Applied Surface Science 270 (2013) 432–438

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis of hollow carbonyl iron microspheres via pitting corrosion method and their microwave absorption properties

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ARTICLE INFO

Article history:
Received 20 November 2012
Accepted 8 January 2013
Available online 14 January 2013

Keywords:
Carbonyl iron
Hollow microspheres
Pitting corrosion
Microwave absorption

ABSTRACT

In this paper, we report a new method to prepare hollow carbonyl iron microspheres, which is called pitting corrosion method. The comparison of the morphology, specific surface area and apparent density of the initial and pitting corroded carbonyl iron microspheres demonstrate that the pitting corroded carbonyl iron has a hollow structure. The pitting corrosion process is uncovered through the concentration change of ferrous ion in the reaction solution and the TEM images with different pitting corrosion time. The formation mechanism of hollow microspheres via pitting corrosion is analyzed. Furthermore, this pitting corrosion method can also be used to prepare other hollow metal particles, such as Ni, Co, and Cu particles. The electromagnetic parameters of the samples before and after pitting corrosion are measured. The calculated reflection loss of the pitting corroded sample for single layer of 0.5 mm or 1.0 mm thickness at 2–18 GHz is much better than that of the initial one. The mechanism of the improvement of the microwave absorption properties is discussed.

1. Introduction

In recent years, hollow micro/nanostructures have attracted increasing interest owing to their potential applications in catalysis [1,2], drug delivery [3,4], bioencapsulation [5,6], medical diagnostics [7] and sensor [8,9]. As one type of important hollow materials, hollow metal micro/nanostructures have been extensively investigated in the past several years [10–13]. Template assisted method is usually used to prepare hollow metals, and different materials such as silica [14], polystyrene latex [15], and selenium [16] have been used as templates to direct the formation of hollow metals. Galvanic-replacement reaction is another effective method to prepare hollow metal micro/nanostructures, which has been used to synthesize some noble metals such as Ag nanocages [17], hollow Au octahedral [18] and hollow Pt nanospheres [19]. In this method, the salt of a more noble metal (B) is reduced with preformed micro/nanocrystals of a less noble metal (A), resulting in deposition of B on the surface of A. After complete consumption of A, hollow structure of metal B can be obtained. Although the great progress in control synthesis of hollow metals have been made, it is still necessary to develop simpler and more suitable for large-scale production methods for the synthesis of hollow metal micro/nanostructures.

The fast advancement of gigahertz (GHz) electronic systems for civil and military applications has attracted a growing interest in absorbers of microwave [20–22]. The ideal microwave absorber requires thin coating, low density, broad absorbing band and strong absorption [23]. Carbonyl iron, a typical magnetic microwave absorbing material, is one of principal constituents of microwave absorber [24–26]. However, the density and absorption properties of the commercial carbonyl iron restrict its use in the applications requiring thin and light absorber. Hollow structures can benefit the lightweight of materials, and there are several studies about a kind of hollow core–shell composite materials, hollow glass microspheres plated with different magnetic microwave absorbing materials [23,27–29]. In those cases, the hollow structures rely on the hollow glass microspheres that occupy specific weight and have no direct absorption. It can be expected that hollow mono-component carbonyl iron particles have advantages, such as lighter weight than solid particles and stronger absorption than the hollow core–shell composite materials mentioned above. However, to the best of our knowledge, there are only a few reports on the synthesis of hollow iron particles [30]. Therefore, there is a challenge to synthesize hollow iron particles.

Pitting corrosion is a form of localized corrosion that leads to the creation of small holes in metal. This kind of corrosion is extremely insidious to be avoided in metal industry, as it causes little loss of material with small effect on its surface, while it damages the deep structures of the metal. Inspired by the pitting corrosion mechanism, herein we report a method to synthesize hollow carbonyl iron microspheres. The hollow structures of the pitting corroded

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http://dx.doi.org/10.1016/j.apsusc.2013.01.044

