Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 2013, 25(Suppl.) S27–S31
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Study on preparation and microwave absorption property of the core-nanoshell composite materials doped with La

Liqiu Wei[1], Ruxin Che[1,*], Yijun Jiang[2], Bing Yu[1]

1. College of Environmental and Chemical Engineering, Dalian Jiaotong University, Dalian 116028, China
2. School of Physics, Peking University, Beijing 100871, China

Abstract

Microwave absorbing material plays a great role in electromagnetic pollution controlling, electromagnetic interference shielding and stealth technology, etc. The core-nanoshell composite materials doped with La were prepared by a solid-state reaction method, which is applied to the electromagnetic wave absorption. The core is magnetic fly-ash hollow cenosphere, and the shell is the nanosized ferrite doped with La. The thermal decomposition process of the sample was investigated by thermogravimetry and differential thermal analysis. The morphology and components of the composite materials were investigated by the X-ray diffraction analysis, the microstructure was observed by scanning electron microscope and transmission electron microscope. The results of vibrating sample magnetometer analysis indicated that the exchange-coupling interaction happens between ferrite of magnetic fly-ash hollow cenosphere and nanosized ferrite coating, which caused outstanding magnetic properties. The microwave absorbing property of the sample was measured by reflectivity far field radar cross section of radar microwave absorbing material with vector network analyzer. The results indicated that the exchange-coupling interaction enhanced magnetic loss of composite materials. Therefore, in the frequency of 5 GHz, the reflection coefficient can achieve –24 dB. It is better than single material and is consistent with requirements of the microwave absorbing material at the low-frequency absorption.

Key words: magnetic fly-ash hollow cenosphere; La; core-nanoshell composite materials; magnetic properties

Introduction

Microwave absorbing material plays a great role in electromagnetic pollution controlling, electromagnetic interference shielding and stealth technology, etc. (Petrov and Gagulin, 2001). An ideal microwave absorbing material owns many advantages such as tiny thickness, low density, wide bandwidth and flexibility simultaneously. Therefore, it is eager to develop the high-performance microwave absorbing materials.

Rare earth magnetic alloys with abundant magnetic properties are concerned at present, due to the unique 4f electronic structure of rare earth. A large magnetic moment and magnetic moment of strong spin-orbit coupling and other characteristics determine the lower symmetry of its crystal structure. Magnetic electrons (4f electrons) lie in an inner shell layer, where spin orbit interaction and crystal field effects are strong. This kind of material has high magnetic moment, magnetic anisotropy, magnetostriction coefficient as well as magneto-optical effects; and it has low magnetic ordering transition temperature (called “four highs and one low”). The complex structure of magnetic ordering and other characteristics, especially in the formation of rare earth complexes with other elements, the abundant magnetic, electrical and optical properties will be reflected (Pan and Li, 1999; Wang et al., 2005). Among the many nano-materials, rare earth compound are well received because of their properties and the wide range of applications. The literature (Xu and Xiong, 2004) shows that, doped a certain rare earth to Fe (Mn) oxide can significantly improve the magnetic properties of the Fe (Mn) of oxide.

The magnetic fly-ash hollow cenosphere (MFHC) is a byproduct of thermal power plant. This is turning waste into treasure for the application of cenosphere. When a coal-burning boiler works, the majority of iron minerals in the coal form Fe_2O_3, Fe_3O_4 with the carbon, carbon monoxide acting. They combine with the new silicon, aluminum, calcium cenosphere material. The density is 3.1–4.2 g/cm^3, and pile density is 1.9–1.8 g/cm^3 (Jia et al., 2006). Application of MFHC relates to various fields such as physical, chemical, mechanical, electrical insulation and other aspects because of its special performance (Jia et al., 2006). Its most notable feature is the high density, mechanical strength and good stability. It can prepare the high-performance microwave absorbing materials.

* Corresponding author. E-mail: mailjyl@yahoo.com.cn

In this article, the core-nanoshell composite material is put forward, in which MFHC is core and the nanosized ferrite doped with La is shell. The exchange-coupling interaction happens between ferrite of MFHC and the nanosized ferrite coating. It can get the complex phases system and enhance the magnetic properties.

1 Materials and methods

1.1 Pre-treatment of magnetic fly-ash hollow cenosphere

The MFHC was screened under 5000 and 7000 head, and then carried out classification for each magnetic particle size. The magnetic fields were 0.05, 0.098 and 0.2 T (Teslas).

