Preparation and Electromagnetic Properties of Ni-Co Coated W-type Barium Ferrite Hollow Microspheres

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Abstract: The Ni-Co coated W-type barium ferrite ($BaZn_{0.6}Co_{1.4}Fe_{16}O_{27}$) hollow microspheres (W-BFHMs) have been prepared by the self-reaction quenching technology and heat treatment at 1250 ℃. The W-BFHMs is a type of light microwave absorbing material in GHz frequencies and its average particle size is 60 μm. A conductive and magnetic Ni-Co layer was coated on the surface of W-BFHMs by electroless plating. Effects of plating time on the particle size, morphology, phase structure and microwave absorption properties of Ni-Co coated W-BFHMs are investigated through SEM, XRD, particle size analyzer and vector network analyzer. The results show that the Ni-Co deposits in the sag and the trench firstly and grows as the branch after filling the sag and the trench. With the increase of the plating time from 5 min to 25 min, the magnetic loss increase from 0.15 to 0.35, while the dielectric loss is not significantly change due to the incompletely covered. The effective absorbing bandwidth increase from 1 GHz to 2.7 GHz, while the absorption peak decrease from -12 dB to -32dB when the plating time is 25 min.

1 Introduction

The development of the radar stealth technology and the target shape technology are more and more limited to the tactical index. Application ranges have been limited due to shortcomings of bandwidth, low efficiency and large density. It is urgent need to develop new high performance light microwave absorbing materials [1-2].

Hollow microsphere materials are the important direction of the light microwave absorbing materials. At present, more research is concentrated on the electromagnetic absorption material of coating layer (such as Ni、Co、Fe-Ni、Fe-Co) [3,4,5]. However, the basic materials are given priority to the fly ash microspheres or hollow glass microspheres, which do not have the microwave absorbing properties. Zhao Yan [6] plated Co on the surface of hollow microspheres and analysed the electromagnetic properties in 2~18 GHz. Sung-Soo Kim [7] plated a layer of Co-Fe alloy thin films on hollow ceramic microspheres. High absorption rate and thin matching thickness are predicted in the composite layers. K. N. Ge [8] plated Ni on the surface of the fly ash microsphere by the method of electroless plating. The effective frequency bandwidth and absorption peak are 16.6~18 GHz and -13.57 dB. Although these methods of compound of the microwave absorbing materials decrease the weight, but the loss mechanism of one layer electromagnetic absorption material is single and the impedance matching characteristics is relatively poor. It is difficult to meet the requirements “thin, light, wide and strong” of new microwave absorbing materials.

The W-BFHMs have been prepared by self-reaction quenching technology (SRQT) and heat treatment. W-BFHMs have the advantages of low density, high temperature resistant, corrosion resistance, etc. On the other hand, W-BFHMs have electromagnetic absorption performance. Therefore, W-BFHMs are taken as the base material. The Ni-Co layers on the surface are plated by electroless plating. The change of the microstructure and dual loss mechanism of double-layer hollow microspheres have been studied under different ultrasonic electroless plating time.

2 Experiment

2.1 Preparation of W-BFHMs principle and process

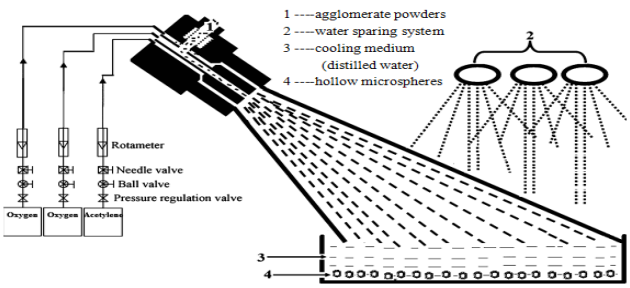


Fig.1 Principle diagram for preparation of hollow microspheres using SRQT

The preparation principle diagram of hollow microspheres has been showed in Fig. 1. The agglomerate powders are sprayed into the flame filed through a CP-D$_{III}$-type high-energy flame-spraying gun. When reaching the ignition temperature, the self–propagation high–temperature synthesis (SHS) reaction occurs promptly and the temperature of reaction system exceeds the melt point of products. Simultaneously, large volume of gas is produced which results in the hollow structure of drops. Then, the drops are quenched quickly into the cooling medium (the distilled water). Because the gas cannot escape from the drops, hollow microspheres are obtained immediately after drying and filtering the quenching products. Put the hollow microspheres into the tubular electric furnace heating to 1250 ℃ at a rate of 5℃/min. After five hours heat treatment, the products of W-BFHMs have been prepared.

