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Effects of microstructure and filling ratio on electromagnetic properties of Co microspheres

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ABSTRACT

Cobalt microspheres with diameters of 1.5–3.5 μm were synthesized by a liquid phase reduction method. The effects of hydrogen annealing on microstructure evolution and electromagnetic properties of Co microspheres were investigated. The influence of filling ratio on the electromagnetic properties of specimens containing Co microspheres as fillers was also examined. The results indicated that the annealing leads to increase in Co microspheres' permittivity as the improved conductivity that developed during annealing contributes to enhanced dielectric relaxation. High filling ratio is found to be favorable for achieving high electromagnetic properties and thus higher electromagnetic absorbing performances, which is of technical significant for application in low frequency band. Coatings containing 30, 45 and 50 vol% Co particles as fillers present excellent EMA performance, even very thin thickness is applied. High electromagnetic wave absorbing efficiency of −10 dB was observed at thickness of 1.5 mm in C band and the electromagnetic wave absorption bandwidth reaches up to 6.3 GHz (6.7–13 GHz) when the filling volume is 45 vol%.

1. Introduction

Ferromagnetic metal/alloy particles are considered as most promising candidates for electromagnetic wave absorbing (EMA) fillers since they possess excellent electromagnetic properties [1,2]. A few catalogs of ferromagnetic metal/alloy particles have been developed to meet the need from EMA technology and superior performance has been obtained [3–5]. Among these materials, Fe based alloy particles present high EMA efficiency [6]; however; they cannot be used at high temperature due to its low Curie temperature (T_c). In contrast, Co particles possesses satisfactory saturation magnetization (M_s), multiple crystal structures [7] and high Curie temperature (1130 °C) and thus are expected to present excellent EMA performance in targeting bands in wide temperature range [8,9]. EMA performance of the coatings containing Co particles as fillers, including the absorption frequency, the effective absorption band width (EABW, the width the band where reflection loss is higher than 10 dB) and the EMA efficiency, is closely related to the particles' morphology [10], and microstructures [11,12] as well as the filling ratio of fillers [8].

A lot of efforts have been made to prepare Co particles with various morphologies including disk-shaped [13], spherical, flower-like [14,15], rod-like Co [16], wires, rings and belts [17]; and the effects of morphology on electromagnetic properties were systematically examined. Han et al. synthesized hierarchical Co particles via a liquid phase reduction method and observed high reflection loss in 8–10 GHz band in the corresponding coatings [18]. Co particles with hierarchical architectures assembled by radially grown nano-sheets were synthesized via a similar process, and excellent EMA performance was obtained in 10–18 GHz range [19]. Solvent-thermal route was also used to prepare Co particles with hierarchical architectures [14,20] and the corresponding coating with a thickness of 2 mm exhibited high EMA performance in 4–8 GHz band. These researches have suggested the feasibility to obtain high EMA performance through the application of well-defined Co particles and the effect from the morphology was preliminarily investigated.

To compare with the efforts focused on the morphology control, the investigation on the microstructure and the filling ratio is scarce, which would restrict the flexibility of the EM properties tailoring. For instance, flaky or dendrite-like particles are shown to present high permittivity, but such morphologies cannot be used for tailoring the dielectric relaxation frequency. On the other hand, particles prepared via solution-chemistry method generally present low permeability due to the presence of crystal imperfects

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and non-ferromagnetic inclusions. These defects can hardly be removed within the scope of solution-chemistry synthesis but can be eliminated via annealing. Additionally, the excellent property of fillers is currently diluted away as the filling ratio is limited to below 30 vol% in most cases. A few researches have been performed to examine the roles of microstructures and filling ratio. Zhen and Hou examined the microstructure evolution of Co particles during annealing and noted the resulted improvement in EM properties [21,22], suggesting the feasibility to tailor electromagnetic properties via heat treatment. Liu and Kong [23] investigated the effect of filling ratio in carbonyl iron particles and found that high filling ratio is favorable for obtaining high EM properties. These previous studies preliminarily suggested the possibility to control or optimize EM properties via tailoring the particle microstructures and the filling ratio.

Herein, we synthesized Co microspheres with well-defined morphology via a simple reduction method and then investigate the effect microstructure and filling ratio on Co microspheres. We demonstrated that it is possible to tailor the microstructure via annealing and hereafter optimal electromagnetic properties and EMA performance can be achieved. The effect of Co particle's filling ratio on electromagnetic performance was also investigated.

2. Experimental

2.1. Materials

All chemicals were analytical grade and used as received without further purification. $CoCl_2 \cdot 6H_2O$, NaOH, $N_2H_4 \cdot H_2O$ (85%), and ethylene glycol (EG) were purchased from Sino pharm Chemical Reagent Co., Ltd.

2.2. Synthesis

Co microspheres were prepared via a facile liquid-phase reduction method [18]. A typical synthesis as follow: 0.02 mol $CoCl_2 \cdot 6H_2O$ was dissolved in 200 mL EG with water bath of 85 °C in a beaker under continuously mechanical stirring, followed by the addition of 0.13 mol NaOH for adjusting the pH value, and then 15 mL $N_2H_4 \cdot H_2O$ was added to the solution. The reaction was allowed to occur for 1 h before the reaction completes. The obtained products were centrifuged at 3000 rpm for 5 min and washed for five times with distilled water and another three times with absolute ethanol. Finally, the products were dried in a vacuum oven at 60 °C for 24 h.

