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Microwave absorption property of Ni–Co–Fe–P-coated flake graphite prepared by electroless plating

Wenbin Yang[a,b,*], Yanyan Fu[a,b], An Xia[a,b], Kai Zhang[c], Zhi Wu[d]

[a] State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, China
[b] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, China
[c] Institute of System Engineering, China Academy of Engineering Physics, Mianyang 621900, China
[d] Institute of Electronic Engineering, China Academy of Engineering Physics, Mianyang 621900, China

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ABSTRACT

Ni–Co–Fe–P alloy coating was covered on surface of flake graphite by electroless plating process. Morphology, composition, structure, magnetic property and microwave absorbing property of the Ni–Co–Fe–P alloy plating were characterized by scanning electron microscopy (SEM), energy diffraction spectrum (EDS), X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR), vibrating sample magnetometer (VSM) and vector network analyzer, respectively. The results indicated that uniform Ni–Co–Fe–P alloy plating was deposited on surface of flake graphite by the electroless plating and the coating was composed of 9.75 wt% Fe, 7.98 wt% Co, 4.13 wt% P and 78.14 wt% Ni. The Ni–Co–Fe–P alloy plating was stable in the air and the plated flake graphite was magnetic. The complex relative permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) and permeability ($\mu = \mu' - j\mu''$) of the samples were measured in the range of 0.1–10 GHz. The reflection loss (RL) was calculated using the theory of absorbing wall, and the results showed that the minimum RL of the plated flake graphite with a thickness of 3 mm was −12.8 dB at 4.6 GHz. The plated flake graphite is a kind of ideal microwave absorbing material.

1. Introduction

With the development of electronic technology, electromagnetic interference pollution has become an extremely serious problem due to the wide application of electromagnetic waves in gigahertz (GHz) range for electronic systems, radar system telecommunications, and so on [1–6]. It has resulted in a growing and intense interest in electromagnetic-absorber technology. A number of materials have been described, which are capable of absorbing electromagnetic radiation [7–11]. However, the conventional microwave absorption materials such as metal powders of iron, cobalt, nickel, metal alloys and ferrites are expensive and quite heavy, which restricts their use in applications requiring low price and lightweight mass. Therefore, the demands to develop microwave absorptive materials with "thin, lightweight, wide, strong" characteristics are increased.

It is well known that electroless plating with advantage of low cost, simple process, high shielding efficiency of coating, excellent environment stability and other notable features is widely applied in preparation of metal composites [12–16]. In recent years, various microwave absorption materials were prepared by electroless plating technology [17–24]. Meanwhile, flake graphite has already caused extensive concerns as microwave absorption materials because of its advantages of low density, low cost, high corrosion-resistance, high temperature-resistance and good electrical conductivity [25,26]. Ni–Co–Fe–P alloy is a kind of high-quality soft magnetic material, and it has high hardness, strong corrosion resistance, excellent oxidation resistance and good microwave absorption property.

In this paper, Ni–Co–Fe–P alloy coating was successfully deposited on surface of flake graphite by electroless plating technology and morphology, composition, structure, magnetic property and microwave absorption property were characterized by scanning electron microscopy (SEM), energy diffraction spectrum (EDS), X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR), vibrating sample magnetometer (VSM) and vector network analyzer, respectively.

2. Experimental

2.1. Preparation

The flake graphite cannot be plated directly because it does not possess the catalytic activity of electroless plating. It was pretreated to produce catalytic activity through the following procedures: degreasing, coarsening, sensitization and

* Corresponding author at: State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, China. Tel.: +86 816 2419631; fax: +86 816 2419201.
E-mail address: yangwenbin@swust.edu.cn (W. Yang).