The reaction equations is showed in Eq. (1) and (2).

$$3Fe+3Fe_2O_3+BaCO_3+ZnCO_3+CoCO_3+KClO_4 \rightarrow ZnFe_2O_4+BaFe_2O_4+CoFe_2O_4+Fe_3O_4+3CO_2+KCl \quad (1)$$

$$5Fe_2O_3+0.6ZnFe_2O_4+1.4CoFe_2O_4+BaFe_2O_4 \rightarrow BaZn_{0.6}Co_{1.4}Fe_{16}O_{27} \quad (2)$$

According to the molecular formula, the mole ratio of Eq. (1) and (2) have been determined. The analytical reagent raw materials of Fe powders, $BaCO_3$, Fe_2O_3, $CoCO_3$, $ZnCO_3$ and $KClO_4$ were selected.

Firstly, the raw materials were put into the LJM-5L ball mill and anhydrous ethyl alcohol was taken as the medium sphere to be churned for 6 h. After that, the epoxy resin was added into the mill to be stirred for another 2 h. Epoxy resin was used to cooperate with sucrose and to enlarge the contact area of the components in the agglomerate powders. It can be transformed to CO, CO_2, and H_2O in SHS reaction due to the high temperature. Secondly, the mixtures were dried and carbonized at 200°C until no smoke releases. The agglomerate powders were selected with 38~45μm for the experiment.

2.2 Preparation of Ni-Co coated W-BFHMs

The Ni-Co layers have been coated on the surface of W-BFHMs by the method of ultrasonic electroless plating. Ultrasonic electroless plating is a technology of preparing composite powder and can form a uniform layer of other metal materials [9,10]. Electroless plating is an electrochemical reaction. The reaction was conducted in alkaline conditions. $H_2PO_2^-$ occur the oxidation reaction while Ni^{2+} and Co^{2+} occur the reduction reaction. The premise conditions of reaction is the material surface needs certain active center, to make the electrochemical reaction occurs. Therefore, pretreatment on the material is needed before processing. In addition, adding appropriate complexing agent can prevent the formation of Ni and Co hydroxide precipitation before ultrasonic electroless plating.

The pretreatment before plating is composed of four steps of roughening(30 min), sensitization(15 min), activation(10 min) and reduction(10 min). The temperature of four steps is at room temperature. 2 g of the pretreatment W-BFHMs was placed in 500mL plating solution which have 10 g

$NiSO_4 \cdot 6H_2O$, 10 g $CoSO_4 \cdot 7H_2O$, 8.5 g $NaPH_2O_2 \cdot H_2O$ and 57.5 g $Na_3C_6H_5O_7 \cdot 2H_2O$ at 80 ℃, pH=9.0.

2.3 Characterization and detection methods. The morphology of the W-BFHMs and Ni-Co coated W-BFHMs were detected by scanning electronmicroscope (SEM, QUANTA FEG-250). The phase composition was studied by X-ray diffraction (XRD, BRUKER D2 PHASER). Particle size distribution was measured by Laser Particle Size Analyzer (Beckman Coulter LS 13 320, testing from 0.04 μm to 2000 μm). The density of W-BFHMs was determined by Archimedes Method.

The microwave absorbing specimens were prepared by molding with paraffin. The mix weight ratio of Ni-Co coated W-BFHMs and paraffin are 3:2. The specimens have a toroidal shape with the thickness at 2.0 mm, and the outer and inner diameters are respectively 7.0 mm and 3.0 mm. The ε', ε'', μ' and μ'' versus frequency were measured by coaxial reflection-transmission method with Vector Network Analyzer (Agilent-N5242A) in 0.5-18 GHz.

The microwave absorbing characteristics can be represented by the reflection loss (RL), as shown in Eq. (3) and (4). Z_{in} is the normalized input impedance related to the impedance in free space. The ε_r is the complex relative permeability and the μ_r is permittivity of the material, d is the thickness of the absorber, and the c is the velocity of light and f is the frequency of microwave.

