/kg}$)^[19]. The decrease in M_s for the cobalt particles is usually ascribed to the formation of oxides on the particle's surface and to the decrease in crystallinity^[20]. Moreover, other impurities can coexist with the products, although the samples are washed several times before the magnetic measurements. The decrease of the saturation magnetization of cobalt particles compared to that of bulk material might be partly due to a very small quantity of impurities absorbed on the cobalt microspheres. The coercivity H_c of the cobalt particles is $176 \times 79.6 \text{ A m}^{-1}$, as shown in the inset of Fig.4. The coercivity increases greatly, compared to the value of bulk cobalt ($10 \times 79.6 \text{ A m}^{-1}$)^[19]. According to the chains of spheres model, the coercivity H_c under the fanning mechanism^[21] is

$$H_{C,n} = \frac{\mu}{R_3} (6K_n - 4L_n) \quad (1)$$

where, μ and R are the dipole moment and diameter of the spherical particles, respectively; K_n and L_n are the constant interaction between magnetic particles. The coercivity H_c is inversely proportional to the diameter of the cobalt particles R , which means the value of the coercivity increases with the diameter of the cobalt particles decreasing. The effect of surface anisotropy may result in the increase of the coercivity, which is ascribed to the nanoflakes of the quasi spherical cobalt particles. Another factor that leads to the

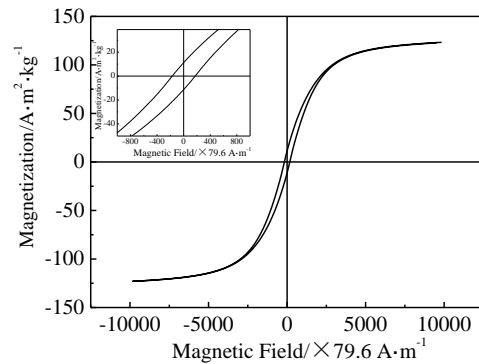


Fig.4 Hysteresis loops of the cobalt particles

higher coercivity is the magnetocrystalline anisotropy of the cobalt particles. The XRD data indicates that the crystal structure is the mixture of the fcc and hcp structure. The hcp-structure possesses larger magnetocrystalline anisotropy. In summary, the increasing of the coercivity might be due to the small size of cobalt particles, the summary effect of surface anisotropy and magnetocrystalline anisotropy.

The permittivity (ϵ_r) and permeability (μ_r) of composite specimens containing cobalt particles as fillers were measured in the microwave range of 1~18 GHz, and the results are shown in Fig.5.

As shown in Fig.5a, it can be seen that the real part permittivity ϵ' of the cobalt particles exhibits less variation ($\epsilon' = 9.84 \sim 10.1$). For the imaginary part ϵ'' , dual-nonlinear dielectric resonances are observed at 9.8 and 15 GHz. For the composites with conductive particles dispersed in paraffin matrix, the interfacial electric polarization should be considered. These quasi spherical cobalt particles consist of nanoflakes in the surface of particles. Such special morphology can generate special orientation and interface polarization^[22,23]. Fig.5b shows the complex permeability of the composites with 50 wt% cobalt particles in the frequency range of 1~18 GHz. The real part of permeability decreases from 1.38 at 1 GHz to 0.96 at 18 GHz with the frequency increasing, and thus the specimen presents excellent frequency dispersion property. Meanwhile, a wide resonance peak for the imaginary part is revealed over the microwave frequency range.

In general, there are two mechanisms of microwave attenuation in the interior of materials: dielectric loss and magnetic loss. As shown in Fig.6, the dielectric loss $\tan\delta_\epsilon$ of the cobalt particles composite exhibits less variation in the microwave range of 1~8 GHz and three peaks in the 8~18 GHz, while the magnetic loss $\tan\delta_\mu$ increases and presents two peaks as high as 0.24 in the 1~18 GHz range. The magnetic loss $\tan\delta_\mu$ of the cobalt particles is larger than the dielectric loss $\tan\delta_\epsilon$. Thus the main contribution of attenuation should be ascribed to magnetic loss.

