Journal of Alloys and Compounds 676 (2016) 251–259

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Two-step milling on the carbonyl iron particles and optimizing on the composite absorption

Yonggang Xu [a, *], Liming Yuan [a], Xiaobing Wang [a], Deyuan Zhang [b]

[a] Science and Technology on Electromagnetic Scattering Laboratory, Shanghai 200438, China
[b] Bionic and Micro/Nano/Bio Manufacturing Technology Research Center, School of Mechanical Engineering and Automation, Beihang University, Beijing 100191, China

ARTICLE INFO

Article history:
Received 13 January 2016
Received in revised form
14 March 2016
Accepted 23 March 2016
Available online 25 March 2016

Keywords:
Composite material
Metals and alloys
Mechanochemical
Magnetic measurements

ABSTRACT

The flaky carbonyl iron particles (CIPs) were prepared using a two-step milling process. The surface 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. Then Hermite interpolation based on the calculated scattering parameters of the tested composite was used to derive the permittivity and permeability of the composite with random volume content. The results showed that the saturation magnetization value of the flaky CIPs decreased as the CIPs was changed to the flakes by high and low speeding milling. The diffraction peaks of the single α-Fe existed in the XRD pattern of CIPs, and the characteristic peaks was broad and the intensity of the diffraction pattern was lower as the high-speeding milling time increased. The sample H2L20 had the largest particle size, the average diameter was 8.64 μm, the thickness was 0.59 μm according to the fitted aspect ratio 14.65. The derived permittivity and permeability using the Hermite interpolation was accurate compared with the tested result, the deviation was about 0.39 + j0.45 and 2.5 + j0.51. Finally, the genetic algorithm was used to optimize the thickness of the CIPs composite of a wide absorbing band of 8–18 GHz. The optimized reflection loss (RL) result showed that the absorbing composites with thickness 1.47 mm had an excellent absorbing property (RL < −10 dB) in 8–18 GHz.

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. [1–3]. 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. The saturation magnetization and the Snoek's limit could be described by the below equation [4,5]: $(\mu_s - 1)f_r = \gamma M_s/(3\pi)$, 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. Both μ_s and f_r could not be increased at the same time, therefore, the spherical CIPs had a limitation in fabricating excellent absorbing materials with thin thickness in the wide frequency. For example, the reflection loss (RL) of composites added 55 vol% CIPs just reached to −3 dB at 2 GHz with 1 mm thickness [6], −5 dB at 4 GHz with 1 mm thickness as 93 wt% CIPs added [7]. As CIPs were shaped to the flakes, the existing easy-plane anisotropy supports a solution on exceeding the Snoek's limit. The parameters μ_s and f_r for the easy-plane anisotropy material can be obtained [8,9]: $(\mu_s - 1)f_r = \gamma M_s\sqrt{H_{ha}/H_{ea}}/(3\pi)$, 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. As a result, the permeability of composites added the same volume content flaky CIPs would increase. The results are attributed to the reduction of the eddy current loss, the orientation of the magnetic moment and the space-charge polarization with the shape change from spherical powders to thin flake particles [10]. The mechanical milling process became an economic process on converting the spherical shape to the flaky shape. Previous research had shown that thin the flaky CIPs could be obtained by high speeding milling

* Corresponding author.
E-mail address: xuyonggang221@163.com (Y. Xu).

http://dx.doi.org/10.1016/j.jallcom.2016.03.192
0925-8388/

on the spherical powders [6,10,11], and the milling process was the one-step milling type. The flaky shape was still an important factor of the absorbing property, the previous study showed that the two-step milling process was proposed to control the milled FeSi particle size and shape [12], although the FeSi particle size was much larger than the CIPs, the milling process could be a potential way on changed the flake size. So, using the two-step milling process on the CIPs could be an effective way of enhancing the particle magnetic property. In addition, as the particles were added to the absorbing composite, the absorbing property of the single-layer absorber was limited due to the simple dispersion of the particles, while the multi-layer absorber could be an excellent structure on improving the absorbing property [13,14]. The genetic algorithm might be an effective way on designing the multi-layer absorber, the CIPs/rubber absorbing composite with high absorption ratio could be obtained after the optimization process. Although the layer thickness and the layer number could be established, the volume content in the absorbing layer was only referring to the measured ones, the random volume content of each layer should be considered to improve the optimized result.