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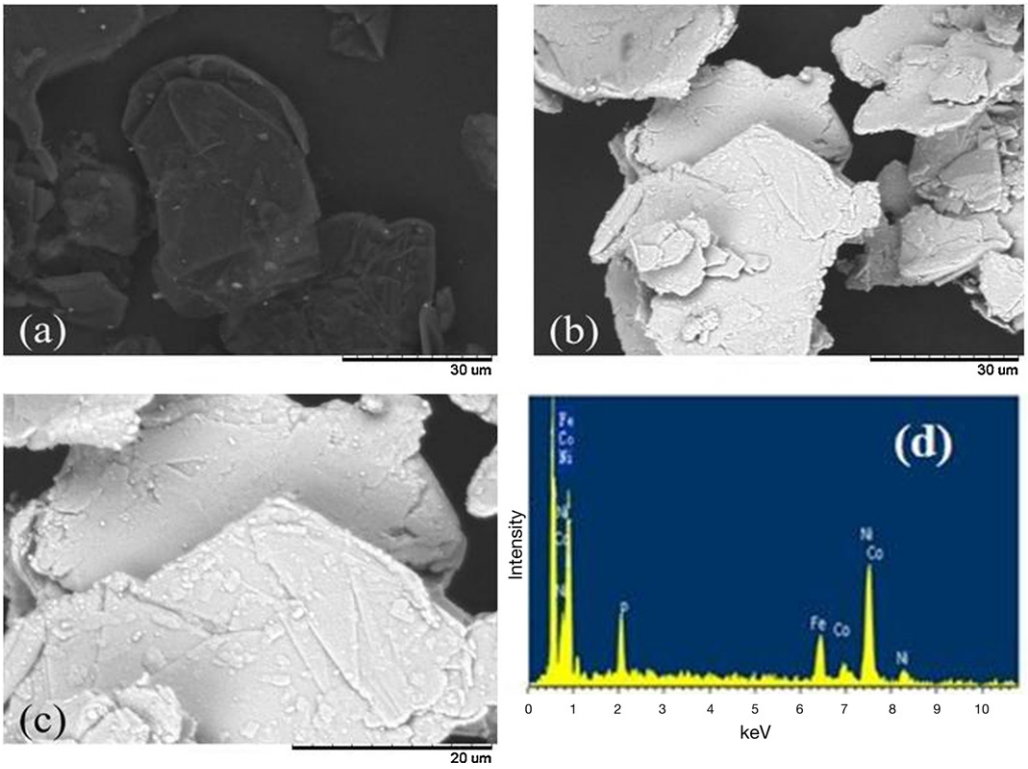

Fig. 1. SEM photos of flake graphite (a) before plating (b) and (c) after plating (d) EDS spectrum after plating.

activation, restoring. The flake graphite was degreased with 50 g/L NaOH, 25 g/L Na_2CO_3 and 25 g/L $Na_4P_2O_7$ solution (at 60 °C for 10 min), and coarsened by using 100 mL/L HF, 200 mL/L HNO_3 solution (at 45 °C for 20 min), then sensitized and activated in 40 g/L $SnCl_2{\cdot}2H_2O$, 1 g/L $PdCl_2$ and 100 mL/L HCl solution for 15 min at 45 °C. In order to avoid impurities into the next bath, the flake graphite was fully washed with distilled water after each step. After these courses, the flake graphite was restored with 100 mL/L HCl solution.

The pretreated flake graphite was plated in an electroless nickel–cobalt–ferrum bath with detailed composition and conditions listed in Table 1.

2.2. Characterization

Morphology of flake graphite before and after plating was investigated using scanning electron microscopy (STEREOSCAN-440, UK, Leica Cambridge Co. Ltd.). Energy diffraction spectrometry (NSS300, USA, Thermoelectricity Co. Ltd.) was performed to identify their chemical composition. Structure analysis of Ni–Co–Fe–P plating on surface of flake graphite was carried out by X-ray diffractometer (D/max-IIA, Japan Rigaku Co. Ltd.). The X-ray diffraction using Cu Kα was operated at an accelerating voltage and current of 45 kV and 40 mA, respectively. Infrared spectrum was characterized by infrared spectrometer (Nicolet 5700, USA, Nicolet Co. Ltd.). Magnetic property of the plated flake graphite was tested by vibrating sample magnetometer (LakeShore 7400, USA, LakeShore Co. Ltd.). The complex permeability and permittivity of the plated flake graphite were measured using vector network analyzer (Agilent E5071C, USA, Agilent Co. Ltd.) in the range of 0.1–10 GHz.

Table 1
Composition and operation conditions of electroless plating.