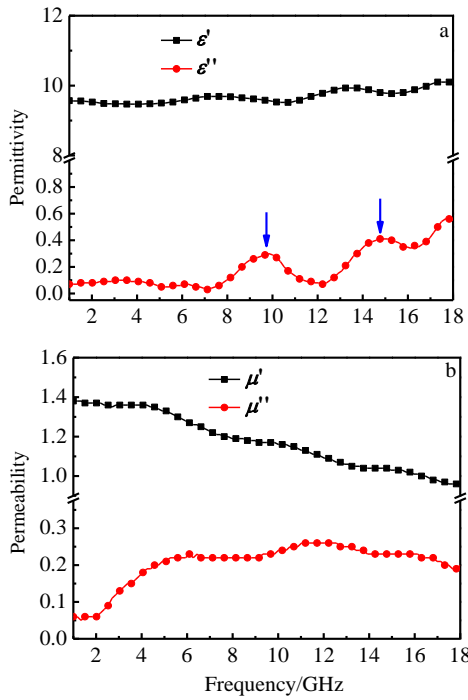


Fig.5 Complex permittivity (a) and permeability (b) of composite specimens with 50 wt% of cobalt particles

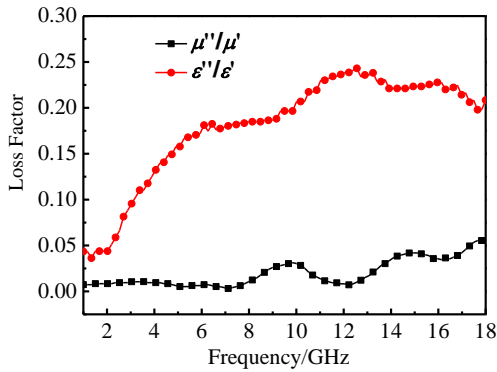


Fig.6 Dielectric loss ($\tan \delta_\epsilon = \epsilon''/\epsilon'$) and magnetic loss ($\tan \delta_\mu = \mu''/\mu'$) for the composite specimens with 50 wt% cobalt particles

The reflection loss (RL) was predicted from the permittivity and permeability for a given frequency and absorber thickness, according to the following equations^[24]:

$$Z_{in} = Z_0(\mu/\epsilon)^{1/2} \tanh[j(2\pi fd/c)(\mu\epsilon)^{1/2}] \quad (2)$$

$$RL = 20\lg|(Z_{in} - Z_0)/(Z_{in} + Z_0)| \quad (3)$$

where, f is the frequency of the EM wave, d is the thickness of the absorber, c is the velocity of the light, Z_0 is the

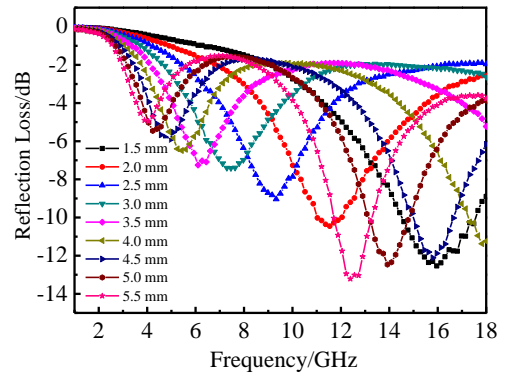


Fig.7 Frequency dependence of the reflection loss (RL) for the cobalt particles/paraffin composite specimens with various thicknesses

impedance of free space, and Z_{in} is the input impedance of the absorber. According to Eqs.(2) and (3), the simulations of the RL of the cobalt particles composites with different thicknesses are shown in Fig.7. A maximum reflection loss of -13.2 dB is achieved at 12.4 GHz for the cobalt particles with a thickness of 5.5 mm, and the effective absorption bandwidth (≤ -10 dB) is 1.6 GHz. According to the results shown above, cobalt particles have strong absorption of microwaves, which may be due to the specific microstructure of cobalt particles.

3 Conclusions

- 1) The quasi spherical cobalt particles, with a mixture of fcc and hcp-cobalt, are synthesized through a simple low-cost liquid reduction method.
- 2) A less saturation magnetization and a larger coercivity for the cobalt particles are achieved compared to the bulk cobalt. Dual-nonlinear dielectric resonances are obtained in the whole frequency range of 1~18 GHz.
- 3) The value of the minimum RL is -13.2 dB at 12.4 GHz for the cobalt particles with a thickness of 5.5 mm, and the effective absorption bandwidth (≤ -10 dB) is 1.6 GHz.

