Improving Impedance Matching of Flaky Carbonyl Iron
Based on the Surface Modification by Binary Coupling Agents

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ABSTRACT: In this paper, the impedance matching of the flaky carbonyl iron was improved by surface modification with binary coupling agents. The microstructure, phase and electromagnetic parameters were detected by scanning electron microscope (SEM), X-ray diffraction (XRD) and Agilent vector network analyzer, respectively. After binary coupling agent applied, the shape and particle size of the flaky CIP have changed significantly, whereas the phase remained α-Fe phase. On the other hand, with the addition of binary coupling agents, the complex permittivity of flaky CIP is reduced, which is beneficial to impedance matching. The doping with 2wt% calcium stearate and 2ml titanate to flaky CIP has a minimum reflection loss peak of −13 dB at the thickness of 2 mm. It is noted that the effective absorption bandwidth (RL<−10dB) is up to 0.8GHz (1.8~2.6GHz). Moreover, the magnetic tangent loss of the samples can be significantly improved by the addition of binary coupling agents. Therefore, the surface modification of binary coupling agent can make flaky CIP get better impedance matching and absorbing performance in S

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band.

**Key words:** absorbing materials; surface modification; coupling agent; microstructure; impedance matching

1. **INTRODUCTION**

With the rapid propagation of the electronic devices, electromagnetic radiation and interference caused by electromagnetic waves threat to human health [1-2]. Thus, the microwave absorbing materials used to suppress electromagnetic radiation and interference have attracted considerable attention [3-4]. High-performance microwave absorbing materials confirmed by broadband, small thickness, minimum reflection loss (RL) and excellent impedance matching [5-6]. At present, the s-band has a wide range of applications in mobile satellite services (MSS), weather radar, terrestrial cellular and broadband circular polarization slot antennas [7].

Flaky shaped carbonyl iron particle (CIP) is an excellent absorbing material for its relatively low electrical conductivity, low eddy-current, high specific saturation magnetization intensity, high Curie temperature, high complex permeability and superior magnetic loss ability [8-10]. Nevertheless, Interfacial polarization results in high complex dielectric constant values of flake iron carbonyl [9]. It worsens the impedance match between microwave absorbing material and air, which is bad for the electromagnetism wave absorption properties [11].

Many efforts have been made to reduce the excessively high dielectric of flake carbonyl iron, such as flake carbonyl iron/Fe₃O₄ composite (CI/ferrites composites) [1], core-shell structure flaked carbonyl iron powder@SiO₂ nanocomposite [5], flake
carbonyl iron combined carbon-based material (carbon nanotubes/carbonyl iron powders complex absorbents) [12], chemical modification [13]. The surface modification by coupling agent doping is regarded as a simple and cheap method, which is beneficial to impedance matching [14-15]. Feng et al. reported of CIP with silane coupling agent KH550 [16], and Song et al. used the surface modification with nanostructure polymer coated on flake CIPs [17]. In addition, the coupling agent can improve the compatibility between the filler and the rubber matrix and change the surface of the absorbing material from hydrophilic to hydrophobic [18].

Up to now, the research of coupling agent mainly has focused on the modification of single coupling agent. However, the modification of binary coupling agent is rarely involved. Based on our previous research [19], the role of binary coupling agent modification on the microstructure and microwave absorbing properties in S band of flake CIP are studied in this paper.

2. EXPERIMENT

2.1 Sample preparation

The flaky CIP was obtained from raw spherical carbonyl iron powder (SCIP) (Co. tianyi, Jiangsu, China) by ball milling method. It has been mentioned in our pervious study [20]. The weight ratio of milling balls and SCIP was 8:1. Absolute ethanol was used during the ball milling process to avoid the aggregation of particles. Calcium stearate and Titanate (DN-101) were selected as the Surface modification during milling process. Based on 100g of CIP, the doping content of calcium stearate is 2 wt % and titanate is 1 ml, 2 ml and 3 ml, respectively. The samples are listed in Table 1.
The ball milling was fixed with 10 hours. The wet milled slurry was dried in a vacuum (DZF-6020 Co. suoyu, shanghai, China) oven at 60 °C for 6h, then the desired surface modified flaky CIP samples were obtained.

| Sample number | Coupling Agents                        |
|---------------|----------------------------------------|
| 1#            | 2 wt % Calcium stearate                |
| 2#            | 2 wt % Calcium stearate + 1 ml Titanate |
| 3#            | 2 wt % Calcium stearate + 2 ml Titanate |
| 4#            | 2 wt % Calcium stearate + 3 ml Titanate |

2.2 Characterization methods

The morphology of the samples was observed by scanning electron microscope (SEM). The phases of the samples were detected by X-ray diffraction (XRD). The electromagnetic parameter for samples was prepared by dispersing the powders in paraffin wax, and the weight fraction of powder is 85%. The powder wax composites were die-pressed to form cylindrical toroidal specimens with 7.0 mm outer diameter, 3.04 mm inner diameter, and around 3 mm thickness. The measurements of complex permeability $\mu$ and permittivity $\varepsilon$ for the specimens were carried out using a vector network analyzer (Agilent PNAN5244A) in the range of 1-18 GHz.