The present work is to investigate the microwave absorbing property of composites filled with two-step milled CIPs. First the flaky CIPs were fabricated using the two-step milling process. Secondly, the complex permittivity and permeability of CIPs composites were analyzed, and the optimized two-step milling process was selected. Finally the microwave absorbing property of the CIPs/rubber composite was optimized by simulating the RL in an application frequency using the genetic algorithm.

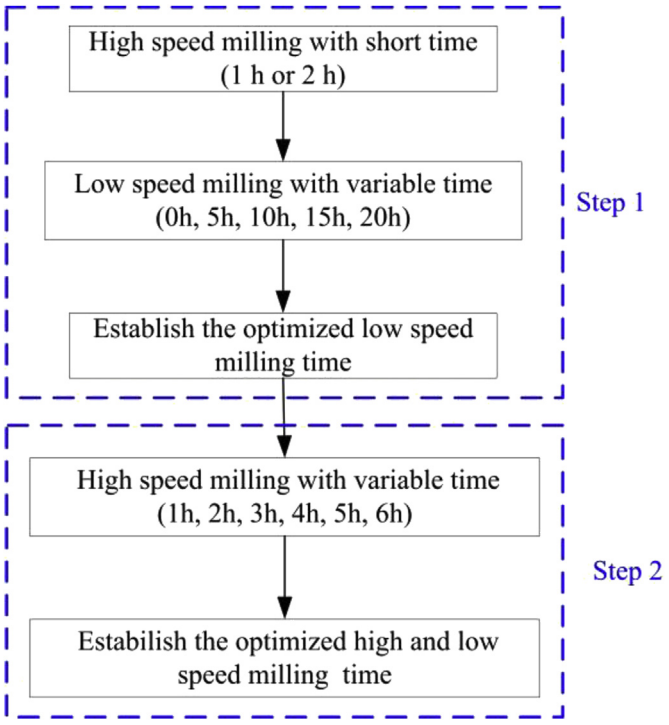

Fig. 1. The optimized process on the milling time using two steps.

2. Material and methods

2.1. Two-step milling on the CIPs

The two-step milling on the CIPs included two parts, the first one was the high speed milling process on the particles, and the second one was the low speed milling process on the particles. 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 deoxidation 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. The main axis in the planetary ball milling machine rotated with the velocity ratio of 100: 400 to the zirconia jar on its axis. As the milling time was selected, the zirconia jar was rotated at the high or low velocity respectively. After the milling process, the powders were sieved by a permanent magnet, washed using the ethanol to remove the stearic acid unbounded to the flaky CIPs, and then drilled in a baking oven.

The paper focused on the optimized milling time in the two-step milling process. The high speed milling velocity was set 500 r/min and the low speed milling velocity was selected as 250 r/min. The high speed milling time was 1 h, 2 h, 3 h, 4 h 5 h or 6 h, and the low speed milling time was 0 h, 5 h, 10 h, 15 h or 20 h. The optimizing milling process on the CIPs was designed as shown in Fig. 1. The time of the high speed milling and low speeding milling process was optimized in two steps. The first step was to optimize the low speed milling time, two high speeding milling times (1 h and 2 h) were selected in order to decrease the optimized numbers, the particles were milled with velocity 500 r/min for 1 h or 2 h respectively, then the milled particles was milled with velocity 250 r/min for 0 h, 5 h, 10 h, 15 h and 20 h. As a result, ten samples (*HiLj*, $i = 1$ or 2, and $j = 0, 5, 10, 15$ or 20, the symbol *HiLj* denotes the particle which was milled with high milling time i h and low milling time j h, the other symbol could be explained similarly) could be obtained, and the ten kind particles were mixed into the rubber with volume content 50% respectively, the electromagnetic measurement sample could be fabricated. The permeability was selected to evaluate the optimized milling time, the sample with the high imaginary part of permeability could be considered as the optimized particles, then the optimized low-speeding milling time was established. The second step was to optimize the high speed milling time, as the optimized low milling time was set in the first step, the high speed milling time was selected as 1 h, 2 h, 3 h, 4 h, 5 h or 6 h. Then several samples could be obtained and fabricated to evaluate the optimized high speed milling time. Finally, the optimized high and low speed milling time could be selected, and the optimized particle could be established, and the absorbing samples with variable volume content could be calculate to optimize the multilayer absorbing patch.

2.2. 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. Raw commercial flaky CIPs were supplied by Shanxi Xinghua Powder Co. Ltd, China. The average diameter of spherical CIPs was 3 μm. Samples filled with the single spherical or flaky CIPs with the volume content from 5% to 50% 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 [15,16]. The testing samples for EM parameters