References

- 1 Wang Z H, Han Z, Geng D Y et al. *Chemical Physics Letters*[J], 2010, 489(4-6): 187
- 2 Zhuo R F, Qiao L, Feng H T et al. *Journal of Applied Physics*[J], 2008, 104(9): 094 101
- 3 Qiao L, Han X H, Gao B et al. *Journal of Applied Physics*[J], 2009, 105(5): 053 911
- 4 Qiao L, Wen F, Wei J Q et al. *Journal of Applied Physics*[J], 2008, 103(6): 063 903
- 5 Wu M Z, Zhang H J, Yao X et al. *Journal of Physics D: Applied Physics*[J], 2001, 34(6): 889
- 6 Pan S K, Lin P H, Wang L et al. *Rare Metal Materials and Engineering*[J], 2014, 43(4): 803

- 7 Zhuo R F, Feng H T, Liang Q et al. *Journal of Physics D: Applied Physics*[J], 2008, 41(18): 185 405
- 8 Sun Y P, Feng C, Liu X et al. *Materials Research*[J], 2014, 17(2): 477
- 9 Oyharçabal M, Olinga T, Foulc M P et al. *Composites Science and Technology*[J], 2013, 74: 107
- 10 Musal H M, Hahn H T, Bush G G. *Journal of Applied Physics*[J], 1988, 63(8): 3768
- 11 Liu Q Y, Guo X H, Chen J L et al. *Nanotechnology*[J], 2008, 19(36): 2618
- 12 Dutta P, Dunn B C, Eyring E M et al. *Chemistry of Materials*[J], 2005, 17(20): 5183
- 13 Puentes V F, Krishnan K M, Alivisatos P. *Applied Physics Letters*[J], 2001, 78(15): 2187
- 14 Zhu Y C, Zheng H G, Yang Q et al. *Journal of Crystal Growth*[J], 2004, 260(3-4): 427
- 15 Tong G X, Yuan J H, Wu W H et al. *CrystEngComm*[J], 2012, 14(6): 2071
- 16 An Z G, Zhang J J, Pan S L. *Materials Chemistry and Physics*[J], 2010, 123(2-3): 795
- 17 Li M, Xie K N, Wu Y Z et al. *Materials Letters*[J], 2013, 111: 185
- 18 Li T, Liu Y, He D L et al. *Rare Metal Materials and Engineering*[J], 2012, 41(9): 1527
- 19 Zhang Y J, Yao Q, Zhang Y et al. *Crystal Growth & Design*[J], 2008, 8(9): 3206
- 20 Li X G, Murai T, Saito T et al. *Journal of Magnetism and Magnetic Materials*[J], 1998, 190(3): 277
- 21 Zhou W, Zheng K, He L et al. *Nano Letters*[J], 2008, 8(4): 1147
- 22 Tong G X, Wu W H, Qiao R et al. *Journal of Materials Research*[J], 2011, 26(13): 1639
- 23 Wang X H, Zhu Z Y, Manchon A et al. *Applied Physics Letters* [J], 2013, 102(11): 111 604
- 24 Matsumoto M, Miyata Y. *IEEE Transactions on Magnetics*[J], 1997, 33(6): 4459

球形钴颗粒的制备及吸波性能研究

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摘要: 以 $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ 为钴源, $\text{C}_4\text{H}_4\text{KNaO}_6 \cdot 4\text{H}_2\text{O}$ 为络合剂, $\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$ 为还原剂, NaOH 为pH调节剂, CTAB为形貌控制剂, 通过液相还原法成功制备出了具有特殊形貌的球形钴颗粒。采用扫描电子显微镜 (SEM), X-射线衍射仪 (XRD), 振动样品磁强计 (VSM) 以及矢量网络分析仪对钴颗粒形貌、晶体结构、静磁性能以及微波频段内的电磁参数进行表征。研究表明钴颗粒的比饱和磁化强度为 $123 \text{ (A m}^2\text{)/kg}$, 矫顽力为 $176 \times 79.6 \text{ A m}^{-1}$ 。钴颗粒在9.8、15 GHz时出现明显介电损耗峰。钴颗粒复磁导率实部随着频率增加逐渐降低, 显示了良好的频散特性, 而虚部在微波频段内呈现宽化的共振峰, 经分析为自然共振和交换共振共同作用所致。根据传输线原理计算反射损耗, 发现当厚度为5.5 mm时在12.4 GHz处得到最大反射损耗-13.2 dB, 此时有效损耗频宽 ($\leq -10 \text{ dB}$) 为1.6 GHz, 表明实验制备的钴颗粒具有良好的吸波特性。

关键词: 球形钴颗粒; 液相还原法; 静磁性能; 电磁参数; 吸波性能

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