Study on the Electromagnetic Properties in Low Frequency of the Mechanical Modified Carbonyl Iron

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Abstract. In order to obtain a high permeability and improve the microwave absorption properties in low frequency, this paper applied high-energy ball milling technology prepared flaky carbonyl iron powders (CIPs) with high permeability, and studied the Influence of milling time on the morphology, structure, impedance matching and low frequency microwave absorption properties. The result shows that the CIPs particles became flake shape and the deformation rate gradually increased with the increasing of milling time, in addition the permittibity and low frequency permeability increased significantly. The performance of electromagnetic attenuation was increased with the deformation rate ascent, but the impedance matching performance was decreased. The CIPs with the ball milling time of 8 h at 300 r/min has the best shape and excellent low frequency microwave absorption properties, with the minimum reflectivity reaching to -17 dB at 4.2 GHz. The minimum reflectivity of flake CIPs can reach to -26 dB at 7.2 GHz when the ball milling time is 6 h. The microwave absorption frequency can be adjusted by controlling the ball milling time, and study the relationship between them has great significance.

Introduction

As a typical magnetic loss absorbing materials, CIPs compare with ferrite has higher permeability, good thermal stability and thinner match thickness, so CIPs is a promising material in absorbing areas. Currently study the CIPs properties of low frequeny is a hot spot[1]. By introducing the theory of the shape anisotropy, compared with spherical particle the flaky shape can break the snoke limit and obtain higher permeability in low frequency[2], for enhancing low frequency absorbing properties is significant. Walser, etc[3]. is proved in theory, when the flake shape deformation rate is in 10-1000, its' permeability can improve 10-100 times. So the flaky shape of CIPs is decide its permeability. Therefore explore suitable processing is the core of flaky shape preparation. In the flaky shape of magnetic metal powder processing technology, the most commonly used in three ways: liquid phase reduction method, amorphous fast quenching method and high-energy ball milling[4,5].

High-energy ball milling is use mechanical action make spherical shape into flaky shape, and the advantages of it was large output and high efficiency. Wherein the milling time is an important factor affecting the final shape of CIPs particles. ZHAO Li-ying, etc[6]. from the milling time analyzed the variation of the electromagnetic parameters; WANG Wei, etc[7]. studied the flaky shape CIPs internal strain impact on microwave absorption properties. However, the current method of using high-energy ball milling existence drawbacks of long milling time and didn't research the impedance matching performance and microwave absorption properties in low frequency. In this paper, by increasing rotating speed and select suitable proportion of ball to powder to improve production efficiency, exploring the milling time impact on electromagnetic properties in low frequency, and using matlab analysis different milling time CIPs impedance matching performance and absorbing properties in low frequency.

Experiment

Materials. In our experiment, the raw CIPs (particle size 1-3μm, purity 99%); Select alcohol as the process control agent. We fabricated flaky CIPs in a model Y2-80M2-4 ball milling device with a modified hardened ZrO_2 pot and 6 mm ZrO_2 ball.

Preparation process is as follows, adjust ball-to-powder weight ratio of 80:1. The operating frequency was set to bo 10 Hz. 200 ml alcohol was added as a process control agent. According to the above experimental conditions respectively milling 4 h, 6 h, 8 h, 10 h, 12 h. All the as-milled samples were separated by magnetic separation, and then dried at 60^{o}C in air for further characterization.

Analysis and test. The microstructure and morphology of the samples were analyzed by an KYKY-6200 scanning electron microscope. The average width(L) and thickness(d) of the as-milled particles were calculated after counting statistically at least 100 particles when we screened the SEM images. XRD test used BRUKER D2PHASER X-ray diffraction. To obtain the cylindrical toroidal samples for microwave measurement, we fully mixed 28 vol% of the as-obtained powders with paraffin wax, and then pressed them into annular disks with an outer diameter of 7.00 mm, an inner diameter of 3.04 mm, and a length of the composite samples were measured using an Agilent N5242A vector network analyzer over the 0.5-18 GHz. The reflection loss(RL) was calculated according to the equation:

$$R = 20\lg\left|\frac{Z_{in}\text{-}1}{Z_{in}+1}\right|$$

The input impedance equation as follow:

$$\mathrm{Z_{in}} = \left(\frac{\mu}{\varepsilon}\right)^{1/2}\tanh\left[j\left(\frac{2\pi fd}{\mathrm{c}}\right)(\mu\varepsilon)^{1/2}\right]$$

f is frequency; d is the coating thickness; c is the speed of light in vacuum.

