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Original Research Paper

Preparation, characterization and microwave absorption properties of barium-ferrite-coated fly-ash cenospheres

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ABSTRACT

Magnetic composites of barium ferrite coated on fly-ash cenospheres (BFACs) were prepared by sol–gel auto-combustion method. To promote surface activity, we modified fly-ash cenospheres (FACs) surfaces using γ-aminopropyltriethoxysilane (APS) as coupling agent and silver nitrate as activating agent before coating barium ferrite films on FACs. The morphology, composition, crystal structure, magnetic and microwave absorption properties of these composite powders were characterized by scanning electron microscope, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, vibrating sample magnetometer, and vector network analyzer. Continuous and uniform coatings of barium ferrite were found on the surfaces of the FACs. The BFACs powders-epoxy composite possesses excellent microwave absorption properties in the 2–18 GHz frequency range. The maximum microwave reflection loss reaches −15.4 dB at 8.4 GHz with a thickness of 3.0 mm, and the widest bandwidth less than −12 dB is 6.2 GHz with a sample thickness of 2.0 mm. The intrinsic reasons for microwave absorption were also investigated. Applications of this composite material in magnetic recording, electromagnetic wave shielding, and lightweight microwave-absorbing fields are promising.

1. Introduction

With fast advancement of wireless communication, microwave-absorbing materials have attracted considerable attention for applications outside special fields such as silent rooms, radar systems, and military applications. Recent studies [1–4] identify barium ferrite ($BaFe_{12}O_{19}$) as a potential superior microwave absorber because of its high saturation magnetization, theoretical maximum coercivity, high magnetic anisotropy field, and excellent chemical stability. However, as a bulk material, barium ferrite is quite heavy, which restricts its applications in those requiring lightweight materials such as advanced microwave absorbents, high-density magnetic recording media, and electromagnetic wave (EMW) shielding. As one of the ways to overcome this problem, core–shell structure composites have been suggested. Core–shell structure composites, consisting of two dissimilar compositional and structural domains, should have enhanced physical and chemical properties and a broader range of applications than their single component counterparts.

Fly-ash cenospheres (FACs) are a by-product generated in coal-fired power plants. For many years, their disposal has posed an environmental problem. Nevertheless, FACs possess favorable characteristics such as sphericity, nontoxicity, lightweight property, and high strength, and hence are marked as substrates on which to fabricate lightweight and functional composites [5]. Cu [6,7], Ag [8], Co–Fe thin films [9], Ni–P [10], Ni–Co–P alloy films [11] and ferrites [1,12,13] are often coated onto FACs to produce core–shell composites, which are useful as conductive fillers for EMW shielding and microwave-absorbing materials. Currently developed methods for coating cenospheres include electroless plating [6,7,11], magnetron sputtering deposition [14–16], heterogeneous precipitation-thermal reduction method [17–19], and sol–gel auto-combustion method [1,12]. Among these methods, the sol–gel auto-combustion technique is the focus of the present study due to the inexpensive precursors, simple operation, time saving process, and resulting homogeneous nano-sized powders [20,21]. Hence, many researchers have prepared composites of hollow FACs coated with barium ferrite films. However, irregular coating and poor adhesion between shell layer and inorganic substrate weaken performance. To improve this situation, we employed a low-cost two-step pretreatment to FACs, including a coupling process with γ-aminopropyltriethoxysilane (APS) and an activating step using silver nitrate as activator to improve the adhesion between the barium ferrite film and FACs and to deposit more of the barium ferrite particles onto FACs surfaces. Thus, by the sol–gel auto-combustion method, a new kind of composite material of barium ferrite films coated on FACs (BFACs) was obtained. The

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morphology, composition, crystal structure, magnetic, and microwave absorption properties of powders of these BFACs composites were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and vector network analyzer. The analyses are described and discussed below. Additionally, the formation mechanism of the composite material is also discussed.

2. Experiment

2.1. Materials and chemicals

FACs (chemical composition: 57.69% SiO_2, 29.54% Al_2O_3, 3.76% Fe_2O_3, 2.87% K_2O, 2.48% CaO, 0.93% TiO_2 and 0.27% Na_2O; particle density: 0.5–0.7 g/cm^3) were obtained from Nanjing Yangzi Petrochemical Company. The coupling agent, γ-aminopropyltriethoxysilane (APS), was supplied by Nanjing East Glass Instrument Company. Other major chemicals, such as ethanol, HNO_3, $AgNO_3$, $NH_3{\cdot}H_2O$, $C_4H_4KNaO_6{\cdot}4H_2O$, $Ba(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$ and citric acid were purchased from Nanjing Chemical Reagents Company. All chemicals were of analytical grade, and deionized water was used throughout the work.