MFHC was soaked with CH_2Cl_2 for 10 min to remove surface organic residues. Then ultrasonic cleaning technology was used with NaOH solution (0.5 mol/L) for 30 min, which solved the problem of corrosion during removing impurities and greasy dirt with acid or alkali liquor. Meanwhile it removed the left liquid in crevices of cenosphere, which increased the surface activity of the particles, breaked the unity between the particles, and improved the quality of coating processes (Li et al., 2002; Zheng et al., 2008). The transmission electron microscope (TEM) images of MFHC before and after pre-treatment are showed in **Fig. 1**.

1.2 Synthesis

The core-nanoshell composite materials were prepared through high-energy ball milling at room temperature, using analytical grade $Fe(NO_3)_3{\cdot}9H_2O$, La_2O_3, MFHC and additive as starting chemicals. First, stoichiometric amounts starting chemicals were mixed and put into the ball mill with 200 revolutions per minute for 30 min at room temperature to get a kind of viscid substance. Then, the obtained viscid substance was dried at 60°C for 2 hr. Finally, the samples were sintered at 500°C for 1 hr. The final product was core-nanoshell composite powder.

1.3 Characterization

The thermal analysis was carried out by thermogravimetry and differential thermal analysis (TG-DTA; STA409CD, Netzsch, Germany) with a heating rate of 10°C/min in the air. The crystal structure of sample was examined by D 5005 Bruker X-ray diffractometer (XRD; Smartlab, Rigaku Corporation, Japan) with Cu-$K\alpha$ radiation.The microstructure was observed by scanning electron microscope (SEM; JSM-7401F, JEOL Ltd., Japan) and transmission electron microscope (TEM; JEM-2100, JEOL Ltd., Japan). The vibrating sample magnetometer analysis (VersaLab, Quantum Design, USA) measure the magnetic properties; and the microwave absorbing property of the sample was measured by reflectivity far field radar cross section (RCS) of radar microwave absorbing material (RAM) with vector network analyzer (T5280, Trascom Instruments Co., Ltd., China).

2 Results and discussion

2.1 TG-DTA curves of sample

The pyrolysis processes of the sample were investigated by TG-DTA curve. **Figure 2** shows the main varying regions occur at 160 and 350°C. The DTA curve shows that the first endothermic peak is at 160°C, it is aroused by the evaporation of impurities; at about 350°C, there is a second endothermic peak which is aroused by nitrate decompositions. After 500°C, TG curve gradually flattened. A stable temperature is attained for the core-nanoshell composite absorbers at 500°C. The additive can provide and keep the heat in the high-energy ball milling, so the solid-state reaction shorten the sintered time and reduce the sintered temperature.

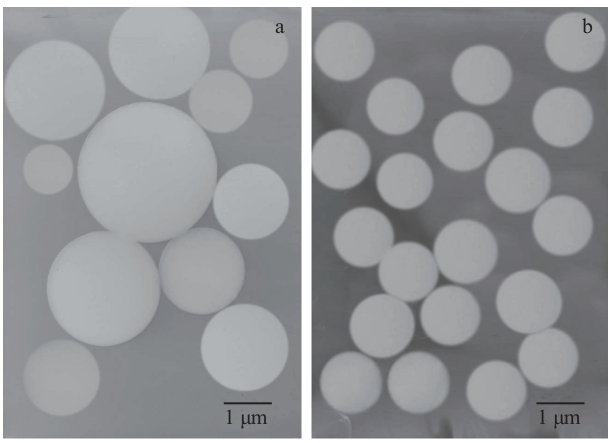

Fig. 1 Transmission electron microscope (TEM) images of magnetic fly-ash hollow cenosphere (MFHC) before (a) and after (b) pre-treatment.

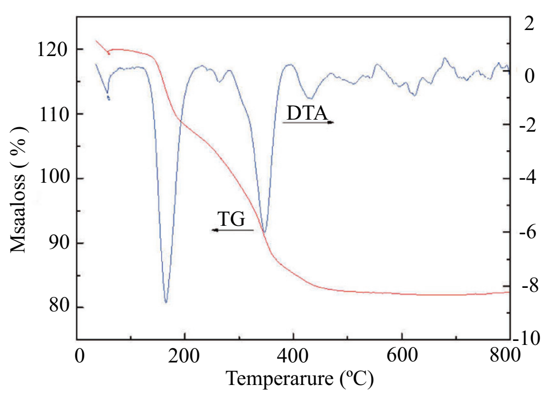

Fig. 2 Thermogravimetry and differential thermal analysis (TG-DTA) curve of the sample.