3. RESULTS AND DISCUSSION

3.1 Microstructure of carbonyl iron modified
Fig. 1 shows the SEM micrographs of the flaky CIP which were modified by coupling agents. It can be seen the distinctly difference in microstructures between the modification of single and binary coupling agent. It is indicated that the particles of sample 1# which is prepared by using the calcium stearate exhibit an irregular flake shape along with a relatively large particle size and sharp edges. However, the shape of samples (samples 2#, 3# and 4#) which are modified by composite coupling agents (calcium stearate and titanate) gradually become more regular and oblate edges. Moreover, the particle size and the degree of refinement gradually increase with the increasing of titanate. The minimal particle size for sample 2# is about 4-10 $\mu m$, while that of sample 4# has the largest particle size of 10-15 $\mu m$. In addition, the sample 4# has a relatively uniform size distribution. The thicknesses of all particles are below 1 $\mu m$, it is beneficial to decrease eddy current loss [21]. Thus, the modification of binary coupling agents can improve the microstructure of flaky CIP more effectively.
Fig. 1 SEM images of carbonyl iron samples modified by coupling agents

3.2 Phase analysis

The XRD patterns for the samples are shown in Fig. 2. All samples show a distinct diffraction peak at about 44°. It corresponds to the crystal plane (110) of the $\alpha – Fe$ phase. The close examination pattern illustrates that there is no shift in the peak position with the increase in the type of coupling agents. That means that the flaky CIP lattice constant does not change with the modification of the binary coupling agents [22].
3.3 Effect of coupling agents on complex permittivity of carbonyl iron

Fig. 3 shows the frequency dispersion of the complex permittivity within the 1-18 GHz. In general, as can be seen that the value of $\varepsilon'$ and $\varepsilon''$ remain vibrating with the frequency. As the frequency increases, $\varepsilon'$ of all samples show a slow decreasing trend in 1-12 GHz. The value of $\varepsilon'$ shows strong frequency dispersion above 12 GHz, which may be attributed to intrinsic electric dipole polarization and interfacial polarization [23]. Yang et al explained the complex permittivity of FCIP rises after wet-milling due to the interfacial polarization [24]. However, in our research, $\varepsilon'$ of sample 3# is lower than that of other samples between 1-4 GHz. At about 2.2 GHz, $\varepsilon''$ of sample 3# drops to about 10, which is the lowest compared to other samples. The modification of the binary coupling agents leads to a significant decrease in the complex permittivity in this study. The similar results also are reported by Zare et al. [25] and Xie et al. [19]. By contrast, the decrease in complex permittivity is likely due to the decrease in interfacial polarization by the modification of the appropriate
amount of binary coupling agents. In addition, as we know, lower complex permittivity helps to achieve better impedance matching [26]. Therefore, the flaky CIP can obtain better impedance matching with the modification of the appropriate amount of binary coupling agents.

![Graphs showing real and imaginary permittivity](image)

**Fig.3** Complex Permittivity of carbonyl iron samples modified by coupling agents

### 3.4 Effect of coupling agents on complex permeability of carbonyl iron

Fig.4 shows the frequency dependence of the complex permeability at 1-18 GHz. In terms of overall trends, both $\mu'$ and $\mu''$ decrease with the increase of the frequency. It is mainly due to the eddy current loss and ferromagnetic resonance of the flaky CIP [27]. In the Fig.4, $\mu'$ of samples does not change significantly with the modification of complex coupling agents. As can be seen from the $\mu''$, all samples firstly increase and then decrease. And the value of $\mu''$ arrives to maximum at about 3 GHz. The jump of $\mu''$ for all samples may result from the multi-resonance [28]. In general, the modification of binary coupling agents does not have a significant effect on the complex permeability of flaky CIP.
Fig. 4 Complex Permeability of carbonyl iron samples modified by coupling agents

3.5 Skin-effect criterion

The imaginary part permeability is related to thickness ($d$) and electric conductivity ($\sigma$):

$$\mu'' = \frac{2}{3} \pi \mu_0 (\mu')^2 d^2 \sigma,$$  \hspace{1cm} (1)

where $\mu_0$ is the permeability of vacuum. Equation (1) can be transformed into this form:

$$\mu'' (\mu')^{-2} f^{-1} = \frac{2}{3} \pi \mu_0 d^2 \sigma.$$ \hspace{1cm} (2)

If the magnetic loss is only caused by the skin effect, the value on the left side of the equation (2) should be constant when the frequency is varied, which is called the skin-effect criterion. Figure 5 shows the value of $\mu'' (\mu')^{-2} f^{-1}$ for samples. The value of $\mu'' (\mu')^{-2} f^{-1}$ for samples is nearly uniform and constant over the frequency ranges of 1-8 GHz, implying that eddy current loss greatly contributed to $\mu''$ and magnetic loss over these frequency regions [29]. However, the value of $\mu'' (\mu')^{-2} f^{-1}$ for samples has a large change extent in the high frequency. As reported by Qiao [30], it is considered that a large change extent occurs because the magnetic loss in the flak particles is mainly caused by natural resonance. Therefore, the magnetic loss in this
study may be related to natural resonance.