The RL value is calculated by the metlab at the thickness 2.0mm with the Eq. (3) and (4) [11,12].

$$\mathrm{RL} = 20\lg\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \tag{3}$$

$$Z_{in} = \left(\frac{\varepsilon_r}{\mu_r}\right)^{1/2} \tanh\left[j\left(\frac{2\pi fd}{c}\right)(\mu_r\varepsilon_r)^{1/2}\right] \tag{4}$$

3 Results and discussion

3.1 Effect of the morphology and element at different electroless plating time. The SEM images of W-BFHMs and Ni-Co coated W-BFHMs at different ultrasonic electroless plating time have been shown in Fig. 2. Fig. 2(a) and 2(b) are W-BFHMs without electroless plating.

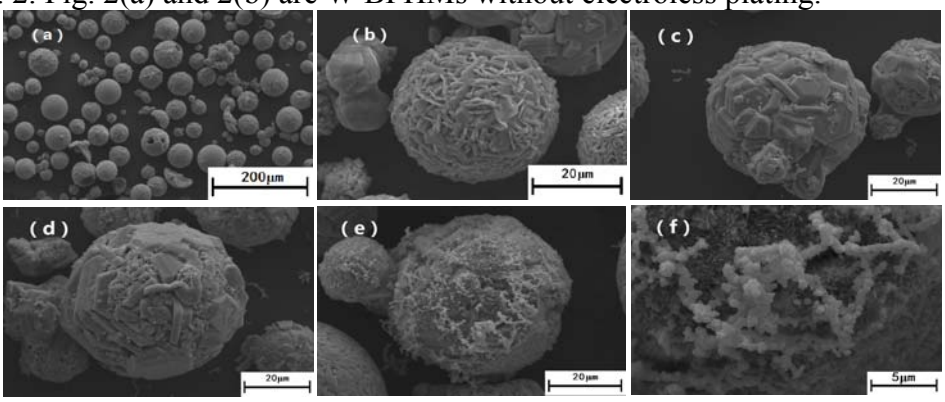
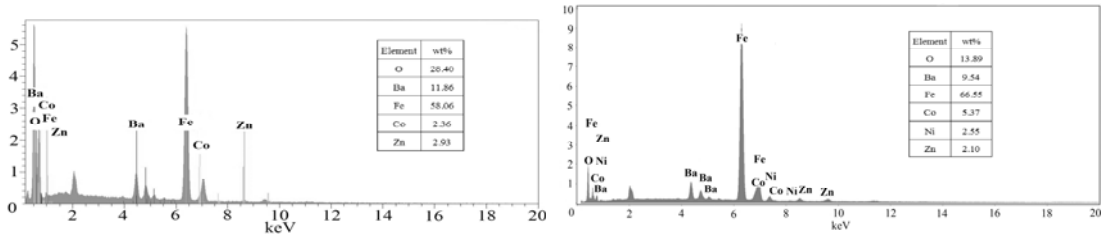


Fig. 2 SEM images of the W-BFHMs and the Ni-Co coated W-BFHMs

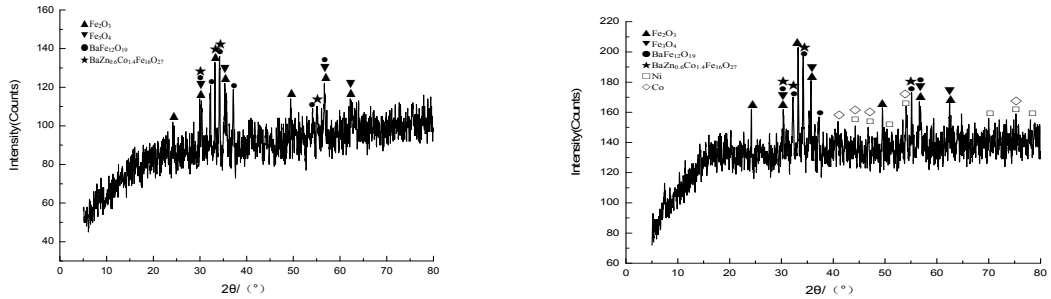
It can be seen that W-BFHMs are mainly composed of a large number of closed spherical particles and individual opening spherical particles. The average particle size is 60 μm. Fig. 2(c), 2(d) and 2(e) are plated with time 5 min, 15 min and 25 min, respectively. It can be seen that at the early reaction on the surface of the W-BFHMs, tiny Ni-Co particles begin to appear. With the increase of reaction time, particle increased continuously. With these branches interlacing and stacking, the morphology is formed as shown in figure 2(f). It is mainly due to the lack of reaction time and the concentration of the roughening solution. This is not conducive to the adhesion and growth of nickel particles in the early of reaction and the rate of reaction is reduced.



