Study on Electromagnetic Wave Absorption performance of Dendritic-like Co

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Abstract. Dendritic-like Co particles consisting of leaf-shaped nano-units were successfully synthesized by chemical reduction method. The absorbing particles have abundant multi-stage branches. Since the crystal structure, size and special morphology have an important influence on the microwave absorption performance, the X-ray diffractometer, scanning electron microscope, vibration sample magnetic measurement and vector network analysis are used to characterize the dendritic Co. Absorbing mechanism was analyzed systematically. The nano-sized, multi-stage branches, porous structures and rough surfaces of the prepared particles all contribute to the penetration, scattering and attenuation of EM waves. Hence the composite, in the test band, especially in the S-band (2-4 GHz), presents excellent microwave absorption properties.

1. Introduction

In recent years, microwave technology has been widely used in transportation, satellite communications, ship radar, power grid and other fields. The latest 5G network communication technology has been promoted in the Internet of Vehicles and Automated Driving, Remote Surgery, Smart Grid and other industries. However, the national defense safety problems and ecological environment caused by electromagnetic radiation are becoming more and more serious. Therefore, it is a key and urgent task to develop electromagnetic absorbing materials that can reliably and effectively reduce radiation[1, 2].

Magnetic metal powder has the advantages of higher snooker’s limiting frequency, high saturation magnetization, high relative permeability at radar wave frequency, etc[3]. In addition, it can rely on dielectric loss and magnetic loss to consume electromagnetic waves that has a wide range of applications in the field of electromagnetic protection and stealth. Inevitably, electromagnetic waves will arouse magnetization of magnetic metal materials, resulting in eddy current effect and decreased absorption efficiency[4]. Nano-type structure (such as flower, sea urchin, dendritic) is a hyper-branch structure formed by nanoparticles with different shapes and sizes, which can effectively weaken the skin effect and eddy current effect[1, 5, 6]. What’s more, this structure introduces quantum effect and small size effect, etc. This nano-type structure has shown superior performance in the field of microwave absorption and has attracted wide attention of many researchers. Sun et al. prepared dendritic α-Fe by hydrothermal and redox method. When the thickness of sample was 1.5 mm, the
minimum reflection loss RL was -22.5 dB\cite{7}. Yu et al. prepared flower-like carbonyl iron powder by in-situ reduction. The experimental results showed that the flower-like carbonyl iron powder had excellent electromagnetic absorbing property in the X (8-12 GHz) band, compared with the spherical carbonyl iron powder. Minimum reflection loss increased by 46\%, and effective reflection loss (RL < -20dB) band broadened by 57\%\cite{3}. It can be seen that the absorbing performance of the nano-typed absorbing material was greatly improved. However, in order to realize engineering applications, it is still a challenge to prepare high-performance electromagnetic absorbing materials. In particular, most of the electromagnetic waves in the civilian field are concentrated in the S-band (2-4 GHz). Thus, the development of the absorbing materials in the S-band is important to electromagnetic protection.

In this paper, dendritic Co structure self-assembled by nano-leaf cells was synthesized by chemical reduction method. These leaf units with a thickness of about several nanometers can effectively suppress eddy currents. The shape is highly anisotropic and helps to exceed the limits of Snoek. The prepared dendritic Co has a rich grain boundary and can induce strong intrinsic electric dipole polarization. Due to the large number of first, second, third or even higher branches, multiple interfacial polarizations can be formed, and a continuous network is easily formed between the dendritic particles. All of these factors contribute to favorable microwave absorption properties.

2. Experiment

2.1. Synthesis of dendritic Co particles

The specific preparation steps of the dendritic Co were as follows: First, CoCl$_2$·6H$_2$O (14.28 g) was weighed and dissolved in 300 ml of absolute ethanol, and mechanically stirred until the CoCl$_2$·6H$_2$O powder was completely dissolved to form a transparent solution. Then, NaOH (12 g) powder was added into the above-mentioned solution of CoCl$_2$ and mechanically stirred for 20 min to obtain a homogeneous mixed solution. Then, 30 ml of ethylenediamine (C$_2$H$_8$N$_2$) and 30 ml of hydrazine hydrate 80\% (N$_2$H$_4$H$_2$O) were slowly added dropwise, accompanying by mechanical stirring for 10 min. The whole reaction process lasted for 1 h. A black solid appeared on the bottom of the flask after the reaction was completed. The black precipitate was separated by a magnet and washed repeatedly with deionized water and absolute ethanol. Finally, the separated black solid was transferred to a vacuum drying oven at a temperature of 80° C. The final product was obtained by drying for 12 h.

2.2. Testing and characterization

To be able to analyze the chemical composition of the product, crystal structure was examined by X-ray diffraction XRD (copper K$\alpha$ radiation source). The morphology and size of the product were also observed by field emission scanning electron microscopy (SEM).

