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Electromagnetic properties of Co flaky particles prepared via ball-milling method

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ABSTRACT

Flaky cobalt particles with different aspect ratio were produced with ball-milling method. The phase structure and morphology of the particles were identified by XRD analysis and SEM observation. The static magnetic and electromagnetic properties of the particles were measured and effects of shape, microstructure and filling fraction were investigated. Phase transition from *fcc* lattice to *hcp* lattice occur due to the drive of ball-milling is responsible for the largely increased coercivity. Particles with high aspect ratio are found to possess high permittivity and permeability, compelling the frequency of absorption peak to shift to low frequency. Coatings using cobalt particles milled for 20 h as fillers present a RL peak of −33 dB at 8 GHz at the thickness of 2.5 mm together with a broad effective absorbing (RL below −10 dB) bandwidth covering 6–10 GHz.

1. Introduction

Electromagnetic wave absorbing (EMA) materials that serve at elevated temperature have become more and more vital in defense systems. Carbon fibers and SiC fibers have been explored for application as high temperature EMA materials for years [1,2]. These series of materials present high dielectric loss efficiency but do not possess ferromagnetic properties and thus exhibit unsound electromagnetic matching characteristics, which then inhibits the improvement of EMA performances. Additionally, application of C fibers and SiC fibers is usually combined into complicated fabrication process of components and the flexibility is thus limited. Particles of Fe and related alloys are excellent EMA materials [3–5] as they possess high permeability and tailorable permittivity when used at mild temperature. Their permeability however decreases quickly when exposed to temperature near to the Curie point (770 °C), which thus limits the application at high temperatures. Cobalt, possessing much higher Curie temperature (1130 °C) and satisfactory saturation magnetization (M_s, 165 emu/g), exhibits the potency to present high permeability at higher temperature. Considering the fact that permittivity is usually much higher than permeability in metallic particles, it's then significant to obtain high permeability for obtaining good impedance matching and for obtaining excellent EMA performances. Besides, application of ferromagnetic particles is more flexible than C and SiC fibers since they can be filled into matrix to fabricate coatings rather than being built-into rigid components.

High and properly tailored electromagnetic properties are crucial for obtaining excellent EMA performances, as previous research suggested [6,7]. Among various factors that affect electromagnetic properties, particle shape is found the most vital one [8–11]. Recent work has indicated that, flaky particles usually possess much higher anisotropy to compare with spherical ones due to the lower geometric symmetry. Meanwhile, the thin thickness of flaky particles may also sever the purpose of suppressing the eddy current effect that occurs in metallic particles. Both these merits are helpful for obtaining high permeability and have inspired a lot of research in the past a few years. Gong [8] synthesized CoFe alloy flakes (NF) and spheres (NP) of nanometer scale and observed that CoFe NFs presented higher permeability than CoFe NPs. Also, coatings using CoFe NFs presented a higher EMA efficiency (RL_{max} of −57.8 dB, at about 2.3 GHz) to compare with that observed in case of CoFe NP (−16.6 dB, at 18 GHz). Ma [12] prepared Co flakes several micrometer in diameter and around 80 nm in thickness through hydrothermal reduction and observed excellent EMA performance. Li [13] prepared Co nano-flakes via liquid phase reduction method and observed μ' as high as 2 at 2 GHz in a specimens with quite low filling ratio (13 vol%).

Flaky cobalt particles of micrometer or nanometer scale are

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usually prepared through solution chemistry methods with very small yield in previous research, which limits the practical application of this series of particles as EMA fillers. Besides, fine particles prepared through this method are chemically active and likely to oxide, which also restricts applications exposed to open weather. Ball milling is a convenient method to produce flaky particles in large quantity. It has been successfully applied in preparing flaky Fe or Fe based alloy particles [14–17] and high performance EMA fillers were where from fabricated. The application of ball milling in Co particles however has not been reported and the evolution in particle shape and EM properties was not clear.

The current study was thus inspired to investigate the evolution in morphology, microstructure and EM properties of Co particles. Flaky cobalt particles of different micro sizes were prepared in large scale via a ball-milling process in the current research. Influences of particles' shape and microstructure on electromagnetic properties were systematically investigated.

2. Materials and experimental details

Commercially available gas-atomized cobalt particles (mesh -400, 99.9 wt% in purity) were used as the starting material. The as-received particles, certain anhydrous ethanol and some GCr15 steel balls were put into jars of 250 ml and then the ball-milling process was carried out with a planetary ball-mill system at 500 rpm for up to 20 h. For all processes, the weights of ball, particle and ethanol were kept at 350 g, 70 g and 45 g, respectively. Milled particles were gathered after the milling process completed, washed for 3 times with anhydrous ethanol and then dried for 12 hours at 60 °C in an oven.