(a) **(b)**

Fig.3 EDS patterns of the W-BFHMs and after ultrasonic electroless plating (5 min)

The energy spectrums of W-BFHMs and after ultrasonic electroless plating are analyzed in Fig. 3. The results show that the products consist of Ba, Fe, Co, Zn and O elements before ultrasonic electroless plating(Fig. 3(a)), without Ni element. However, the product of Ni-Co element increase after ultrasonic electroless plating (Fig. 3(b)).



(a) **(b)**

Fig. 4 XRD pattern of the W-BFHMs and after ultrasonic electroless plating (5 min)

The crystal type develops completely to hexagonal shape crystal structure ($BaZn_{0.6}Co_{1.4}Fe_{16}O_{27}$) after heat treatment at 1250 ℃ which has been shown in Fig. 4(a). It is shown that the Ni-Co element increase after ultrasonic electroless plating in Fig. 4(b) .

3.2 Effect of the electromagnetic properties at different electroless plating time

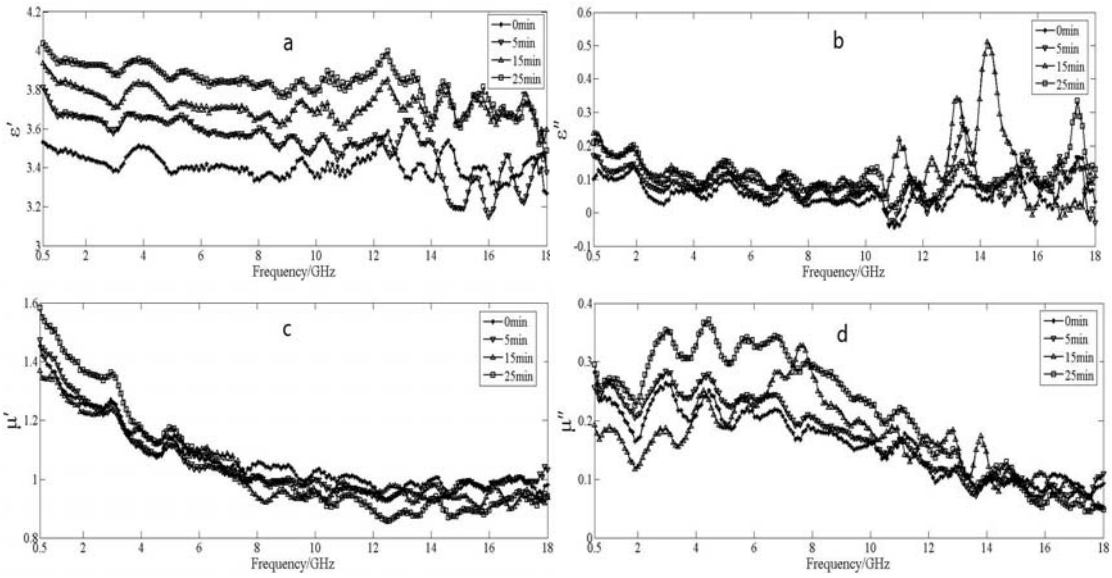


Fig. 5 Curves of electromagnetic parameters at different electroless plating time

Fig. 5 shows the curves of electromagnetic parameters (ε', ε'', μ' and μ'') of the Ni-Co coated W-BFHMs at different electroless plating time (0, 5 min, 15 min and 25 min).

The Figure 5(a) shows curves of electromagnetic parameters ε' of the W-BFHMs at different ultrasonic electroless plating time. It can be seen that with the increase of frequency, the real part of complex permittivity ε' remains generally around a value. But with the increase of plating time ε' increased from 3.4 to 4. However, the imaginary parts of permittivity ε'' are not change significantly between 0.5~12 GHz, only a slight increase of peak between 10 ~16 GHz as shown in figure 5(b).

