Journal of Magnetism and Magnetic Materials 394 (2015) 266–273

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Magnesiothermic reduction of rice husk ash for electromagnetic wave adsorption

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A R T I C L E I N F O

Article history:
Received 3 October 2014
Received in revised form
7 January 2015
Accepted 27 June 2015
Available online 30 June 2015

Keywords:
Magnesiothermic reduction
Rice husk ash
Electromagnetic wave adsorption
Dielectric loss

A B S T R A C T

The increase in electromagnetic pollution due to the extensive exploitation of electromagnetic (EM) waves in modern technology creates correspondingly urgent need for developing effective EM wave absorbers. In this study, we carried out the magnesiothermic reduced the rice husk ash under different temperatures (400–800 °C) and investigated the electromagnetic wave adsorption of the products. The EM absorbing for all samples are mainly depend on the dielectric loss, which is ascribed to the carbon and silicon carbide content. RA samples (raw rice husk ashed in air and was magesiothermic reduced in different temperatures) exhibit poor dielectric properties, whereas RN samples (raw rice husk ashed in nitrogen and was magesiothermic reduced in different temperatures) with higher content of carbon and silicon carbide display considerable higher dielectric loss values and broader bandwidth for $RL < -5$ dB and -10 dB. For RN samples, the maximum bandwidth for -5 dB and -10 dB decrease with carbon contents, while the optimum thickness decrease with increasing SiC content. The optimum thickness of RN400–800 for EM absorption is 1.5–2.0 mm, with maximum RL of between -28.9 and -68.4 dB, bandwidth of 6.7–13 GHz for $RL < -5$ dB and 3.2–6.2 GHz for $RL < -10$ dB. The magnesiothermic reduction will enhance the potential application of rice husk ash in EM wave absorption and the samples benefited from low bulk density and low thickness. With the advantages of light-weight, high EM wave absorption, low cost, RN400–800 could be promising candidates for light-weight EM wave absorption materials over many conventional EM wave absorbers.

1. Introduction

Due to the expanded utilization of electromagnetic (EM) wave in various fields, one of the most challenging problems is EM interference and pollution, which could cause disturbance on the devices and systems and even threaten the health of animals and human beings [1–4]. In response to the need for protecting human beings from EM wave irradiation and preventing the military equipment from being detected by radar waves, the development of effective EM wave absorption materials have attracted a world of attention. An ideal EM wave absorber is necessary to have light-weight, low density, strong absorption, broad bandwidth for EM wave absorption and multi-functionality on the basis of thin matching thickness [5–7].

Electromagnetic wave absorbers can be basically classified into two categories: magnetic and dielectric absorbing materials by loss characteristics. Traditional magnetic EM wave absorbers such as ferrite and metallic powders [8–11], exhibited the strong absorption and wide absorbing band-width, but are restricted by their large density and low high-temperature resistant [12,13]. Compared to magnetic EM wave absorbers, conventional dielectric EM wave absorbers include conductive polymers [14,15], carbon [16], and silicon carbide [17,18], are much more light weight and high temperature stability, but also exhibit inevitable disadvantages of poor adsorption of EM wave and narrow absorb bandwidth [6]. Many studies also reported composite materials of EM absorbing [19,20], which aim to balance the advantages and disadvantages of magnetic materials and dielectric materials. However, they often involved complicated synthesis processes and high cost. Therefore, researchers are still urged to fabricate ideal EM wave absorber by economical and uncomplicated approach.

Rice husk as one of the byproducts of rice and was treated as an abundantly agriculture waste in most rice producing countries. The most common disposal of rice husk in rural area is burning at open field, causing environmental pollution. Therefore, many efforts have been devoted to find value addition to rice husk and exploit their application in many fields. For its high content of silica, rice husk ash can be used as a possible substitute for condensed silica fume in concrete [21], a source for silica in cement manufacture [22], and fillers in polymers to enhance the

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http://dx.doi.org/10.1016/j.jmmm.2015.06.074

properties of mechanical, thermal and chemical [23]. With unique and natural nano-porous structure and high carbon content, rice husk can also be an important starting material for the synthesis of absorbent and catalyst [24–26]. In addition, rice husk also has the potential to be used as an alternative material for the EM wave absorber, which has been investigated by many researches [27–29]. In our previous study, we have investigated the EM parameters of rice husk ash and especially their relationship with the physic-chemical characteristics of rice husk ash [30].

Recently, great efforts have been focused on synthesizing porous silicon from rice husk by magnesiothermic reduction [31]. Magnesiothermic reduction is a promising technique by using low-temperature magnesium vapor to convert silica to silicon or SiC without losing structure regularity. The overall reaction can be described as SiO_2 (s)+2Mg (g)→2MgO (s)+Si (s). To date many attempts have been devoted to the fabrication of nanostructured silicon anodes for lithium ion batteries due to its small size, porous nature and unparalleled theoretical capacity [32–34]. The magnesiothermic reduction process is also used for transformation of SiO_2/C nanocomposite to SiC, the overall reaction can be described as $SiO_2+C+2Mg\rightarrow SiC+2MgO$ [34]. Silicon carbide is a wide gap semiconductor possesses many advantages such as high temperature stability, high thermal conductibity, outstanding chemical and radiation resistance and more, which are suited for high-temperature, high-power, high-frequency, and high-radiation environments [35]. On the other hand, SiC is also a good electromagnetic wave absorbing material with wide range of electrical resistivity [36]. In the past decades, many researches have been focused on investigating the absorption properties of SiC nanopowders, SiC fibers and SiC nanowaires [37–39], and also utilized as an auxiliary absorbent with other materials or doped with trace elements to enhance the absorption capacity [40–42]. Nevertheless, as per our knowledge, there are no works have been done to investigate the EM wave properties of porous silicon and silicon/carbon from rice husk ash though magnesiothermic reduction.