Results and discussion

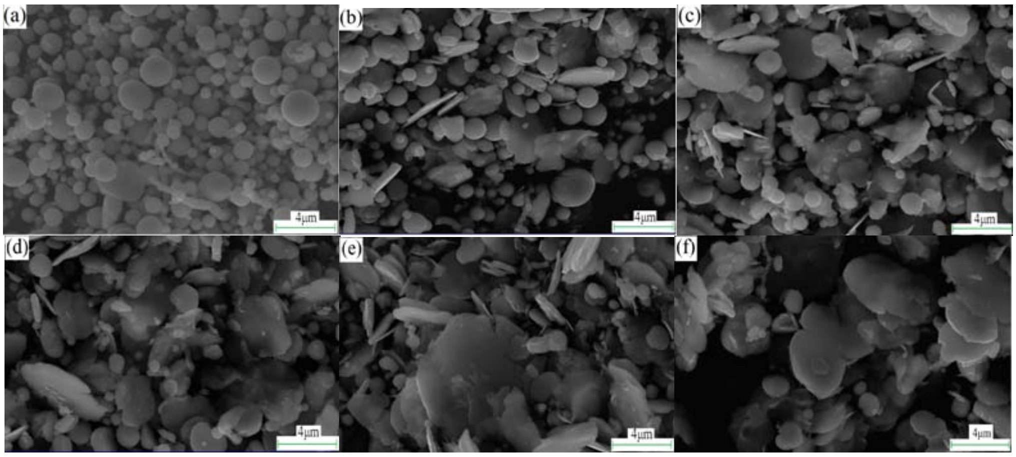


Fig. 1 SEM photographs of CIPs at different ball milling time
(a) raw CIPs; (b) 4 h; (c) 6 h; (d) 8 h; (e) 10 h; (f) 12 h

Effect of milling time on the morphology of CIPs. Fig. 1 shows the SEM photographs of CIPs with the different ball milling time. As can be seen by Fig. 1 with increasing milling time, CIPs received shear, impact and other mechanical force from ZrO_2, its structure goes through the change from spherical to pie shape to flake shape. Raw CIPs diameter is 1-3 μm spherical particles, after 4 hours milling, due to the short mechanical interaction, the big particles was became pie shape but the small particles was still spherical. After 6-8 h milling time, small particles gradually became flake shape and flake thickness gradually reduced, during this process, due to alcohol absorbs some energy and the milling time was suitable, so it didn't show a lot of debris. After 10-12 h milling time, flake shape structure was too thin and work hardening effect lead to particle breakage. Shown in Fig. 1 e, f, has a lot of debris in irregular shape and grain refinement indirectly. Table 1 shows particle size of CIPs at different ball milling time.

Table 1 Particle size of CIPs at different ball milling time

Milling time/ h	Width/ μm	Thickness/ μm	Aspect ratio	Number of the pictures
4	5.2	0.6	8.7	b
6	6.0	0.5	12.0	c
8	7.5	0.3	25.0	d
10	6.7	0.3	22.3	e
12	5.5	0.3	18.3	f

Effect of milling process of CIPs crystal structure. The XRD patterns of the flake CIPs as shows in Fig. 2 that (a) is the raw CIPs and (b) is CIPs after 12 h ball milling. From Fig. 2, pattern only contains CIPs diffraction peaks, understood that raw CIPs has low impurity content and alcohol protected CIPs unoxidized; Comparison found that after ball milling, the peak height was reduced, FWHM was slight increase and diffraction angle slightly shifted. These phenomena shown the degree of crystallinity declined. Perhaps because after mechanical effect the grain size were reduced and mechanical action led to increase of grain internal defects, so the grain was divided[8].

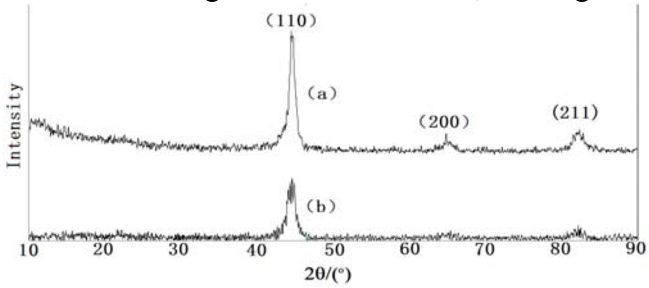
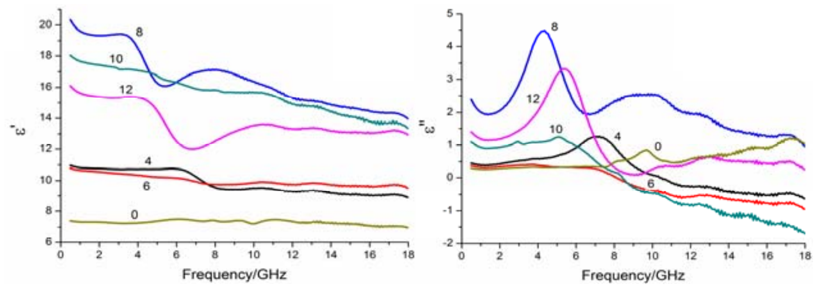


