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Electromagnetic absorbing property of the flaky carbonyl iron particles by chemical corrosion process

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ABSTRACT

The flaky carbonyl iron particles (CIPs) were prepared using a milling process at the first step, then the chemical corrosion process was done to optimize the particle shape. The particle morphology was characterized by the scanning electron microscopy, the static magnetic property was evaluated on a vibrating sample magnetometer and X-ray diffraction (XRD) patterns were done to analyze the particle crystal grain structure. The complex permittivity and permeability were measured using a vector network analyzer in the frequency range of 2–18 GHz and the reflection loss (RL) was calculated. The results showed that the saturation magnetization value of the CIPs decreased as the CIPs was corroded to the small flakes in chemical corrosion process. The diffraction peaks of the single α-Fe existed in the XRD pattern of CIPs, and the characteristic peaks was more obvious and the intensity of the diffraction pattern was lower by corrosion. The permittivity and the permeability of the corroded milling CIPs was a little larger than the milling CIPs, it was due to the larger aspect ratio based on the fitting calculation process. At thickness 0.6 mm and 0.8 mm, the corroded milling CIPs composite had the better absorbing property than the other two samples. The frequency band (RL < -5 dB) could be widened to 8.96–18 GHz at 0.6 mm and 5.92–18 GHz at 0.8 mm, and RL less than -8 dB began to exist in 8.96–14.72 GHz at 0.8 mm.

1. Introduction

Radar absorbing materials (RAM) have been widely used in the military applications and the civil aspects such as the stealth coatings, the absorbing patch on the phone, et al. [1–4]. Recently, carbonyl iron particles (CIPs) are widely used due to the micrometer size, the large value of the saturation magnetization and the high Snoek's limit at gigahertz frequency. As CIPs were shaped to the flakes, the existing easy-plane anisotropy supports a solution on exceeding the conventional Snoek's limit [5,6]. The parameters μ_s and f_r for the easy-plane anisotropy material can be obtained [7–9]: $(\mu_s - 1)f_r = \gamma M_s\sqrt{H_{ha}/H_{ea}}/(3\pi)$, where H_{ha} and H_{ea} denote the effective anisotropy field when the magnetization deviates from the easy axis in the hard plane and in the easy plane respectively, γ denotes the gyromagnetic ratio and M_s is the saturation magnetization, μ_s is the static permeability and f_r is the resonance frequency, the left value $(\mu_s - 1)f_r$ would be larger than the common Snoek's limit $\gamma M_s/(3\pi)$. Therefore, the permeability of composites added the same volume content flaky CIPs would increase, the macroscopic phenomena could be observed, including the reduction of the eddy current loss, the orientation of the magnetic moment and the space-charge polarization.

The common mechanical milling process was considered as an economic process on changing the spherical shape into the flaky shape. Previous researches had shown that the thin flaky CIPs could be obtained using the high speeding milling on the spherical powders [10–12]. While using the optimized milling process could get the flaky particle of the desired particle size, such as the two-step milling process on the CIPs (including the high speeding milling for a short time and the low speeding milling for a long time). The flaky shape and size were important factors of the absorbing property, the previous study showed that the variable milling process was proposed to control the milled Fe alloys particle size and shape [12], the two step milling process could be also suitable on changing the flake size. However, the milling process was oftenly a energy-cost process, how to optimize the milling process and make full use of the milling process on fabricating the flaky CIPs could be considered as a promising research field for the excellent absorbing particles.

This paper proposed a combination process of the milling process and the chemical corrosion process to fabricate the flaky CIPs. The high speeding milling process for a short time was used to prepare the flaky particle, then the chemical corrosion process was used to optimize the flaky shape to improve the absorbing

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property. First the flaky CIPs were fabricated using the high energy milling process. Secondly, a typical content of acid was used to oxide the CIPs to change the flaky shape. Finally the complex permittivity and permeability of CIPs composites were tested, and the microwave absorbing property of the CIPs/rubber composite was analyzed by simulating the RL in an application frequency.

2. Material and methods

2.1. High energy milling on the CIPs

Raw commercial spherical CIPs were supplied by Shanxi Xinghua Powder Co. Ltd., China. The CIPs powders were introduced to a zirconia jar, and then a suitable analytically n-hexane, ZrO_2 milling balls and stearic acid were added. The mass ratios of zirconia ball, CIPs, n-hexane and stearic acid were 20:1:1:0.02. The ZrO_2 milling balls included three different diameters, 20 mm, 8 mm and 5 mm, the number of the three balls in one zirconia jar was 2, 50, and 500 respectively. The stearic acid, milling balls, n-hexane and mixed powders were sealed together in the zirconia jar, considering the n-hexane had the de-oxidation effect and the CIPs oxidation could be neglected, it was not necessary to remove the atmosphere. The zirconia jar was fixed in the steel vial which was assembled to the SP2 planetary ball milling machine. As the milling time 4 h was selected, the zirconia jar rotated with the high velocity 500 rpm. After the milling process, the powders were sieved by a permanent magnet, washed using the ethanol to remove the stearic acid unbonded to the flaky CIPs, and then drilled in a baking oven.