Fig. 5  \( \mu''(\mu')^{-2} f^{-1} \) of samples modified by coupling agents

3.6 Loss Tangent analysis

In order to investigate the loss capability of the flaky CIP modified by binary coupling agents, the dielectric (\( \tan \delta_e = \varepsilon''/\varepsilon' \)) and magnetic (\( \tan \delta_\mu = \mu''/\mu' \)) loss tangents for all samples are calculated by using measured electromagnetic parameters. The results are shown in Fig. 6. The dielectric loss tangent of the four curves shows a gentle upward trend, and the use of the binary coupling agents does not have a significant effect on it. But the magnetic loss tangent shows a significant upward trend with increasing frequency. For magnetic materials, dielectric loss and magnetic loss coexist and compete with each other [31]. It can be seen from the figure that \( \tan \delta_\mu \) is always greater than \( \tan \delta_e \). In general, large \( \tan \delta_\mu \) samples have good absorbing performance [32]. It is clearly that the flaky CIP modified by binary coupling agents can get a higher magnetic loss tangent. Therefore, the modification of binary coupling agent can make flaky CIP get better absorbing performance.
3.7 Reflection Loss analysis

According to the transmission line theory, Based on the electromagnetic parameters of the absorbing material, the reflection loss of the absorbing coating at 2 mm thickness is calculated. Calculated as follows [33]:

\[
Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \\
Z_{in} = \sqrt{\frac{\mu}{\varepsilon}} \tanh\left(j \frac{2\pi f d}{c}\right) \sqrt{\mu \varepsilon} \\
RL = 20 \log \left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right|
\]

Here, \( Z_0 \) is the impedance of air, \( \mu_0, \varepsilon_0 \), are the permeability and permittivity of air, respectively, \( f \) is the frequency of the electromagnetic wave, \( d \) is the thickness of the absorber, \( c \) is the velocity of light, \( Z_{in} \) is the input impedance of the absorber, and \( \mu, \varepsilon \) are the complex permeability and complex permittivity of absorber.
respectively.

Figure 7 displays the reflection loss curves of samples with the thickness of 2mm. The RL peak moves to high frequency with the addition of titanate. It shows that the flake CIP containing 2ml titanate (3#) exhibit effective microwave absorption performance the minimum reflection loss ((RL)\text{ min}) is \(-13\) dB at 2.1GHz, and the absorption bandwidth covered 0.8GHz (1.8–2.6GHz) when the RL<\(-10\) dB. For the modified materials of sample 1#, 2# and 4#, the value of (RL)\text{ min} are -11.5 dB at 1.8 GHz, -9.8 dB at 1.8 GHz and -12.2 dB at 1.9 GHz, respectively. The microwave absorbing abilities of binary coupling agent (Calcium stearate+Titanate) exhibite the best microwave absorption properties and relatively wide bandwidth. The results indicate that the addition of binary coupling agents can effectively improve impedance match and absorption properties for flake CIP in this study.

Fig.7 Reflection loss for carbonyl iron samples modified by coupling agents
4. CONCLUSIONS

The microstructure and microwave properties of flaky CIP are heavily depended on the modification of the binary coupling agents in this study. The XRD patterns shows that only the $\alpha - Fe$ phase is achieved for all samples with the addition of binary coupling agents. SEM micrographs display the morphology of the samples which is changed from sharp edge (single coupling agent modification) to passivated edge (binary coupling agents modification). It is indicated that binary coupling agent modification can reduce the complex permittivity and achieve better impedance matching for flaky CIP. The loss tangent illustrates that the flaky CIP which is modified by binary coupling agents can get a better absorbing performance. The $(RL)_{\text{min}}$ of the samples all fall in 1.8-2.1GHz, and the smallest $(RL)_{\text{min}}$ is $-13$dB at 2.1 GHz with the thickness of 2mm. In addition, the role of binary coupling agents can effectively increase the absorption bandwidth of the flaky CIP. Therefore, the use of binary coupling agents can effectively improve the microstructure and impedance matching, reduce the reflection loss and enhance the absorbing performance. Thus, the addition of binary coupling agent in flake CIP can be used in antennas and other fields in s-band.
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