In this paper, rice husk was ashed at 700 °C in air and nitrogen atmosphere, respectively to prepare two kinds of rice husk ash: RHA (ashed in air) and RHN (ashed in nitrogen). The magnesiothermic reduction was conducted at different temperature from 400 °C to 800 °C using RHA and RHN to obtain RA400–800 and RN400–800, respectively. The complex permittivity and permeability values indicate that magnesiothermic reduction for rice husk ash is a promising method to utilize agriculture waste to prepare high EM adsorption, light-weight and porous structure EM wave absorber.

2. Experimental

2.1. Materials

Rice husk was obtained from Quzhou, Zhejiang province, and was washed by deionized water to remove the impurities and dried at 60 °C for 8 h before usage. Its average chemical composition was 79.6% organic substances, 19.02% SiO_2, 0.7% K_2O, 0.28% CaO, 0.14% MgO, 0.13% P_2O_5, 0.06% S, 0.04% Cl, and 0.03% others. Magnesium was obtained from Aladdin Reagents Company (Shanghai, China). HCl (36–38%) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were used without further purification.

2.2. Magnesiothermic treatment of rice Husk

In a typical procedure, a certain amount of rice husk was calcined in a muffle furnace at 700 °C for 3 h in air and nitrogen atmosphere, respectively. The heating rate was 10 °C min^{-1}. After cooled to room temperature, two kinds of rice husk ash samples were obtained (RA and RN). For reduction process, 3 g rice husk ash mixed with 3 g magnesium with the mass ratio was 1:1. The mixture was moved to the muffle furnace at 400 °C, 500 °C, 600 °C, 700 °C and 800 °C for 12 h in argon atmosphere, respectively. After Mg reduction, rice husk silicon/magnesia mixture was immersed in 5 M HCl solution at room temperature to remove magnesia and MgO. The obtained samples were named as RA400–RA800 and RN400–RN800 by using RHA and RHN as starting materials, respectively.

2.3. Characterizations

The phase purity and crystal structure of the samples were determined by a D/max 2550 X-ray diffractometer (XRD) (Rigaku, Japan) with Cu Kα radiation ($\lambda=0.15406$ nm) at a scan rate of 0.02° s^{-1}. The operation voltage and current were maintained at 36 kV and 34 mA, respectively. The surface morphologies were observed by 650 FEG Field Emission Scanning Electronic Microscope (Quanta, USA). Surface area and pore characteristics of the samples were measured by nitrogen adsorption and desorption at 77 K using a Coulter OMNISORP surface and pore analyzer. The EM parameters were examined by a HP8720ES vector network analyzer (Agilent, USA) using T/R coaxial line method at EM wave frequency of 2–18 GHz and thickness of 2 mm using paraffin as substrate. The filling rates were 30% for all measurements. The relative complex permittivity ($\varepsilon=\varepsilon'-j\varepsilon''$) and permeability ($\mu=\mu'/j\mu''$) were calculated from the measured *T*/*R* coefficients. The measurement errors are less than 10% when $\varepsilon''<15$. The resistivity values of RHA were determined by a KDY-1 four-probe resistivity meter with input current of 0.005 mA. Bulk densities of RHA were determined using the following method: a 50 mL cylinder was filled to a specified volume with samples had been dried in an oven at 80 °C overnight. The cylinder was tapped for at least 1–2 min to compact the samples, and then weighed. The bulk density was calculated as

$$\text{Bulk density}\ \left(\text{g cm}^{-3}\right)$$
$$=\text{mass of sample (g)/volume of packed sample}\left(\text{cm}^{3}\right). \qquad (1)$$

3. Results and discussion

3.1. XRD patterns

XRD analysis was performed to determine the phase and composition of the prepared samples. As shown in Fig. 1, all samples except RA800 exhibit a broad band at around $2\theta=22°$, which is the characteristic peak of amorphous silica. Because the melting point of magnesium is around 650 °C, the onset temperature for magnesiothermic reduction should be around 650 °C. Therefore, RA400, RA500, RN400 and RN500 remain essentially amorphous silica, while the RA600, RA700, RA800, RN700 and RN800 exhibit the peaks of silicon (PDF #27-1402), suggesting the amorphous silica was consumed in the reduction process and was converted to silicon. However, no silicon peak revealed in RN600, as opposed to the strong intensity lines of silicon in RA600, indicates that higher reduction temperature required for magnesium reduction of RN than that of RA samples. This phenomenon was attributed to the retention of carbon that blocked the reaction path of the magnesium reduction, which can also explain the intensities of silica peaks of RN600–800 are significantly lower than that of silica peaks of RA600–800. When 800 °C applied in this study, the peak of critobalite (PDF #39-1425) revealed in RA800, resulting