Fabrication and Microwave Absorption Performances of FeNi-CoFe$_2$O$_4$-PANI Composites

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Abstract. Flake FeNi alloys were fabricated by micromachining, CoFe$_2$O$_4$ and PANI were loaded on the surface of the flake FeNi alloys by coprecipitation and in-situ polymerization. Finally the FeNi/CoFe$_2$O$_4$/PANI composites with electromagnetic absorption properties were obtained. The morphology, composition and microwave absorbing properties of the composites were studied by SEM, XRD, FTIR and VNA. The results showed that CoFe$_2$O$_4$/PANI is deposited on the surface of the matrix, and a small amount was dissociated. The permittivity and the low-frequency absorbing property of the composites was improved. At the frequency of 2.2GHz, the lowest reflection reached -12.2dB. By analyzed the electromagnetic properties and using the theory of 1/4 wavelength interference cancellation, the reasons for the improvement of low frequency absorbing properties of composites were explained.

1. Introduction
With the progress of military science and technology, the radar operation frequency used in military has been widening. Such as, the decimeter wave and meter wave play an increasingly important role in military field [1]. The development and application of early warning radar and over-the-horizon radar make the research and development of low frequency absorbing materials extremely urgent. At the same time, in the civil field, electromagnetic radiation has become inevitable in people's daily life. Research shows that electromagnetic radiation in low frequency can cause biological damage to human body [2]. Therefore, the research and application of low frequency absorbing materials is of great significance to the survival ability of weapons and equipment in the battlefield and the improvement of electromagnetic protection ability in civil areas.

FeNi alloy is a typical magnetic metal with high permeability and saturation magnetization. It is commonly used as low frequency absorbing material [3]. However, its application is limited by its high density, easy oxidation and easy corrosion, what's more its single loss mechanism cause the absorption performance in low frequency is also greatly affected [4]. Particle flaking and surface coating are often used to improve FeNi alloy low frequency absorbing performance. For example, Xu Jingfeng [5] et al. fabricated flake FeNi alloy by wet grinding and annealing process, the electromagnetic parameters were greatly improved, and the reflectivity was lower than -10dB in the frequency range of 7~8.5GHz. Wang Qi [6] et al. used ZnO coated Fe$_{0.7}$Ni$_{0.3}$ alloy powder to adjust the permittivity of the composite, but at the same time reduced the imaginary part of the permeability. Xie Jianliang [7] et al. used sol gel method to modify the surface of the flake metal powder, which effectively promoted the impedance matching performance of FeNi alloy and enhanced the low frequency wave absorbing effect.
At present, the researchers often to expand the low frequency properties of FeNi alloy by a single means, and the low frequency absorption effect is limited to C–X band. Polyaniline (PANI) is a conjugated conductive polymer with good stability, high temperature resistance and oxidation resistance [8]. It mainly absorbs electromagnetic waves by using electrical loss. CoFe$_2$O$_4$ as a nano-absorbing material, has superparamagnetic properties and is often used as an additive to improve the electromagnetic properties of the matrix [9]. In this study, CoFe$_2$O$_4$ and PANI were coated on the surface of flake FeNi alloy to obtain FeNi/CoFe$_2$O$_4$/PANI ternary composites. The effects of electromagnetic parameters with multicomponent coating of flake FeNi alloy were studied. The microwave absorbing properties of the composites were compared with the flake FeNi alloy, and the microwave absorbing mechanism of the composites were analyzed.

2. Experiments

2.1. Reagents and instruments

High permeability flake FeNi alloy prepared by ball milling technology; ferrous chloride hexahydrate, anhydrous ethanol, cobalt chloride hexahydrate and phosphoric acid were prepared by Tianjin Damao Chemical Reagent Factory; ammonium persulfate (APS) and aniline (used after degrading distillation) were prepared by Tianjin Yongda Chemical Reagent Factory; ammonia water (25%~28%) was prepared by Shijiazhuang Chemical Reagent Factory; the above reagents were AR reagents. Water was self-made distilled water.

