Journal of Analytical and Applied Pyrolysis 126 (2017) 201–208

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Influence of wastewater sludge pyrolysis char as dopants on the microstructure and electromagnetic wave absorbing properties of iron deficient Mn-Zn ferrite ($Zn_{0.75}Mn_{0.75}Fe_{1.5}O_4$) based on microwave induced sintering method

Feng Liu[a,b], Zhipeng Li[b,*], Yi Ding[c], Yu Tian[a,*]

[a] State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin, 150090, China
[b] School of Marine Science and Technology, Harbin Institute of Technology at Weihai, Weihai, 264209, China
[c] Marine College, Shandong University at Weihai, Weihai, 264209, China

ARTICLE INFO

Keywords:
Wastewater sludge pyrolysis char
$Zn_{0.75}Mn_{0.75}Fe_{1.5}O_4$ ferrite
Electromagnetic parameters
Electromagnetic wave absorbing properties

ABSTRACT

Iron deficient Mn-Zn ferrite was prepared by doping the microwave induced pyrolysis char of wastewater sludge. The effects of doping with different dosages of pyrolysis char on the crystallization phase, micromorphology, crystal microstructures, electromagnetic parameters and microwave absorbing properties were investigated. The iron deficient ferrite samples with microwave sintering at a temperature of 900 °C had a spinal structure, and the main crystallization phase was $Zn_{0.75}Mn_{0.75}Fe_{1.5}O_4$. The crystal grains with the dopants of 20 wt% were homogeneous, and the average grain size was about 36.80 nm. The crystal of ferrite with dopants of 20 wt% had a clear grain boundary, and the crystallinity degree reached 94.76%. Moreover, the electromagnetic parameters (permittivity and permeability) of $Zn_{0.75}Mn_{0.75}Fe_{1.5}O_4$ ferrites were changed due to the dopants improving the electromagnetic wave absorbing properties. The electromagnetic wave reflection loss of the $Zn_{0.75}Mn_{0.75}Fe_{1.5}O_4$ ferrite samples with the dopants of 20 wt% increased to −4.2 dB.

1. Introduction

Wastewater sludge is the inevitable product of wastewater treatment processes in the worldwide [1]. The sludge was rich in carbonaceous organic matters, pathogens, phytonutrients, heavy metals and mineral compositions, which dispersed in the wastewater and were concentrated through the wastewater treatment processes in sewage sludge [1]. Landfill treatment of the sewage sludge was the most commonly used method, but it would cause a series of potential environmental pollution accidents such as polluting groundwater and changing the soil physical and chemical properties [2]. Sludge composting was a way of resource utilization which can improve the organic matter and phytonutrients of soil. However, the sludge fertilizer contained toxic refractory organic and poisonous heavy metals, which could enrich in and transfer through the food chain will do great harm to human health if not appropriately controlled [3].

Thermal decomposition or incineration technique of sewage sludge is a pollution-free way of sludge reduction [4]. The conventional pyrolysis is usually conducted through thermal radiation in the reactor, which results in significant energy losses. However, the advantages of microwave induced pyrolysis were extremely effective and no energy loss. Microwave induced pyrolysis is referred to as dielectric heating, and the atoms or molecules comprising the dielectric exhibit a dipole movement, which generates friction and the electromagnetic energy is dissipated subsequently as heat [5,6]. The refractory organics in sewage sludge were oxidized thoroughly with temperatures above 800 °C, but the heavy metals were enriched in the pyrolysis char. The pyrolysis char (including fly ash), which contained some heavy metals and belonged to the hazardous waste, was difficult to degrade and would bring great harm to the environment and living things [7,8]. Usually, cement solidification process was used for treating the pyrolysis char, however, resource utilization of the pyrolysis char had been employed rarely due to the high-cost and sophisticated technologies.

Manganese-Zinc ferrites (Mn-Zn ferrites) as very important soft electromagnetic materials have been used extensively in civilian facilities [9]. The Mn-Zn ferrites with a spinel crystal structure could absorb and decay electromagnetic waves (EMW) energy by ferromagnetic resonance [10]. For improving the absorbing properties and optimizing

* Corresponding authors.
E-mail addresses: lizhipengcn@hit.edu.cn (Z. Li), hit_tianyu@163.com (Y. Tian).

http://dx.doi.org/10.1016/j.jaap.2017.06.007
Received 16 August 2016; Received in revised form 20 April 2017; Accepted 10 June 2017
Available online 12 June 2017

preparation conditions of ferrite, dopants including silicon dioxide, rare-earth elements and the other transition metal elements were employed in ferrites production [11]. Doping the silicon into the ferrite could improve the grain boundary resistance during the ferrite preparation. The silicon and calcium doped together into the ferrite could change the chemical properties of crystal boundary and decrease the sintering temperature; some rare earth elements or transition metals could affect the electromagnetic properties of ferrite due to their place in the crystal structure [12]. Nowadays, most researches focused on single or a few kinds of dopants in ferrite for improving the electromagnetic properties or optimizing the preparation conditions, however, dopants with complex mixture of more metallic elements had not been paid more attention.