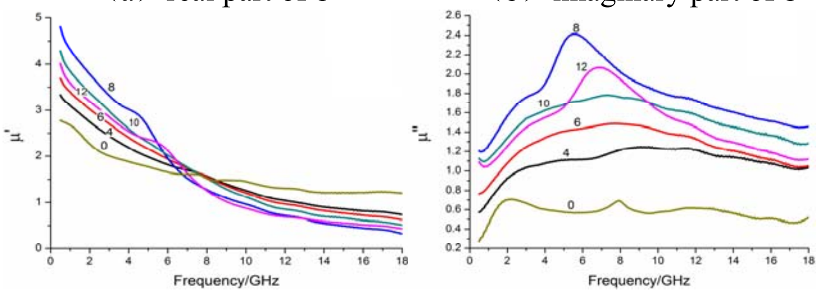
Fig. 2 XRD patterns of raw material (a) and that after ball milling(b)

Effect of milling time on the electromagnetic properties of CIPs. Fig. 3 shows the relationship between the electromagnetic parameters of milling time and CIPs. Fig. 3 (a), (b) shows that with milling time increased, the real part of permittivity was increased between milling time of 0-8 h , the maximum is 21.3, and it was declined after 10 h milling; The real part of permittivity with frequency didn't change significantly, it was slight fluctuations in 4-8 GHz, and stabilize and slowly decreases in other frequency. The reason for the result is that with the deformation rate increased the surface area larger and surface polarization bigger, so the ε′ tended to increase. When the milling time more than 8 h, flake shape CIPs were fractured, so its deformation rate reduce and ε′ reduce. ε″ trend with the milling time is the same as ε′, after 0-12 h ball milling ε″ appear that trend is first increase and then decrease. After ball milling 8 h obtained the ε″ maximum and its peak point is the lowest. ε″ varies with frequency, exist peak in 3-8 GHz, and in other frequency it is stabilize and slow decline. This may be due to the flake shape CIPs polarization orientation and overlap each other forming a conductive network, therefore electron transitions is more easier led to this conclusion[9].

Through Fig. 3(c) we can see that μ′ with milling time show the "seesaw" type, at f=6.5 GHz appeared the fulcrum of μ′. The greater deformation rate of CIPs the larger the initial permeability and descent rate, after 8 h ball milling the initial permeability has maximum reach 4.8. μ′ vary with frequency appear downward trend, rapid decline in the range of less than 6.5 GHz, then with frequency increasd μ′ slow decline. The reason for this phenomenon is different deformation rate caused the anisotropy field different, so the permeability increased when the deformation rate increased. With the frequency increased, CIPs eddy current loss also increased, so it could generate a stronger reversal magnetic field, thereby led to permeability reduced[10]. Fig. 3(d) shows the μ″ variety. With milling time increased, peak of μ″ gradually increase and peak point reduce at 0-8 h; With the frequency increased, μ″ appeared single peak variation that first and then decreased. The reason is that natural resonance is the mainly magnetic loss at 0.5-6 GHz, and with frequency increased the resonance intensity also increased at 6 GHz achieved the maxmum[9]. Eddy current loss is the mainly magnetic loss at 6-18 GHz, so that the reverse magnetic field which led to μ″ decreased with the frequency increase.



（a）real part of ε　　（b）imaginary part of ε



（c）real part of μ　　（d）imaginary part of μ

Fig. 3 The electromagnetism parameter curves of CIPs at different ball milling time

Effect of milling time on CIPs microwave absorbing properties. Permittivity and permeability directly determine the absorbing materials' absorbing properties. To achieve the efficient absorption of microwave, wo need to have two part performance: good impedance match and efficient attenuation. Materials' impedance is closer to impedance of free space, it has the better impedance matching performance. Impedance match can be calculated by the following formula[1]:

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

Attenuation constant representative the attenuation performance, and the larger attenuation constant the attenuation stronger. Formula is as follows[1]:

$$a = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon\text{-}\mu'\varepsilon') + \sqrt{(\mu''\varepsilon''\text{-}\mu'\varepsilon')^2 + (\varepsilon'\mu'' + \varepsilon''\mu')^2}} \tag{2}$$

d is thickness; f is frequency; c is the speed of light in wacuum; μ and ε are the electromagnetic parameters; Z_{in} is the characteristic impedance; a is the attenuation constant.