The morphology of the samples was observed by scanning electron microscopy (SEM) of Hitachi Company SU-4800, XRD was measured by D8 X-ray diffractometer of Brooke Company, Germany, organic composition was measured by NEXUS-670 infrared spectrometer of Nikoli Company, USA, and electromagnetic parameters in the frequency range of 0.5~18 GHz were measured by vector network analyzer N5242A of Agilent Company.

2.2. Preparation of FeNi/CoFe$_2$O$_4$ composites

Take 200 ml distilled water under N$_2$ protection, stir and drain oxygen; weigh 2.7 g ferrous chloride, 1.19 g cobalt chloride according to stoichiometric ratio, dissolved in the above distilled water, stirred in 30°C water bath for 30 min, marked as solution A. Added ultrasonic dispersed flake FeNi into solution A, and raised temperature to 70°C water bath, drop ammonia to PH between 9~11, mechanical stirring for 20 min, wait for the solution discoloration and then stop stirring precipitating for 1 h, used anhydrous water and Ethanol cleaned three times, then separated and dried by magnetic.

2.3. Preparation of FeNi/CoFe$_2$O$_4$/PANI composites

FeNi/CoFe$_2$O$_4$/PANI composites were prepared by adding 2.2 composite powders, 1.5 ml aniline and 2 ml phosphoric acid into 200 ml distilled water, then adding 150 ml aqueous solution containing 3 g APS to the above solution at constant pressure of 0.5 h, mechanical stirring for 12 h, vacuum filtration and drying.

3. Results and discussions

3.1. Sample characterization

The SEM photograph of flaky FeNi powder and composites are shown in Figure 1. Figure 1 (a) is the micro-morphology of flaky FeNi powder. It can be seen that after micromachining, the particles show flaky structure with a width-thickness ratio between 20 and 50, and the surface is smooth. Figure 1 (b) gives the surface morphology of FeNi/CoFe$_2$O$_4$. It can be seen that a large amount of CoFe$_2$O$_4$ is deposited on the surface of flake particles. Ferrite particles synthesized by coprecipitation method are mainly aggregated because of their small size. Figure 1 (c) is the surface morphology of FeNi/CoFe$_2$O$_4$/PANI. A large number of CoFe$_2$O$_4$ and PANI are attached to the surface of flake
particles, in which PANI in situ grows on the surface of flake particles and presents irregular aggregation. In addition, a small amount of free CoFe$_2$O$_4$ and PANI can be seen from Figure 1 (b) (c).

![Figure 1. SEM diagram of FeNi (a), FeNi/CoFe$_2$O$_4$ (b) and FeNi/CoFe$_2$O$_4$/PANI (c).](image)

The XRD spectrum of FeNi/CoFe$_2$O$_4$/PANI is shown in Figure 2. It can be seen that the diffraction peaks are mainly composed of FeNi alloy and coprecipitation products. Compared with standard PDF cards, the coprecipitation product is CoFe$_2$O$_4$ (file no: PDF#22-1086), which belongs to the face-centered cubic system and has spinel structure. In addition, no clear diffraction peaks of PANI are found in the spectra, because PANI peaks mainly existed near 15-25 degrees and are concealed under the strong diffraction peaks of FeNi and CoFe$_2$O$_4$ crystals. Combining the SEM photos of Figure 1 able to confirm the FeNi/CoFe$_2$O$_4$/PANI composites were obtained.

![Figure 2. XRD pattern of FeNi/CoFe$_2$O$_4$/PANI.](image)
The infrared spectra of FeNi/CoFe₂O₄/PANI is shown in Figure 3. The corresponding characteristic peaks of PANI appeared in the spectra, of which 1570, 1500, 1300, 1150 and 828 cm⁻¹ corresponded to the characteristic absorption peaks of C=C in quinoid structure, C=C in benzene ring, C-N, N=Q=N and C-H respectively. In addition, the characteristic absorption peak of Fe-O appeared at 588 cm⁻¹. The characteristic absorption peaks of H-O appeared at 3452 cm⁻¹ due to a small amount of water in the composites. The above infrared spectroscopy analysis further proved that the FeNi/CoFe₂O₄/PANI composite was prepared.