2.2. Chemical corrosion process on the flaky particles

For the surface treatment of the flakes, a 98.3% weight content sulfuric acid H_2SO_4 solution was used. CIPs with weight 30 g were immersed in the deionized water and heated to 50 °C for 30 min. The solution was diluted to the dilute sulfuric acid, the substance amount decreased from 18.4 mol/L to 0.1–0.8 mol/L. The substance amount of the sulfuric acid was 1/5 relative to the CIPs (about 0.54 mol). Then the dilute sulfuric acid was gradually added to the solution added the CIPs, and mechanical stirring process was necessary. As the chemical reaction finished, the CIPs was sieved by a permanent magnet, washed using the ethanol to remove the water and avoid the flaky CIPs oxidation, finally the reacted CIPs could be heated in a baking oven at 120 °C for 24 h.

2.3. Materials preparation and measurement

Methyl vinyl Silicone rubber was used as matrix and 2, 5-dimethyl hexane was used as the vulcanized assistant, both were supplied by LaiZhou Jintai Silicon Industry Co. Ltd., China. Samples filled with the three kinds of CIPs with the volume content of 40% were fabricated respectively. The silicone rubber and absorbents were mixed in a two-roll mixer for 15–30 min. The particle was mixed into the silicone rubber with the uniform dispersion, for the roll-mixer provided a shear force in the mixing process which could overcome the intermolecular van der Waals force and the particle aggregation could be avoided [13,14]. The testing samples for EM parameters measurement were modeled to a toroidal shape with outer diameter 7.0 mm, inner diameter 3.04 mm and thickness 2 mm. All the samples were vulcanized into pieces at 180 °C under a pressure 10 MPa for 5 min.

The morphology of the composites was observed by scanning electron microscopy (SEM CamScan CS3400) to evaluate the dispersion state and microstructure of CIPs. The static magnetic property was then evaluated on a vibrating sample magnetometer (VSM, JDM-13), and the field reached up to $1.5*10^4$ Oe. The phase of powders was estimated by an X-ray diffractometer (D/MX 2200) using Cu K-radiation (wavelength $\lambda=0.154$ nm), and the scan step size was 0.02 deg/s with 50 steps per degree. The effective complex permittivity and permeability of the RAM were measured using the AV3627 vector network analyzer in the frequency range of 2–18 GHz. Then The RL (the same meaning of the reflection coefficient) of the absorber (defined as the ratio of the reflected power to the incident power by testing the absorbers backed by a perfect electronic conductor) could be calculated. For a single-layer absorbing material, the RL of the absorber is given by [15],

$$R = 20 \lg\left|(Z_{in} - 1)/(Z_{in} + 1)\right| \quad (1)$$

where, Z_{in} is the normalized input impedance of the absorbing material, $Z_{in} = \sqrt{\mu_r/\varepsilon_r}\tanh(2\pi dj\sqrt{\mu_r\cdot\varepsilon_r}/\lambda_0)$. ε_r and μ_r are the relative complex permittivity and complex permeability of the absorber respectively, λ is the wavelength, and d is the thickness of the absorbing composites.

3. Results and discussion

3.1. Characteristics of the particles

Fig. 1 shows the morphology of the three type CIPs. It could be obtained that the commercial CIPs was the spherical shape, the milled particles and the corroded particles were of the flaky shape. The particle size of the samples was analyzed using the microscopic statistical method. It could be obtained that the average diameter of spherical CIPs was 3.1 μm. As the particle was milled, the obtained flaky CIPs had the average diameter about 5.2 μm, a little larger than the spherical particle size. While as the flaky particle was corroded the particle size decreased and the average diameter was about 4.3 μm. It could be concluded that the milling process was effective on changing the particle to the flakes. The corrosion process began to happen on the particle surface on the diameter plane. As the CIPs were gradually corroded along the center direction, the edge thickness could decrease in the diameter plane. As a result, the flaky shape could be enhanced after the corrosion process.

The hysteresis loop curves under the applied field of the three type CIPs are shown in Fig. 2. It showed that the loops curves had the typical characteristics of the soft magnetic particles, and the saturation magnetization (Ms) of the three particles was 200.34 emu/g, 195.75 emu/g and 195.02 emu/g respectively, and the Ms value of the CIPs was consistent with the results of other researches [7–9]. The Ms value of the flaky CIPs was decreased as the CIPs was changed to the flakes, but it was not much less than the value of spherical CIPs. It also indicated that the crystallization structure maybe change in the milling process, and the detailed result could be shown in the XRD result.

Fig. 3 shows the X-ray diffraction patterns of the spherical CIPs and the milled flaky CIPs. The diffraction peaks of the single α-Fe existed and the strength of the peaks is obvious. In XRD spectrum of the CIPs the peak at $2\theta = 44.5°$ is the (1 1 0) plane, and the peak at $2\theta = 64.7°$ is the (2 0 0) plane. The XRD spectrum for the CIPs powder indicated the reflections corresponding to the distinct body-centered cubic (BCC) Fe metals. In addition, it was obtained that the characteristic peaks was broad and the intensity of the diffraction pattern was lower as the milling process was done. It indicated that the particle characteristics can be not only influenced by the milling parameters, but also by the crystallite size according to the Scherrer's formula [13]. During the mechanical milling process, CIPs powders adhered on the ZrO_2 balls or vial, collision and milling occurred between the balls and the inner wall