The as-prepared Co microspheres were annealed in H_2 atmosphere at 500, 600, and 800 °C for 120 min, respectively, for microstructure tailoring. The as-prepared Co particles were mixed adequately with NaCl in mortar before annealing at 600 and 800 °C to avoid the aggregation. After the annealing completed, the products were washed for five times with distilled water to remove NaCl and dried in a vacuum oven at 60 °C for 24 h.

2.3. Characterization

The morphology of Co particles was observed using a scanning electron microscope (SEM, FEI Quanta 200 F). The phase identification and structure analysis of particles of various conditions were determined through X-ray diffraction (XRD, Rigaku D/max-rB, Cu Kα). The saturation magnetization (M_s) and coercivity (H_c) of Co particles of various conditions were carried out on a vibrating sample magnetometer (VSM, Lakeshore 7300) at room temperature.

Electromagnetic properties were evaluated through measuring the complex permeability and complex permittivity of paraffin-matrixes specimens performed on a vector network analyzer (VNA, AgilentN5230A). VNA specimens were fabricated via pressing Co-paraffin mixture into a mode. The fabricated specimens are coaxial cylindrical rings with outer diameter of 7 mm, inner diameter of 3.04 mm, and thickness of 3 mm. Different filling ratios of Co particles, namely, 15 vol%, 20 vol%, 30 vol%, 45 vol% and 50 vol% were set when filling Co microspheres in to paraffin matrix.

3. Results and discussion

3.1. Phase structure

The crystal structure of Co particles was examined by XRD. As shown in Fig. 1(a), the characteristic peaks at 2θ of 41.68, 44.76 and 47.57° in the spectra of the as-prepared sample are well-matched with the (100), (002), and (101) planes of *hcp* Co, respectively, confirming the forming of *hcp* Co with lattice parameters of $a=2.5031$ Å, $c=4.0605$ Å (*P63/mmc*; JCPDS no. 05-0727). XRD peaks of as-prepared particles are rather low, indicating the low crystallinity. No other characteristic peaks were detected, suggesting the high purity of as-prepared Co particles. Typical XRD pattern of particles annealed at different temperatures are shown in Fig. 1(b–d). Compared with as-prepared Co particles, XRD peaks of annealed samples are stronger and sharper, indicating significant improvement in the crystallinity. Fig. 1(b) indicates that the obtained product is a mixture of α-Co and β-Co as XRD peaks (at 51.52°) corresponding to (200) plane of *fcc*-cobalt appears. Powders annealed at 600 °C are also mixture of α-Co and β-Co, but the content of α-Co decreases apparently, as shown in Fig. 1(c). As shown in Fig. 1(d), when further increase the annealing temperature to 800 °C, phase-pure *fcc* Co is obtained as peaks corresponding to β-Co can hardly be recognized, indicating that the α-Co has completely converted to β-Co.

Co particles prepared through solution chemistry process inevitably containing high density of crystal imperfects and oxide inclusion and thus exhibit low crystallinity, as shown in Fig. 1(a). These defects or inclusion vanishes when annealed at high temperature in H_2 atmosphere, which will then lead to improved crystallinity. On the other hand, α-Co tends to transit to β-Co when exposed to temperature higher than 425 °C and the formed β-Co can be maintained if the specimen is quickly quenched to room temperature. Based on above observations, it is clear that the

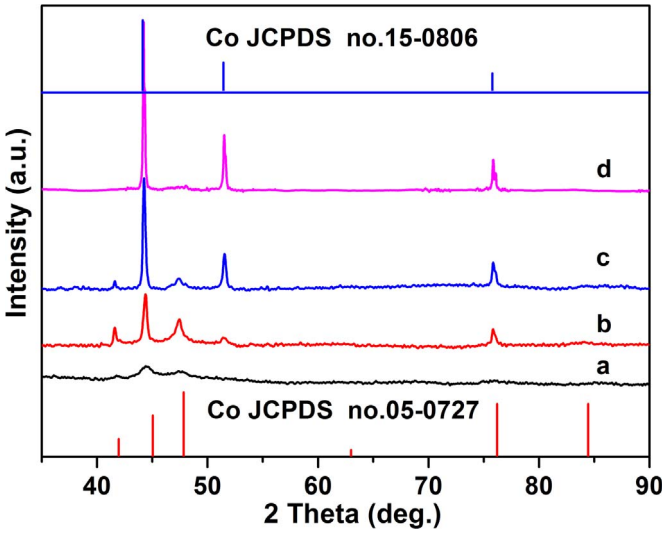

Fig. 1. XRD patterns of as-prepared spherical Co particles (a) and the annealed particles at different temperatures for 120 min in H_2 atmosphere: (b) 500 °C; (c) 600 °C; (d) 800 °C.