For the purpose of studying the electromagnetic absorbing properties of the as-prepared product in the 2~18 GHz band, ring-shaped samples having an outer diameter of 7 mm, an inner diameter of 3.04 mm, and a thickness of 2.78mm were pressed by paraffin-bonded dendritic cobalt. The mass fraction ratio of particles to paraffin wax was 1:2 (sample 1) and 1:1 (sample 2), respectively. The test technique used coaxial reflection/transmission technology.

2.3. Microwave Absorption performance calculation

For a single-layer absorbing material with a metal backing, the usual reflection loss (RL) can be calculated from the following equation according to the transmission line theory\cite{8, 9}:

$$Z_m = \frac{\mu_r\mu'_r}{\varepsilon_r\varepsilon'_r} \tan h \left( \frac{2\pi}{c} \int df \sqrt{\mu_r\varepsilon_r} \right)$$

(1)

$$RL = 20\log \left( \frac{|Z_m - Z_o|}{|Z_m + Z_o|} \right)$$

(2)
Where the complex permittivity $\varepsilon_r$ and permeability $\mu_r$ are measured at a given thickness and frequency. $Z_0$ is the impedance of free space, $Z_{in}$ is the input impedance between free space and the material interface, $c$ is the speed of light, $f$ is the frequency of the microwave, and $d$ is the thickness of absorbing material.

3. Results and discussion

3.1. Characterization of the samples

The SEM images showed that the prepared product has a typical layered dendritic structure. The entire structure had a radius of about 5 microns and radiated from the center by a plurality of leaf-like elements. There was a large space between the leaf-like unit layers, which facilitated the scattering of incident electromagnetic waves. The single leaf-like structure was composed of trunk, secondary branches and tertiary branches. The lateral branches were evenly distributed on both sides of the trunk at a certain angle. The length of the trunk was about 1-5 microns, while the length of the lateral stem was 50 nm-1um. Since the order of adding sodium hydroxide was adjusted based on the previous experimental scheme\cite{10}, the particles showed many small pores and the surface of the structure was rougher than before. The XRD pattern of the dendritic cobalt was shown in figure. 1(d), and the diffraction peaks of these samples were located at $2\theta = 41.54$, 44.54, and 47.36, corresponding to the (100), (002) and (101) planes. It had a good match with the close-packed (hcp) Co crystals (space group P63/mmc1 (194); $a = 0.2503$ nm, $c = 0.4060$ nm; JCPDS No 05-0727)\cite{10}.

3.2. Microwave absorption

As could be seen from figure 2, the permittivity ($\varepsilon$) of the two samples increased as the content of dendritic cobalt particles increased. This reason was that the distance between the particles became shortened when the content of the dendritic cobalt was increased. This would undoubtedly enhanced charge transporting ability, resulting in a stronger space charge polarization, thereby increasing the value of permittivity. The $\varepsilon'$ of sample 1 remained substantially constant at 4.5, and $\varepsilon''$ value was almost constant in 2-12 GHz, while there was large fluctuation in 12-18 GHz. However, sample 2, whether it was the real part ($\varepsilon'$) or the imaginary part ($\varepsilon''$), had large fluctuations throughout the whole test frequency range. This complex nonlinear vibration behavior was caused by space charge polarization, dipole polarization and interfacial polarization, which was usually related to the special structure of dendritic cobalt particles and their distribution in paraffin\cite{11,12}. At the same time, with the increase of frequency, the electric dipole polarization gradually become the dominant factor of metal-insulation system, and the electron polarization caused by the non-coincidence of the equivalent centers might also have a great influence on the dielectric response\cite{13}. The relationship between the complex permeability and frequency was shown in figure 2(c,d). The complex permeability of Sample 2 was substantially higher than that of Sample 1 in the frequency range of 2-18 GHz. The real
permeability ($\mu'$) of sample 1 increased first with frequency and then fluctuated around 1.2, while the overall trend of the real part ($\mu'$) of permeability of sample 2 increased with frequency. The whole ascent process was accompanied by fluctuations and fluctuated greatly in the range of 14-18 GHz. As for the imaginary part of magnetic permeability, the imaginary part ($\mu''$) of permeability of sample 1 had a distinct peak in the 6-8 GHz band, and the sample 2 had multiple peaks.

Figure 2. (a) and (b) are the curves of the real and imaginary parts of permittivity of dendritic cobalt with frequency; (c) and (d) are the curves of the real and imaginary parts of the dendritic cobalt permeability with frequency.