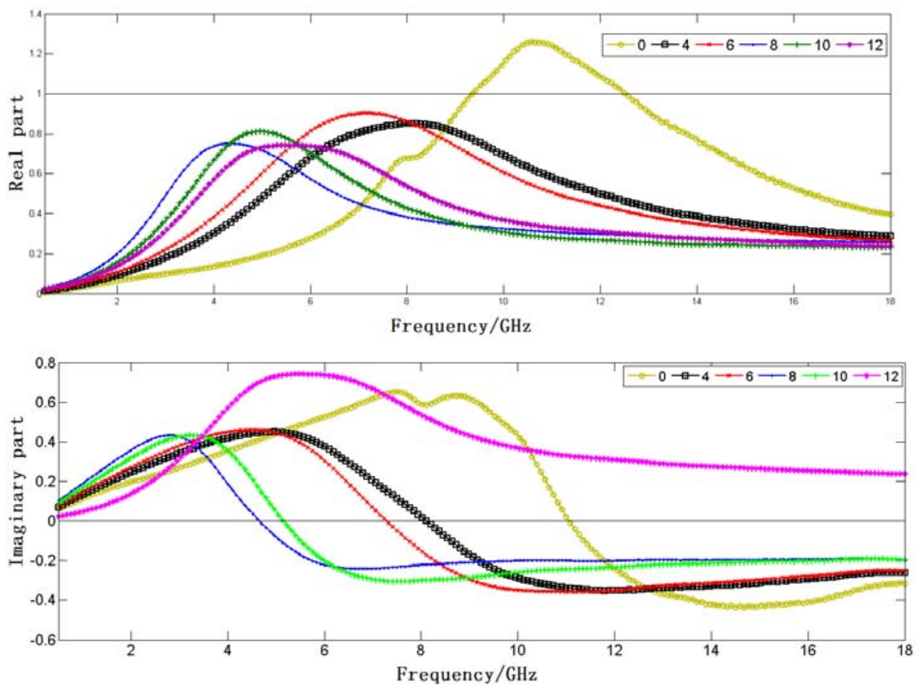


Fig. 4 The impedance matching curves of CIPs at different time

Fig. 4 shows the impedance matching curves of CIPs at different time, as we known the free space impedance (real part is 1; imaginary part is 0), so which curves' real part close to 1 and imaginary part close to 0, it has the better impedance matching. In order to more intuitive compare each curve with free space impedance closeness by matlab polynomial curve fitting means calculated the different between sample curves and the target curve (real part is 1 and imaginary part is 0) in terms of D, so the smaller D is the better impedance matching performance it has. The results are shown in Table 2.

Table 2 The impedance matching performance of CIPs at different ball milling time

Milling time/ h	D of real part	D of imaginary part	Peak point of real part / GHz	Frequency of imaginary part equal 0/ GHz
0	7.8	17.8	10.5	11
4	9.5	18.2	8	8
6	9.3	18.6	7.2	7.1
8	11.1	18.9	4.2	4.2
10	11.3	19.1	4.9	5
12	10.9	18.8	5.3	--

Two conclusions can be drawn by Table 2: firstly, as CIPs deformation rate increased, its impedance matching real part and imaginary part gradually decreased. After 8 h milling, the flake shape CIPs has the maximum deformation rate, therefore impedance matching of it was worst performance. Secondly, with the milling time increased, the best match frequency range to free space were gradually shift to low frequency. The reason is after ball milling the permittivity significantly increased and it was not sensitive to varies with frequency[11], but the permeability increased only in low frequency, so appeared the above phenomenon.

Fig. 5 shows the frequency dependences of attenuation constant *a* for CIPs/paraffin composites with different milling time. As seen from the figure, the value of *a* ascend with frequency in 0.5-18 GHz, the result indicates that the CIPs/paraffin composites show better microwave absorption properties in higher frequency range. Besides, as the milling time increased, CIPs has a bigger *a* in the whole frequency range, indicating the more excellent attenuation and electromagnetic wave absorption.