Chemical	Concentration (g/L)
$NiSO_4{\cdot}6H_2O$	26
$CoSO_4{\cdot}7H_2O$	20
$FeSO_4{\cdot}7H_2O$	20
$NaH_2PO_2{\cdot}H_2O$	20
$Na_3C_6H_5O_7{\cdot}2H_2O$	100
H_3BO_3	30
pH	9
Temperature (°C)	80
Time (min)	20

3. Results and discussion

3.1. Morphology and structure

As shown in Fig. 1(a), the morphology of graphite is flake, and the color of flake graphite before plating is not clear because its conductivity is not good enough. Fig. 1(b) and (c) shows surface morphologies of the plated flake graphite. Compared with that before plating, a layer of continuous and uniform metal alloy is deposited on the surface of flake graphite, and the coverage is in good condition and the structure is compact. The surface of flake graphite after plating is white and bright because of the light reflection and refraction role of the metal alloy. And it can be observed that there are very shallow ravines and small particles on the surface at high magnification. Fig. 1(d) is the EDS of flake graphite after plating. It indicates that the coating is composed of Ni, Co, Fe and P. The spectrum peaks of the four elements have some overlapping phenomena. The main ingredient is Ni, accounting for 78.14 wt%, and there are 9.75 wt% Fe, 7.98 wt% Co, 4.13 wt% P in the alloy plating.

Fig. 2 shows XRD patterns of flake graphite and Ni–Co–Fe–P-coated flake graphite. It can be seen that the diffraction peaks of flake graphite appear at $2\theta = 44.54°$, 54.72° and the strength of peak at 54.72° is very strong. The diffraction peaks of flake graphite exist still in the XRD pattern of the plated flake graphite, but the strength of the peaks is decreased obviously. The result shows that the coverage degree of Ni–Co–Fe–P plating is compact and the thickness reaches at least to μm. In addition, there is an obviously non-crystalline peak at 2θ of 40–50°, which indicates that the alloy coating is nearly amorphous.

Fig. 3 shows the FTIR spectra of flake graphite before and after plating. It can be seen that there are two characteristic peaks (3420 cm^{-1} and 1582 cm^{-1}) of adsorbed water in curves (a) and (b). The peak at 3420 cm^{-1} is ascribed to O—H stretching vibration, and the peak at 1582 cm^{-1} is attributed to O—H bending vibration. In

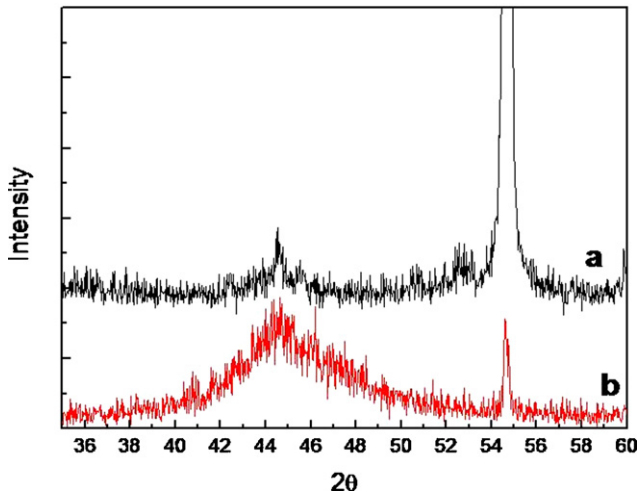

Fig. 2. XRD spectra of flake graphite (a) before plating (b) after plating.

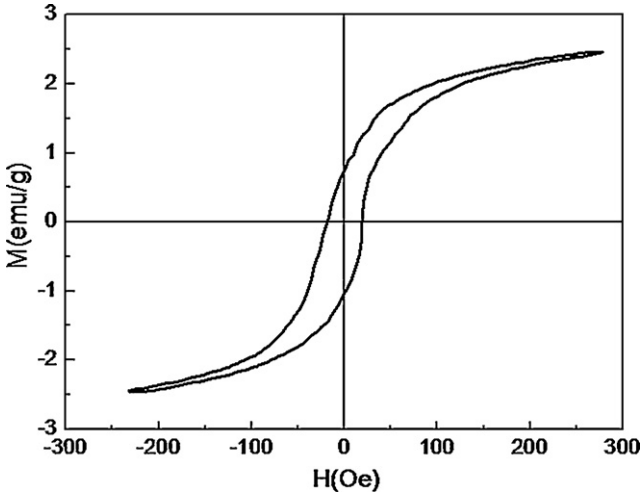

Fig. 4. Hysteresis loop of flake graphite after plating.

addition, there is a characteristic peak of C=O stretching vibration at 1721 cm^{-1} in curve (a), which indicates that the surface of flake graphite before plating can be easily oxidized. While, there is no peak of C=O stretching vibration in curve (b), which indicates that the surface of flake graphite after plating is uneasy to be oxidized and the Ni–Co–Fe–P alloy plating can be stably existed.