![Figure 3. FTIR spectra of FeNi/CoFe₂O₄/PANI.](image)

3.2. Analysis of electromagnetic parameters and absorbing property

After mixing FeNi/CoFe₂O₄/PANI with paraffin at 30% volume ratio, annular sample with inner diameter of 3 mm, outer diameter of 7 mm and thickness of 2 mm were prepared by moulding method. In order to facilitate the comparison of the performance changes after compounding, annular samples were made of flake FeNi alloy powder at the same ratio. Figure 4 shows the electromagnetic parameters of two samples in the range of 0.5-6 GHz. As shown in Figure 4 (a) (b), with the increase of frequency, the real part of permittivity ($\varepsilon'$) of FeNi/CoFe₂O₄/PANI decreases slightly and stabilizes at about 45; the imaginary part ($\varepsilon''$) decreases gradually with the increase of frequency, and the maximum value reaches 5.7. The permittivity of flaky FeNi powder tends to be constant with the vary of frequency. The real and imaginary parts of FeNi powder are obviously lower than that of the composites. The real and imaginary parts of FeNi/CoFe₂O₄/PANIr are 2 and 1.5 times higher than that of flaky FeNi, respectively. This is because PANI is a kind of conductive material with small density and large volume, which makes composites easier to lap for adjacent particles after compounding, thus forming conductive network and increasing permittivity [10]. In addition, according to free electron theory [11], the imaginary part of the permittivity of the material is positively related to the conductivity of the material, because the addition of conductive polyaniline also promotes the increase of the imaginary part of the permittivity. From Figure 4 (c) (d), we can see that the magnetic permeability of the two samples is similar with frequency change. The real part of FeNi/CoFe₂O₄/PANI is slightly lower than that of FeNi alloy, while the imaginary part is slightly higher than that of FeNi alloy. The reason is that CoFe₂O₄ has a certain magnetic property and changes the proportion of magnetic components in the annular sample.
Figure 4. Relative permittivity and relative permeability of FeNi, FeNi/Co$_2$FeO$_4$/PANI.

Figure 5. Reflection loss of each samples (a) and 3D reflection loss curves of FeNi/CoFe$_2$O$_4$/PANI (b).
The reflectivity curves of samples with thickness of 2 mm can be calculated by theoretical model of transmission line [12]. From figure 5 (a) can be seen that the absorption intensity of FeNi/CoFe₂O₄/PANI decreases slightly to -12.2 dB compared with flake FeNi powder, and the absorption peak frequency decreases greatly, moving from 4.7 GHz of FeNi to 2.2 GHz. Low frequency (S band) absorbing performance has been greatly improved. Three-dimensional surface of FeNi/CoFe₂O₄/PANI reflectivity varying with frequency and thickness is shown in Figure 5 (b). It can be seen that the reflectivity decreases first and then increases with the increase of frequency. With the increase of thickness, the absorption peak moves to low frequency gradually and the absorption intensity increases gradually. So we can draw a conclusion that a better low frequency absorbing performance can be achieved by increasing thickness appropriately.

3.3. Analysis of absorbing mechanism
The tangent of the electric loss angle and the magnetic loss angle reflect respectively the electric loss ability and the magnetic loss ability of the absorbing material. The tangent of the electric loss angle (a) and the tangent of the magnetic loss angle (b) of the two samples vary with frequency are shown in Figure 6. It can be seen that the electrical loss of the composites is lower than that of FeNi in the whole frequency range, but the magnetic loss ability of the composites is slightly higher than that of FeNi. This is because the permittivity of FeNi/CoFe₂O₄/PANI is higher than FeNi, but the increase ratio of the real part is higher than imaginary part, which results in the tangent decrease of the loss angle, and the change rule of the magnetic loss angle is also known. Through the analysis of electric and magnetic loss ability, it is found that under the condition of the same magnetic loss ability, the absorption strength of the composites decreases due to the decrease of the electric loss ability.