2.2. Preparation procedures of the composite powders of BFACs

The composite powders of BFACs were synthesized through sol–gel auto-combustion method; a schematic representation of the synthesis procedures is given in Fig. 1.

1. Pretreatment and surface modification of FACs: To improve the adhesion between the shell layer and the core particle, pretreatment is required to eliminate undesirable organic contaminants and broken particles. FACs were treated in acid (10% HNO_3 solution) at room temperature for 30 min; those still floating on the water surface were collected and washed three times with deionized water, followed by drying in a vacuum oven at 80 °C for 2 h. Surface modification of FACs by APS was performed in a water–ethanol mixed solution (5:95 v/v). 2.0 mL APS was added into 100 mL of the above-mentioned mixed solution and stirred for 10 min for uniform distribution and hydrolysis reaction of APS. Next, 5.0 g of cleaned FACs were added under continuous stirring at 75 °C for about 90 min. The modified FACs were filtrated, washed three times with ethanol, and finally dried in a vacuum drying chamber at 80 °C for 2 h.
2. Activation of modified FACs: Further activation treatment of FACs was accomplished in a $[Ag(NH_3)_2]^+$ solution. 5.0 g of FACs modified by APS were stirred in 150 mL of a solution containing 3.28 g/L of $AgNO_3$ and 20 mL/L ammonia, and a solution of 8.75 g/L $C_4H_4KNaO_6\,4H_2O$ (50 mL) was added slowly. The reaction system was magnetically stirred for 3 h at room temperature. The activated FACs were then separated, rinsed three times with deionized water, and dried at 80 °C for 2 h.
3. Preparation of the composite powders of BFACs: In preparing the composite powders of BFACs, the precursor sol of barium ferrite was prepared for the sol–gel process. 0.52 g of $Ba(NO_3)_2$ and 9.37 g of $Fe(NO_3)_3\,9H_2O$ were dissolved into 20 mL of deionized water to form the required aqueous solution of 0.1 M total concentration, followed by the addition of 5.46 g of citric acid. The pH value of the solution was adjusted to 7.0 with appropriate ammonia solution. The solution was slowly evaporated at 80 °C until a just a little of the sol remained. Next, 5.0 g of activated FACs were added into the precursor sol. After ultrasonic vibration for 20 min, the mixed solution was still evaporated at 80 °C until a viscous wet gel formed. The mixture was dried at 120 °C for 24 h and turned into a dry precursor gel. Afterwards, this gel was ignited in air and then left to auto-combust until all of the gel was completely burnt to leave a

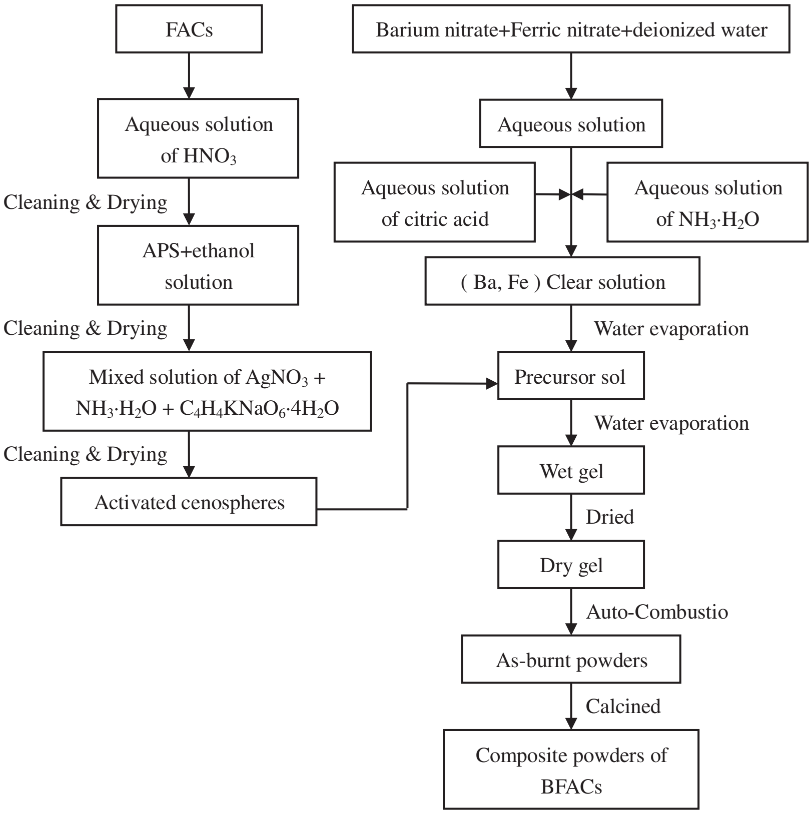

Fig. 1. Flow chart of synthesis procedures of the BFACs composite powders.