3.2. Magnetic property

The magnetic properties of the Ni–Co–Fe–P-coated flake graphite were measured by using VSM at 300 K. The magnetic hysteresis loop of the Ni–Co–Fe–P-coated flake graphite is shown in Fig. 4. It can be seen that the saturation magnetization (M_s), the remnant magnetization (M_r) and the coercivity (H_c) of the Ni–Co–Fe–P-coated flake graphite are 2.41 emu/g, 0.72 emu/g and 19.2 Oe, respectively. The result shows that the Ni–Co–Fe–P-coated flake graphite is magnetic, and it belongs to soft magnetic materials because the area of hysteresis loop and the residual magnetism are small. The Ni–Co–Fe–P alloy coating can improve the magnetic properties of flake graphite, so the microwave absorption properties of the Ni–Co–Fe–P-coated flake graphite can be enhanced.

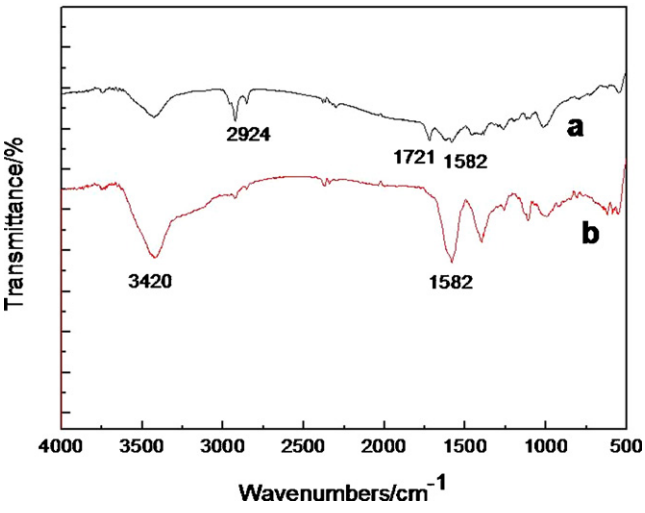

Fig. 3. IR spectrum of flake graphite (a) before plating (b) after plating.

3.3. Microwave absorption Property

The complex permittivity (real part ε', imaginary part ε'') and the complex permeability (real part μ', imaginary part μ'') of flake graphite before and after plating were measured by using vector network analyzer in the frequency range of 0.1–10 GHz. Fig. 5 illustrates the real and imaginary parts of permittivity of flake graphite

