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Synthesis, permeability resonance and microwave absorption of flake-assembled cobalt superstructure

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ABSTRACT

To meet the demands of high-efficient microwave absorption materials, cobalt superstructure was synthesized and characterized. As SEM confirmed, the cobalt superstructure was assembled by flakes. The size of cobalt superstructure was about 10 μm, and the thickness of the flake was about 500 nm. The permittivity and permeability were investigated as a function of frequency in the microwave range of 1–18 GHz. Based on the LLG equation and exchange resonance mode, three magnetic resonances, including one natural resonance and two exchange resonances were discussed. The calculated reflection loss (*RL*) indicated the cobalt superstructure indicated the cobalt superstructure has potential application as a promising candidate for microwave absorption. The maximum RL reached as high as −77.29 dB with a matching thickness of 1.5 mm, and the effective bandwidth with a reflection loss less than −10 dB was 3.6 GHz from 9.85 to 13.45 GHz. For cobalt superstructure, magnetic loss mainly contributed even more than dielectric loss to the microwave absorption.

1. Introduction

In recent years, more and more attentions have been focused on the electromagnetic microwave absorption and electromagnetic interference shielding materials [1–7]. To obtain high-efficient microwave absorption materials, there are two key problems to overcome [8]. One is excellent impedance matching between the materials and air space, and the other one is strong attenuation when microwave goes through the interior of the materials. Among various kinds of microwave absorption materials, magnetic metallic materials have been extensively studied for microwave absorption in recent years. The magnetic metallic materials have high magnetic loss, and strong microwave attenuation therefore could be achieved, because according to Snoek's limit, magnetic materials with high saturation magnetization could be obtained high magnetic loss. However, the materials easily form the conductive network in the insulator, and due to their superior conductivity, eddy current would generate in the conductive network induced by microwave in GHz rang. The Eddy current could result in high microwave reflectivity and low microwave absorption once the microwave is incident on the materials. Namely, this is impedance mismatching between magnetic metallic materials and air space. The problem seriously limits the practical application of magnetic metallic materials, and is also a challenge to many researchers. No doubt that there are academic and practical values to overcome the impedance mismatching, and obtain excellent magnetic metallic materials with excellent microwave absorption.

According to the reported literatures, the magnetic core/shell structures have been designed and synthesized to achieve desired impedance matching [9], such as C/Ni nanocapsules [10], C/FeCo nanocapsules [11], grapheme/Fe_3O_4/SiO_2/NiO nanosheets [2], C/CoNi nanocapsules [12], etc.. The above materials are all coated by the materials with relatively low conductivity, which could make magnetic particles be isolated, which could effectively avoid the formation of conductive network, and then improve the impedance matching, and ultimately obtain the superior microwave absorption materials. There are however two problems for the magnetic core/shell structures. One is that the decreased saturation magnetization due to the particle size in nanoscale, reduces the contribution of magnetic loss to microwave absorption. The other one is the two-step complex routes, which would also limits their wide application. The unique structure of magnetic metallic particles could be considered to be design and synthesized to obtain desire microwave absorption materials.

Here, we chose to investigate cobalt particles because of their high saturation magnetization and Curie temperature, which confirms cobalt particles would possess strong microwave attenuation in a wide temperature range. In this paper, we have synthesized cobalt superstructure through liquid reduction

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method, and the materials were characterized. The results showed that cobalt superstructure was in microscale and high saturation magnetization therefore was obtained. The microwave performances have also been investigated as a function of frequency in the microwave range of 1–18 GHz. The calculated reflection loss indicated the maximum RL reached as high as −77.29 dB with a matching thickness of 1.5 mm, which demonstrated cobalt superstructure had a potential application as a promising candidate for microwave absorption.

2. Experiment section

All chemicals used in this work are of analytical grade and used as received without further purification.

In a typical procedure, 4.72 g $CoCl_2 \cdot 6H_2O$ was dissolved in 100 mL ethyl alcohol with vigorously stirring for 30 min at 40 °C, followed by 10 g NaOH. The reaction temperature was at 65 °C, the power was 1400 W and the ultrasonic frequency was 40 kHz. After that, 20 mL $N_2H_4 \cdot H_2O$ (80 wt%) was quickly added to the above solution, then 30 min later, the solution was cooled to room temperature. The dark gray precipitates were separated, washed with deionized water and absolute ethanol three times, and then dried under vacuum at 40 °C for 24 h to collect the samples.

The X-Ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer in Mo K_α radiation (λ=0.7093 Å) operated at 50 kV and 30 mA. The scanning electron microscopy (SEM) images were recorded using a QUANTA600 scanning electron microscope operated at 25 kV. The magnetization measurement was performed by a Lake Shore7410 vibrating sample magnetometer (VSM). The complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) were determined in the microwave range of 1–18 GHz with an O-ring shaped sample (i.d.=3 mm, o.d.=7 mm and thickness d=2 mm) using an HP8722ESS vector network analyzer.