Phase composition of raw and as-milled cobalt particles was examined on a X-ray diffractometer (XRD, PANalytical X'Pert PRO, CuKα). The morphology of cobalt particles was observed with a scanning electron microscope (SEM, Philips FEI Siron). Static magnetic properties were measured with a vibrating sample magnetometer (VSM, Lake Shore 7404) at room temperature. Electromagnetic properties of specimens with milled cobalt as fillers and paraffin as matrix were measured on a vector network analyzer (VNA, Agilent N5230A) in the frequency range of 2–18 GHz. The volume fraction of fillers in VNA specimens was set at 10 vol%, 23 vol% and 30 vol% respectively to examine the effect of filling rate. The fabricated VNA specimens were coaxial toroidal, 7 mm in outer diameter, 3 mm in inner diameter and 3–3.5 mm in thickness. Microwave absorption performance can be evaluated by the transmission line theory on the basis of the following related formulas [7,18]:

$$Z_{in} = Z_0(\mu_r/\varepsilon_r)^{1/2}\tanh[j(2\pi fd/c)(\mu_r\varepsilon_r)^{1/2}] \quad (1)$$

$$\mathrm{RL} = 20\log\left|(Z_{in} - Z_0)/(Z_{in} + Z_0)\right| \quad (2)$$

3. Results and discussion

3.1. Phase structure and morphology

Fig. 1 shows the x-ray diffraction patterns of cobalt particles as received or ball-milled for different time. The XRD pattern of raw cobalt particles presents two sets of diffraction peaks, one of which can be indexed to the *hcp* lattice of α-Co, another to *fcc* lattice of β-Co. Peaks corresponding to β-Co disappear while those corresponding to α-Co enhanced in the pattern, after ball milled for 4 h, as shown in Fig. 1. This variation in XRD pattern indicates

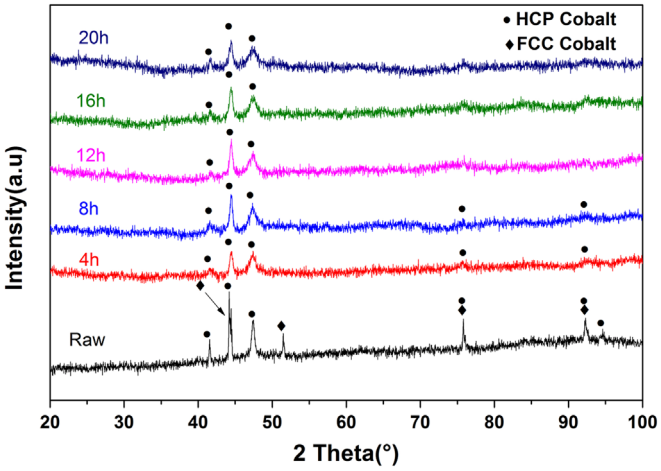

Fig. 1. X-ray diffraction patterns of cobalt particles milled for different time.

that β-Co is transferred to α-Co during the ball-milling. On the other hand, characteristic peaks of α-Co become broader and some peaks disappear as the ball-milling proceeds, as shown in the figure. Similar results were observed in our previous work [9] and other researches [19,20]. This variation is attributed to the increased defects, the decreased grain size and the amorphous phase's forming in the surface layer of the particles due to the intense impact. Grain size of different samples is calculated according to Scherer formula and the calculated results are listed in Table 1. It is found that grain size decease before 8 h and then keep unchanged during the ball milling. Meanwhile, the fact that average grain sizes calculated by (101) peak and (002) peak are different is reasonable on the basis that ball milling will result in non-uniform deformation of grains.

Figs. 2 and 3 shows the morphology of raw and milled particles. The raw particles are spheres with 5–30 μm in diameter, as shown in Fig. 2(a). After milled for 4 h, particles are flattened into flakes with 3–4 μm in thickness. After milled for 8 h, flakes with diameter up to 40 μm and thickness below 1 μm are observed, contributing to a very high aspect ratio (diameter/thickness, AR). As the ball-milling further proceeds, flaky particles are broken into small scraps while the thickness remains at about 1 μm. The largest particle diameter observed at 12 h, 16 h and 20 h is around 25 μm, 15 μm and 10 μm, respectively. Through the whole process, the AR firstly increases and then decreases.

3.2. Static magnetic properties

Fig. 4 shows the magnetic hysteresis loops of raw cobalt particles and particles milled for different time. The measured static magnetic properties are listed on Table 2. Saturation magnetization (M_s) fluctuates slightly all along the milling proceeds but remains at the level similar to that of raw particles. Since M_s of β-Co (165 emu/g) is quite near to that of α-Co (162 emu/g) [21],

Table 1
Grain size calculated by different x-ray diffraction peaks according to Scherer formula.

Samples (milling time)	Grain size (nm) calculated by (002) peak	Grain size (nm) calculated by (101) peak
Raw (0 h)	36	21
4 h	19	13
8 h	17	12
12 h	21	10
16 h	18	11
20 h	19	10