The microwave induced pyrolysis char of wastewater sludge was a complex mixture contained silicon, calcium, aluminum, copper, iron and a small amount of rare earth elements. Doping the microwave induced pyrolysis char of wastewater sludge into the ferrite might improve the electromagnetic properties. Mn-Zn ferrite ($Zn_{0.5}Mn_{0.5}Fe_2O_4$ ferrite) was synthesized with microwave-induced pyrolysis char of sewage sludge as dopant had been reported in previous study [10]. A new phase of iron deficient ferrite ($Zn_{0.75}Mn_{0.75}Fe_{1.5}O_4$) had been formed, which was responsible for the acquisition of magnetic properties for the materials, and its content even determined the saturation magnetization values [13]. In this study, the effect of doping the microwave induced pyrolysis char of wastewater sludge on the new phase of iron deficient Mn-Zn ferrite ($Zn_{0.75}Mn_{0.75}Fe_{1.5}O_4$ ferrite) preparation was investigated. Meanwhile, the microwave induced crystallization and rapid thermal annealing process were utilized in the iron deficient Mn-Zn ferrites preparation. The iron deficient Mn-Zn ferrites were examined to obtain crystalline microstructure and absorbing EMW properties of ferrites. The reuse of wastewater sludge pyrolysis char for iron deficient Mn-Zn ferrites preparation could reduce the potential environment pollution of hazardous materials in the pyrolysis char.

2. Materials and methods

2.1. Preparation of microwave induced pyrolysis char

The preparation method of microwave induced pyrolysis char was similar to that described in previous study [10]. Microwave heating furnace with emitting frequencies near 2.45 gigahertz (GHz) was used for microwave induced heating experiment, which was consisted of a rectangular microwave cavity resonator, a magnetron for generating high power microwave pulse, a power continuous-adjustable control system to supply the output power within the range of 0.5 kW to 2.7 kW, a pyroelectricity infrared sensors system and a synchronous data acquisition system. The tar and gas were produced during the sewage sludge pyrolysis process passed through the tar products collection unit with an ice-water bath, and then the residual gas was fully absorbed by alcohol, and the gas was collected by reservoir bag finally. During microwave induced pyrolysis process, the preparation of pyrolysis char of sewage sludge was completed within about 15 min with 800 ~ 1500 W of microwave input power. It could be seen from previous study [10] that the silicon dioxide and metal oxides were the major constituents in the pyrolysis char, which were accounting for about 85% of the pyrolysis sludge char by weight.

The main chemical properties of pyrolysis sludge chars are given in Table 1. The pyrolysis experiments of wastewater sludge (50 g, moisture content 81.2 wt%) were carried out by microwave-assisted method and traditional method in an electric furnace. Solid char yields of wastewater sludge were different by microwave-induced pyrolysis and traditional pyrolysis method (in an electric furnace), and the weight yields of sludge char achieved were about 7.54 wt% and 10.38 wt%, respectively. It was suggested that the pyrolysis of sludge was more thoroughly by microwave-assisted method. The main components of pyrolysis sludge char produced by microwave assistant

Table 1
Components of pyrolysis sludge char analyses with microwave assistant and traditional method (in an electric furnace) (expressed as wt%).

Pyrolysis method	Si	Fe	Al	Mg	Ca	Mn	Zn	Pb	Cu	Ti
Microwave assistant	19.189 ± 2.765	6.038 ± 294	5.433 ± 0.864	1.141 ± 0.239	4.109 ± 0.188	0.163 ± 0.003	1.133 ± 0.021	0.014 ± 0.001	0.064 ± 0.002	0.027 ± 0.002
Traditional method	12.657 ± 3.031	3.294 ± 1.176	2.981 ± 0.545	0.588 ± 0.076	1.947 ± 0.085	0.074 ± 0.001	0.461 ± 0.001	0.006 ± 0.001	0.037 ± 0.001	0.012 ± 0.001
Pyrolysis method	Cd	Ba	Sr	Ce	K	Na	Hg	Cr	P	Cl
Microwave assistant	0.004 ± 0.001	0.193 ± 0.006	0.024 ± 0.002	0.032 ± 0.011	1.655 ± 0.024	0.651 ± 0.031	–	0.016 ± 0.004	3.628 ± 0.743	0.084 ± 0.027
Traditional method	–	0.082 ± 0.004	0.016 ± 0.003	0.018 ± 0.009	0.723 ± 0.008	0.346 ± 0.015	–	0.007 ± 0.002	2.021 ± 0.578	0.148 ± 0.034