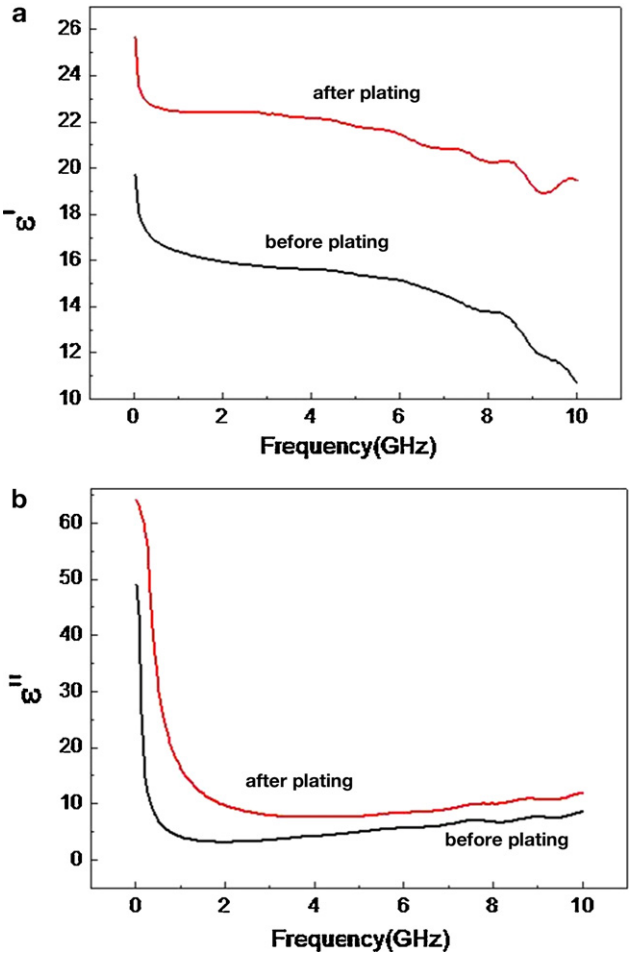

Fig. 5. Frequency dependence of real (a) and imaginary (b) part of the complex permittivity of flake graphite before plating and after plating.

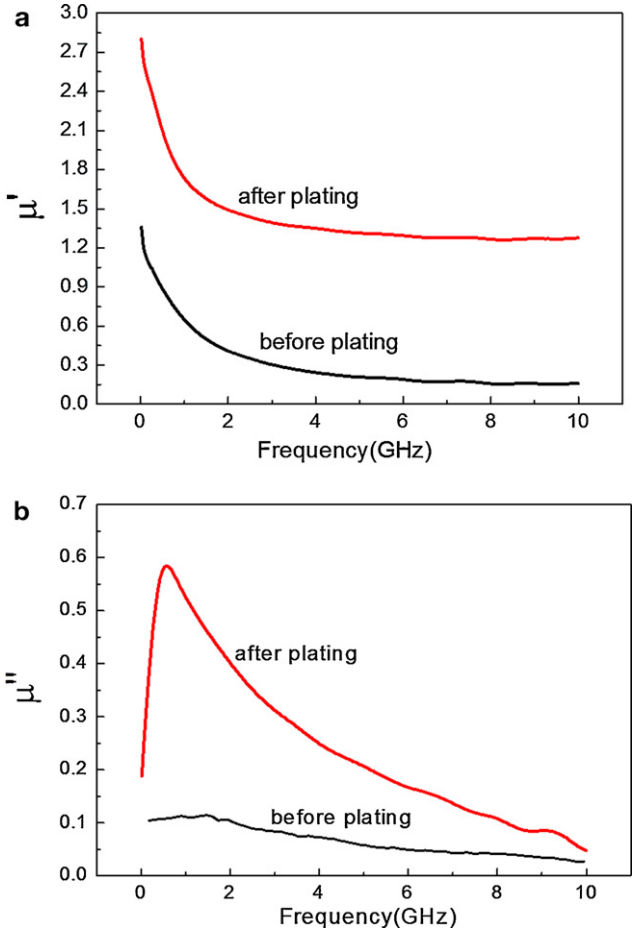

Fig. 6. Frequency dependence of real (a) and imaginary (b) part of the complex permeability of flake graphite before plating and after plating.