3. Results and discussion

Fig. 1 shows the XRD pattern for as-prepared samples. The peaks located at 2θ=18.856°, 21.402° and 35.957° are indexed as the (100), (101) and (103) planes of hcp-cobalt, respectively (space group: P63/mmc (194); JCPDS card: 05-0727, a=2.503 Å, c=4.0621 Å). The peaks located at 2θ=23.086° and 40.556° match well with the (200) and (222) planes of fcc-cobalt, respectively

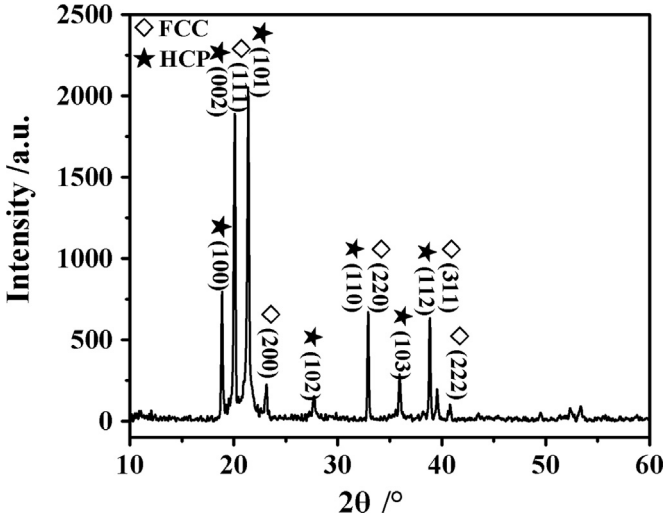

Fig. 1. The XRD pattern of as-prepared samples.

(space group: Fm3m (225); JCPDS card: 15-0806, a=3.545 Å). The other peaks could be considered as overlap peaks of the two crystal structure, which is due to the peak locations too close to distinguish. In general, cobalt has two crystal structures: a low temperature hexagonal closed-packed (hcp) and a high temperature face-centered cubic (fcc). The transition temperature is 427 °C between the two crystal structures. The stacking fault could form in the reaction process with the variation of reaction condition, which is ascribed to the low stacking fault (Co, 31 ± 5 mJ m^{-2})[13]. As well know that the stacking fault formed in hcp-cobalt can be considered as fcc structure, and the stacking fault formed in the fcc-cobalt can be considered as hcp structure. The XRD pattern demonstrated the as-prepared cobalt superstructure is a mixture of fcc and hcp-cobalt. The formation of mixture of crystal structure may be attributed to the formation of the stacking fault [14,15].

Fig. 2 shows the SEM images of the cobalt superstructure. It can be seen that as-prepared samples are flake-assembled structure. The size of the cobalt superstructure is about 10 μm, and the thickness of the flake is about 500 nm. According to the diffusion-limited aggregation mechanism, the cobalt superstructure were obtained by the interaction between the stochastic diffusive force and directive force [16]. At first, amounts of cobalt nuclei formed during the nucleation process. Then the cobalt nuclei grow to cobalt monomers with cobalt atom aggregating continually on the surface of cobalt nuclei. With the cobalt ions and the reduction agent deceasing in the reaction liquid, the cobalt monomers oriented grow to the cobalt superstructure with three-dimensional flake-assembled hierarchical superstructure [17].

Fig. 3 shows magnetic hysteresis loops of the cobalt superstructure at room temperature. We can see in the figure that the saturation magnetization (M_s) is 155.39 emu/g, only less 7.5% than that of single hcp-cobalt (168 emu/g) [17]. The high saturation magnetization means that the strong microwave absorption could be achieved according to Snoek's limit. Compared to the bulk cobalt (10 Oe), a coercivity (H_c) of 174.13 Oe is achieved for cobalt superstructure, which is attributed to shape anisotropy and magnetocrystalline anisotropy [18].

Fig. 4 presents frequency dependence of electromagnetic parameters for cobalt superstructure in the microwave range of 1–18 GHz. As shown in Fig.4(a), both the real and imaginary part of permittivity (ε'') increase with frequency increasing. Also, multi-nonlinear dielectric resonance peaks are observed at 7.85, 12.91 and 16.40 GHz. It is interpreted as the result of atomic and electronic polarization [19–21]. From Fig.4(b), it can be seen that the real part of permeability (μ') decreases, exhibiting excellent frequency disperse properties. Meanwhile, multiple magnetic resonance peaks are exhibited at 6.73, 10.98 and 15.32 GHz in the range of 1–18 GHz. Fig. 4(c) shows the dependence of dielectric and magnetic loss on the frequency in the range of 1–18 GHz. The magnetic loss is obviously larger than dielectric loss, which demonstrates magnetic loss mainly contributes even more than dielectric loss to microwave absorption for cobalt superstructure. Meanwhile, dielectric and magnetic loss all manifestly display multiple resonances corresponding to permittivity and permeability, respectively, and the multiple resonances are beneficial to widen the microwave absorption bandwidth.

As mentioned above for cobalt superstructure, the microwave absorption is mainly attributed to magnetic loss. To study the mechanism of magnetic loss, we introduce the equation $\mu''(\mu')^{-2}f^{-1} = (2/3)\pi\mu_0 d^2\sigma$ [10,22,23], where μ_0 represents the vacuum permeability, d represents the thickness of composite and σ represents the electric conductivity of composite. If $\mu''(\mu')^{-2}f^{-1}$ is independent of frequency in the frequency range of 1–18 GHz, the magnetic loss mainly stems from the current eddy. If not, the magnetic loss is ascribed to natural and exchange resonance. Fig. 4