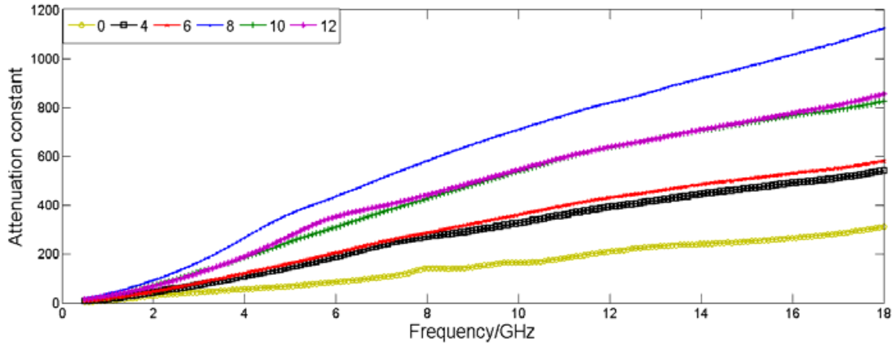


Fig. 5 The decay constant curves of CIPs at different ball milling time

Fig. 6 show the reflectivity of CIPs with different milling time at 2 mm in the frequency range of 0.5-18 GHz. The reflectivity and others of the samples are statistically listed in Table 3.

Table 3 Reflectivity of CIPs at different ball milling time

Milling time/ h	Absorbing peak/ dB	Peak point/ GHz	-10dB bandwidth/ GHz	Covering frequency domain/ GHz
0	-21.5	11.3	8.5-14	5.5
4	-22	8	6-10	4
6	-26	7.2	5.5-9	3.5
8	-17	4.2	3.2-5.5	2.3
10	-20	5	3.8-6.2	2.4
12	-17	5.7	4-7.2	3.2

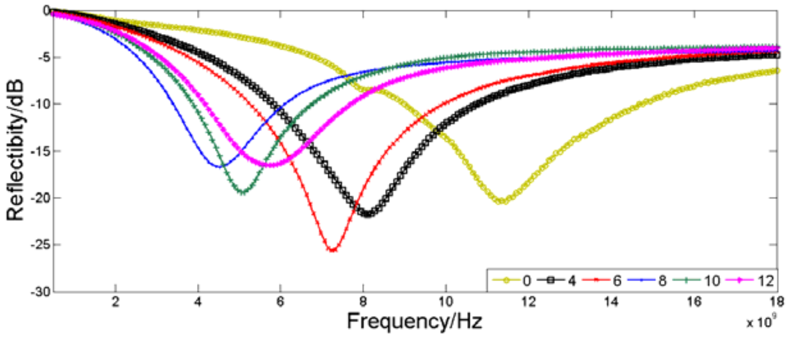


Fig. 6 Reflectivity curves of CIPs at different ball milling time

As shown in Fig. 6 and Table 3, the reflectivity of samples all appeared single peak, and the bigger samples' deformation rate the better absorbing property of low frequency. Peak point changes from 11.2 GHz of raw CIPs to 4.2 GHz after 8 h ball milling, however, the value of reflectivity descend of CIPs with different milling time, from -26 dB to -17 dB, and the length is gradually descend, from 5.5 GHz to 2.3 GHz. The result may be interpreted by the following two factors:

(1) Because to be aqueezed and cold welding with the adjacent particles the deformation rate of CIPs is ascend, and particle size of raw CIPs exist variation range, so each samples' are non-continuous composites powders from small to large, thus forming a series of non-continuous absorbing units, and each unite corresponds to different matching frequency and attenuation, thereby it is better to ascend the low frequency absorbing property[12].

(2) The flaky CIPs have shape anisotropy and it cause higher permeability in low frequency. As we can see from Fig. 4 with the deformation rate ascend the match frequency shifted towards lower frequency range, so the CIPs after 8 h ball milling has the lowest peak point and absorption intensity.

Conclusions

1) By high-energy ball milling method can effectively change spherical CIPs particles into a flaky shape, and with increase the milling time the deformation rate of CIPs gradually ascend, and after milled 8 h achieve the maximum. If the milling time longer than 8 h, the CIPs particles were crushed, so the deformation rate and performance of absorbing get worse.

(2) The flaky CIPs structure having a stronger anisotropic field, at low frequency (2-8 GHz) the permeability has been significantly improved, and the permittivity at 2-18 GHz significantly increased because it doesn't has dispersion characteristic.

(3) After ball milling the CIPs low frequency matching performance is increased, but the match strength is descend; with the deformation rate of CIPs increased the attenuation ability ascend; The CIPs with the ball milling time of 8 h at 300 r/min has the best shape and excellent microwave absorption properties in low frequency, with the minimum reflectivity reaching to -17 dB at 4.2 GHz. The minimum reflectivity of CIPs achieve can reach to -26 dB at 7.2 GHz when the ball milling time is 6 h.

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