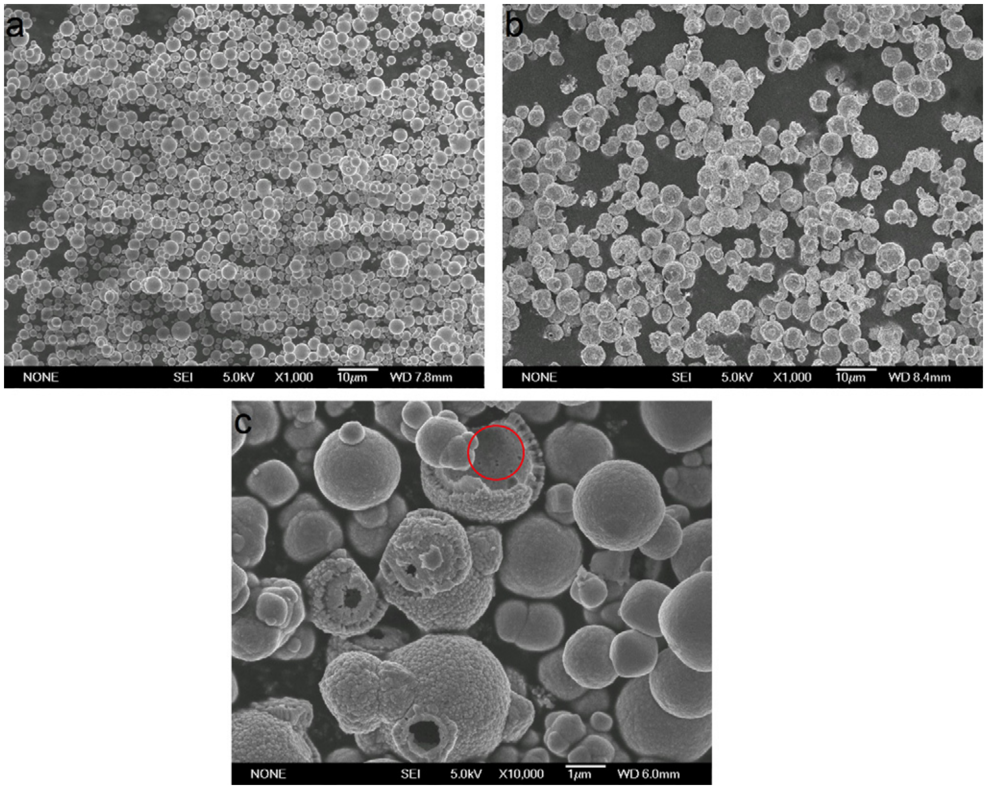

Fig. 1. SEM image of the samples: (a) the initial carbonyl iron; (b) and (c) the pitting corroded carbonyl iron.

carbonyl iron microspheres were confirmed by several measurements. Furthermore, we prepared other hollow metal particles, including Ni, Co, and Cu particles, by using the pitting corrosion method. The microwave absorption properties of the pitting corroded are more excellent than those of the initial carbonyl iron microspheres and the mechanism of the improvement of the microwave absorption properties was discussed.

2. Experimental

The raw material was sphere-shaped carbonyl iron powder, purchased from Tianyi Ultra-fine Metal Powder Co. Ltd., Jiangsu province, China. In a typical synthesis of hollow carbonyl iron microspheres, the initial carbonyl iron microspheres (0.4 g) were dispersed in 40 mL ferric chloride ethylene glycerol (EG) solution (0.18 M) (the solvent can also be water or ethanol), then stirred at room temperature for 10 min. After the reaction, the powder sample was filtered off, rinsed with dilute nitric acid (2 wt%), and then with water and ethanol, and dried in a vacuum furnace.

The size and morphology of the samples were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and transmission electron microscope (TEM, H-800). The BET surface area of the samples was determined by N_2 adsorption–desorption isotherm measurement at 77 K (Surface area analyzer, SA 3100). The apparent density of the samples was measured with a Hall flowmeter.

In order to measure the electromagnetic parameters, the samples were homogenously dispersed in paraffin with a mass fraction of 80% (powder) and then formed into a cylindrical sample (7 mm in outer diameter and 3 mm in inner diameter) with a coaxial mould, respectively. The effective complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$) of these samples in the frequency range from 2 to 18 GHz were measured using an HP-8722ES network analyzer. The reflection loss was calculated according to the transmission line theory [22], expressed as follows

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

Z_{in} is the normalized input impedance of a metal-backed microwave absorbing layer.

$$Z_{in} = \sqrt{\frac{\mu_x}{\varepsilon_x}}\tanh\left[j\left(\frac{2\pi fd}{c}\right)\sqrt{\mu_x\varepsilon_x}\right] \quad (2)$$

where f is the frequency of the electromagnetic wave, d is the thickness of the absorber, and c is the velocity of light.

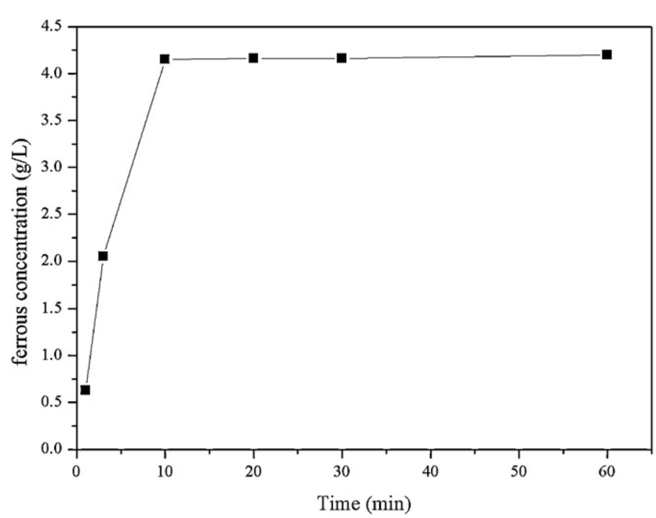

Fig. 2. Concentration changes of Fe^{2+} as the pitting corrosion time increase.