The figure 5(c) shows that the real parts of permeability μ' reduce with the increase of frequency after 8 GHz basically stable at 1. With the increase of plating time, it increase before 6 GHz and decreases after 6 GHz. The figure 5(d) shows that the imaginary parts of permeability μ'' significantly increase within 0~12 GHz and the peak increases from 0.2 (0 min) to 0.35 (25 min).

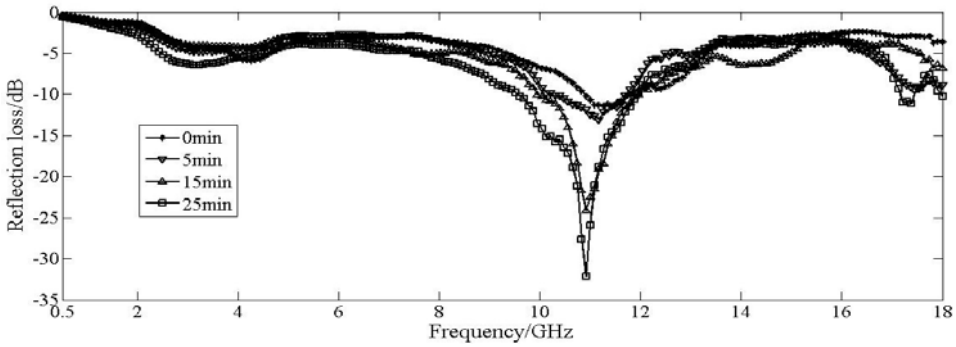


Fig. 6 Curve of Reflection loss at different ultrasonic electroless plating time

It is shown that the W-BFHMs have microwave absorption performance and its magnetic loss peak is at 12 GHz within 0.5~18 GHz in Fig. 6. In the same way, the loss mechanism of Ni-Co as the magnetic material is given priority to natural resonance. Therefore, when a certain amount of Ni-Co coated on the surface of W-BFHMs, on the basis of the original magnetic loss was further improved.

The Fig. 6 shows that effective absorbing bandwidth (less than -10 dB) of W-BFHMs is less than 1 GHz whin 0.5~18 GHz and the absorption peak is only at -12 dB. With the increase of plating time, it is shown that the Ni-Co coated W-BFHMs have stronger absorption capacity. When the plating time is 5 min, its effective absorbing bandwidth is 10~11.8 GHz, and the absorption peak is -14 dB; When the plating time is 15 min, its effective absorbing bandwidth is 9.9~12 GHz and the absorption peak is -24 dB; When the plating time is 25 min, the effective wave absorption bandwidth is 9.3~12 GHz and the absorption peak is -32 dB. So, with the increase of Ni-Co coated plating time, its effective absorbing bandwidth become widely from 1 GHz to 2.7 GHz and absorption peaks increase from -12 dB to -32 dB. At the same time, the microwave absorption performance also presents different degrees of enhancement within 2~8 GHz.

4 Conclusions

(1) By the self-reaction quenching technology, heat treatment and ultrasonic electroless plating, W-BFHMs and Ni-Co coated W-BFHMs have been prepared with the average particle size of 60 μm. The W-BFHMs are mainly composed of spherical hollow microspheres. Ni-Co deposits in the sag and trench of hexagonal lamellar crystal of W-BFHMs firstly, it grows like the branch after filling the sag and trench.

(2) At the different electroless plating time, the real part permittivity ε' increases from 3.4 to 4 and the imaginary part of permittivity ε'' does not change significantly between 0.5~12 GHz, only a slight increase of peak between 10~16 GHz; the real part of permeability μ' slight increase before 6 GHz (from 1.4 to 1.6), while decreased after 6 GHz (from 1 to 0.9), the imaginary part of permeability μ'' significantly increases within 0.5~12 GHz and the peak increases from 0.2 (0 min) to 0.35 (25 min). The change of electromagnetic loss mechanism of Ni-Co coated W-BFHMs mainly displays in the increase of magnetic loss. Its magnetic loss mainly comes from the natural resonance.

(3)The microwave absorption performance of Ni-Co coated W-BFHMs at the plating time of 25 min has improved significantly. Its effective absorbing bandwidth is from 1 GHz to 2.7 GHz and absorption peaks increase from -12 dB to -32 dB with the increase of plating time. So it can be expected that strong dielectric loss and the obvious absorption peak appear in 12~16 GHz when the W-BFHMs have been fully coated.

Acknowledgements

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