Figure 3 showed the reflection loss (RL). Sample 1 had multiple absorption peaks located at 7 GHz, 14 GHz, 17 GHz, and minimum reflection loss (RL) was -16 dB. Sample 2 had a minimum reflection loss of -16.3 dB at 8.9 GHz and effective bandwidth (RL < -10 dB, electromagnetic wave absorption of 90%) at 7.5-10.1 GHz. As the thickness increased, the absorption peak gradually shifted to low frequency, and multiple absorption peaks appeared. In the thickness from 2mm to 5mm, the absorption band of sample 2 covered 2-10GHz, which means that it has good absorption at low and medium frequencies.

Figure 3. (a), (b) are the reflection loss curves of samples with dendritic Co and paraffin mass fraction ratios of 1:2 and 1:1 at different thicknesses; (c) normalized impedance matching; (d) loss factor

It was well known that the good absorption characteristics of electromagnetic absorbing materials need to meet two conditions: impedance matching and loss factor $\alpha$. The loss factor $\alpha$ is a kind of characterization of the ability of absorbing material to absorb electromagnetic waves, which is used to describe the integral attenuation ability based on the following equation:\[14\]
The higher the loss capability, the stronger the ability to absorb electromagnetic waves. From figure 3(c), when the thickness was 2 mm, the two samples had good impedance matching near 6 GHz and 9 GHz, respectively, and the frequency range was the best absorption position at the current thickness. In addition, the loss factor of sample 2 was significantly higher than that of sample 1, which also showed that sample 2 had a better effect of absorbing electromagnetic waves. This might be because the content of the dendritic cobalt absorbing particles in the sample 2 was higher than that in the sample 1, and the dense absorbing particles could easily form a continuous network, and the electromagnetic waves entering the inside of the material could be quickly dissipated as a current.

In order to better understand the loss mechanism of dendritic cobalt particles, the dielectric loss tangent \( \tan \delta_\varepsilon = \varepsilon''/\varepsilon' \) and magnetic loss tangent \( \tan \delta_\mu = \mu''/\mu' \) of sample 2 were calculated. In the range of 2-10 GHz and 16.2-18 GHz, the magnetic loss tangent of the dendritic cobalt was higher than the tangent value of the electrical loss, which indicated that the loss mechanism in these two frequency bands was mainly magnetic loss, and the dielectric loss was dominant in other frequency bands. Generally, main mechanisms causing magnetic loss are hysteresis loss, domain wall resonance loss, eddy current loss, natural resonance and exchange resonance loss. Under weak external magnetic field, the hysteresis loss is very weak and can be ignored\(^{[14, 15]} \). Magnetic domain wall resonance occurs in the low frequency range of 1~100MHz for multi-domain wall material\(^{[17]} \). Thus, the loss of electromagnetic waves is mainly caused by eddy current loss, natural resonance and exchange resonance loss. The contribution of the eddy current loss can be judged according to the change of the value of the formula \( C_0 = \mu''(\mu')^{-2}f^{-1} = 2\pi\mu_0\sigma \) with the frequency\(^{[18, 19]} \). If the magnetic loss is only from eddy current losses, then the value of C0 should remain constant as the frequency changes\(^{[20]} \). As shown in figure 4 (b), the C0 value of the dendritic cobalt particles decreases with increasing frequency, and there is significant fluctuation, so the influence of the eddy current on the magnetic permeability is negligible. A peak appears in C0 curve in the 6-8 GHz band, mainly due to the appearance of the ferromagnetic resonance of nanomaterials, so the magnetic loss is contributed by natural resonance. Multiple formants appear in the frequency band above 12 GHz. According to Aharoni's theory, the frequency of natural resonance should be lower than the exchange resonance\(^{[21]} \). Therefore, it can be inferred that the peak appearing after 12 GHz is an absorption peak caused by exchange resonance.

![Figure 4. (a).Dielectric loss angle and magnetic loss angle;(b) the value of \( \mu''(\mu')^{-2}f^{-1} \) in 2-18GHz](image)

**4. Conclusion**

In this paper, the absorbing particles of dendritic cobalt were successfully prepared by chemical reduction method. The structure is a super-branched structure formed by self-assembly of nano-leaf cells. On the one hand, the nano-leaf unit effectively overcomes the skin effect and eddy current effect of the magnetic metal material, and improves the high-frequency magnetic permeability; on the other hand, the rich secondary structure is favorable for wave propagation and scattering; Rough surface, porous structure and large specific surface area are beneficial to the interface polarization, thus
enhancing the loss of electromagnetic waves. The experimental results show that the absorption band of sample 2 covers 2-10 GHz when the thickness is changed from 2 mm to 5 mm, which means that it has a good absorption effect at low and medium frequencies. Therefore, the dendritic cobalt absorbing particles prepared in this paper have a good application prospect in electromagnetic protection.

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