![Figure 6. Dielectric loss tangent (a) and magnetic loss tangent (b) of two samples.](image)

Absorbing materials not only rely on the internal electrical and magnetic losses to attenuate electromagnetic waves, but also have a large amount of energy was lossed by the reflection wave interference loss (1/4 wavelength interference cancellation phenomenon) at the interface between the front and back of the absorbing materials [13]. When parallel electromagnetic waves incident perpendicularly on the surface of absorbing materials, part of them are reflected by the front interface, part of them are reflected by the metal backplane after entering the absorbing material, and then emitted from the surface of absorbing materials. When the thickness of absorbing materials is odd multiple of 1/4 wavelength of electromagnetic wave, the phase difference between the incident wave and the outgoing wave will be 180 degrees, and the reflection loss peak will be formed by canceling each other’s reflection characteristics. The theoretical equation of 1/4 wavelength interference cancellation is as follows:
In the equation, \( t_m \) is the thickness of absorber, \( f_m \) is the frequency of electromagnetic wave, \( \varepsilon_r \) is the relative permittivity, and \( \mu_r \) is the relative permeability. \( n \) indicates that when the thickness of absorber is an odd multiple of the 1/4 wavelength, the material satisfies the theory of interference cancellation of 1/4 wavelength.

\[
t_m = \frac{nc}{4f_m\sqrt{\varepsilon_r\mu_r}}\quad (n = 1, 3, 5, \ldots)
\]  

(1)

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![Figure 7](image_url)

**Figure 7.** The \( \lambda/4 \) thickness curve and the curve of electromagnetic wave reflectivity of two samples (a) and \( \sqrt{\varepsilon_r\mu_r} \) of two samples (b).

The thickness curve of 1/4 wavelength at \( n=1 \) and the corresponding reflectivity curve is shown in Figure 7 (a). It can be seen that the thickness of absorbing material calculated by equation (1) corresponds to the absorption peak frequency is 2 mm, which is consistent with the set thickness of absorbing coating. Therefore, the peak variation of reflection loss caused by composites is mainly determined by the theory of 1/4 wavelength cancellation. According to the theory of 1/4 wavelength interference cancellation, the shift of reflection loss peak at the same thickness is entirely determined by \( \sqrt{\varepsilon_r\mu_r} \). Figure 7 (b) shows the \( \sqrt{\varepsilon_r\mu_r} \) versus frequency curves of the two samples. It can be seen that the \( \sqrt{\varepsilon_r\mu_r} \) of FeNi/CoFe\(_2\)O\(_4\)/PANI is higher. According to equation (1) \( t_m \) is identical, thus \( f_m \) decreases. Therefore, the reason why the absorption peak frequency of FeNi/CoFe\(_2\)O\(_4\)/PANI composites shifts to low frequency was explained by the 1/4 wavelength cancellation mechanism.

4. Conclusions
   (1) Through co-precipitation and in-situ polymerization technology made the CoFe\(_2\)O\(_4\) and PANI coated on the surface of flake FeNi alloys, achieved the FeNi/CoFe\(_2\)O\(_4\)/PANI composites with both electrical and magnetic loss property.
   (2) Comparing with flake FeNi alloys, it was founded that the permittivity of the composites increases greatly and the imaginary part of permeability increases slightly. When the matching thickness \( d=2\)mm, \( R_{L\min} \) reached -12.2dB, \( f_m \) decreases from 4.7GHz to 2.2GHz, showed good low frequency (S-band) absorbing property.
   (3) The reason for the change of absorption intensity between composites and FeNi was explained by the tangent of electric and magnetic loss angle. The internal reason for the decrease of absorption peak frequency of the composites was explained by the theory of interference cancellation of 1/4 wavelength.
wavelength. FeNi and the composites all allow to the theory of interference cancellation of 1/4 wavelength. The higher $\sqrt{\varepsilon\mu_r}$ of FeNi/CoFe$_2$O$_4$/PANI, so it has the lower absorption peak frequency.

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