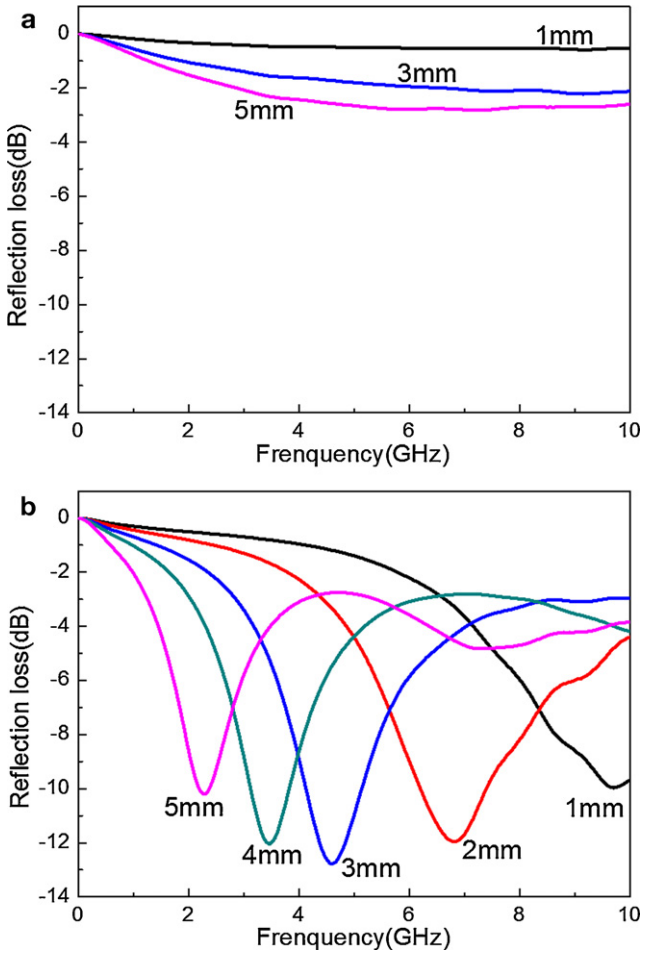

Fig. 7. Frequency dependence of the RL of flake graphite at various thickness (a) before plating (b) after plating.

before and after plating as a function of frequency. It can be seen that the real and imaginary parts of permittivity of the plated flake graphite have similar change trends with those before plating. The values of real part ε' and imaginary part ε'' are abruptly decreased in the range of 0.1–1 GHz, which shows that the dielectric losses of flake graphite before and after plating are changed significantly in low frequency region. Then the value of real part ε' is gradually decreased with the increasing of frequency, but the value of imaginary part ε'' is gradually increased with the increasing of frequency. The real and imaginary parts of permeability of flake graphite before and after plating as a function of frequency are shown in Fig. 6. It is found that the values of real part μ' of flake graphite before and after plating are decreased with the increasing of frequency and tend to be constant ultimately. The value of imaginary part μ'' is increased in the range of 0.1–1 GHz, then is decreased with the increasing of frequency. The changing degree of imaginary part μ'' of the Ni–Co–Fe–P-coated flake graphite is higher than those before plating, which is attributed to the metallic behavior of Ni, Co and Fe in Ni–Co–Fe–P alloy coating.

The RL curve can be calculated according to the theory of absorbing wall. For the composite layer terminated by metal plate, the normalized input impedance Z_{in} at the surface is given by:

$$Z_{in} = \sqrt{\frac{\mu_\gamma}{\varepsilon_\gamma}} \tanh\left[j\frac{2\pi}{c} fd\sqrt{\mu_\gamma \varepsilon_\gamma}\right] \quad (1)$$

where ε_γ and μ_γ are the relative complex permeability and permittivity of the composite medium, respectively, and f is the frequency of electromagnetic wave, d is the thickness of the absorber, and c is the velocity of electromagnetic wave in free space. The RL is related to Z_{in} by:

$$\mathrm{RL(dB)} = 20lg\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \quad (2)$$

Thus, the surface reflectance of an absorber is determined from six characteristic parameters: f, d, ε'_γ, ε''_γ, μ'_γ, μ''_γ. Using the values in Figs. 5 and 6, the theoretical values of RL of flake graphite before and after plating with different thickness can be obtained. Fig. 7 shows the RL of flake graphite before and after plating at various thicknesses. It can be seen that the microwave absorption of flake graphite before plating is very weak in the frequency range of 0.1–10 GHz, and the Ni–Co–Fe–P alloy coating improves the microwave absorption property of flake graphite greatly. As shown in Fig. 7(b), the microwave absorption peaks of the Ni–Co–Fe–P-coated flake graphite are shifted to low frequency with increasing sample thickness. The maximum attenuation of the incident wave is observed with a thickness of 3.0 mm for the Ni–Co–Fe–P-coated flake graphite, and the bandwidth of <−5 dB reaches 3.0 GHz and the minimum RL value of −12.8 dB is obtained at 4.6 GHz.

4. Conclusions

Ni–Co–Fe–P alloy coating was successfully deposited on surface of flake graphite by electroless plating technique. The composition of the alloy plating is 78.14 wt% Ni, 9.75 wt% Fe, 7.98 wt% Co, and 4.13 wt% P. The coating is amorphous and stable in the air. The Ni–Co–Fe–P-coated flake graphite is magnetic. The microwave

absorption property of the Ni–Co–Fe–P-coated flake graphite is much better than that of flake graphite before plating, and the value of the minimum RL reaches −12.8 dB at 4.6 GHz with the thickness of 3.0 mm.

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