Synthesis of uniform porous Fe micro-flakes with excellent magnetic properties in GHz range

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Abstract. Porous Fe micro-flakes with uniform size and well-defined shape have been successfully synthesized by hydrogen thermal reduction of the α-Fe_2O_3 precursor flakes. The thicknesses and planar sizes of those porous flakes fall into the range of 208-375nm and 10-23 μm, respectively. Static magnetic properties and high frequency permeability of the porous Fe micro-flakes have been charactered. The porous Fe micro-flakes with large saturation magnetization and small coercivity values have also show high real and imaginary permeability values. The two wide magnetic loss peaks could be owing to the magnetic anisortropy dispersion which is caused by the porous structure. What's more, it implies that the composites with porous Fe microflakes can be used for the purpose of electromagnetic noise attenuation over a wide frequency range.

Introduction

Many physical and chemical properties of particles in nano-scale and micro-scale, such as electronic, magnetic, optical, catalytic properties, strongly depend on sizes and shapes. Therefore, obtaining those particles with controllable sizes and shapes has attracted great attention [1, 2]. There are many methods to prepare those particles, for instance, ball milling, solution method, vapor method and so on [3]. Two dimension structures have low weight, large surface area, specific facets and more active sites when comparing to zero dimension and one dimension structures [4].

Recently, with the rapid development of wireless communication technologies in gigahertz (GHz) range, such as mobile telephones, intelligent transports and satellite broadcast systems, the accompanying electromagnetic interferences (EMI) are increasingly serious [5, 6]. Hence, the electromagnetic wave absorption materials are promising to solve this problem. Generally speaking, the electromagnetic wave absorption materials are divided into two types: dielectric materials and magnetic materials. Dielectric materials achieve absorption though dielectric loss which is caused by electric polarization, while magnetic materials that is mainly though magnetic loss related to dynamic magnetization process [7]. Ferromagnetic metal particles have attracted much more attention than ferrite due to the higher permeability and higher operating frequency [8]. Particularly, two dimension ferromagnetic metal particles have extended snoek's law which is owing to the strong shape anisortropy but still retained high permeability in GHz range [5]. Thus, flake-like ferromagnetic metal particles should realize excellent electromagnetic wave absorption properties.

In general, for the metal flakes prepared by milling, the sizes are discrete and the shapes are irregular. However, the metal flakes with uniform size and shape can be prepared by solution method. But, since the high reduction potential, Fe flakes can be hardly obtained by liquid reduction process [9]. Fortunately, iron oxide can be prepared by solution method [10]. And then, Fe flakes can be obtained by reducing the precursor by hydrogen [11].

In this contribution, we intend to prepare plate-like α-Fe_2O_3 by hydrothermal approach. Then the precursor has been reduced by hydrogen annealing to acquire the porous flaky Fe. The porous Fe

flake not only can be uniform size and shape, but also can be a candidate in absorbing the electromagnetic noise.

Experiments

In this study, the quality of all chemicals used is in the analytical grade and used without further purification. α-Fe$_2$O$_3$ micro-flakes were synthesized by a facile hydrothermal route. In the fabrication process, 60 mL distilled water were divided equally with the serial number "A" and "B". Subsequently, 0.05 mol Fe(NO$_3$)$_3$·9H$_2$O and 0.45 mol NaOH were dissolved in "A" and "B" to form two homogeneous solutions, respectively. Solution "A" and "B" were mixed rapidly with vigorous stirring for nearly 10 minutes. The mixture was placed into a 100 mL Teflon-lined autoclave and then hydrothermally treated at 473 K for 10 h and cooled down to room temperature. The collected powder products were washed several times in deionized water and industrial alcohol, and then were dried at 333 K for 12 hours.

Porous Fe micro-flakes were prepared by hydrogen-thermal reduction. α-Fe$_2$O$_3$ micro-flakes were reduced in hydrogen atmosphere at 773K for 1 h. The reduced products were cooled in N$_2$ atmosphere to room temperature naturally in the furnace.

A scanning electron microscope (SEM, JEOL, JSM 7600F) was used to observe and analyze the morphologies of the collected powder sample. The dimensions (length, width and thickness) of ribbons were measured by the software named "Smile View®". X-ray diffraction (SHIMADZU, XRD 7000) was used to analyze the phase structures and a hysteresis loop has been taken by a vibrating sample magnetometer (VSM) to characterize room temperature static magnetic properties for the particles. To investigate the microwave performance, a vector network analyzer (Agilent 8720ET) was used to measure μ in 0.5-10 GHz by inserting a toroidal shape sample into the coaxial waveguide. The toroidal sample was a mixture of particles and wax. And the volume fraction of the particles is 18.34%. The inner diameter, outer diameter and thickness of the samples are 3.0, 7.0 and 3 mm, respectively.
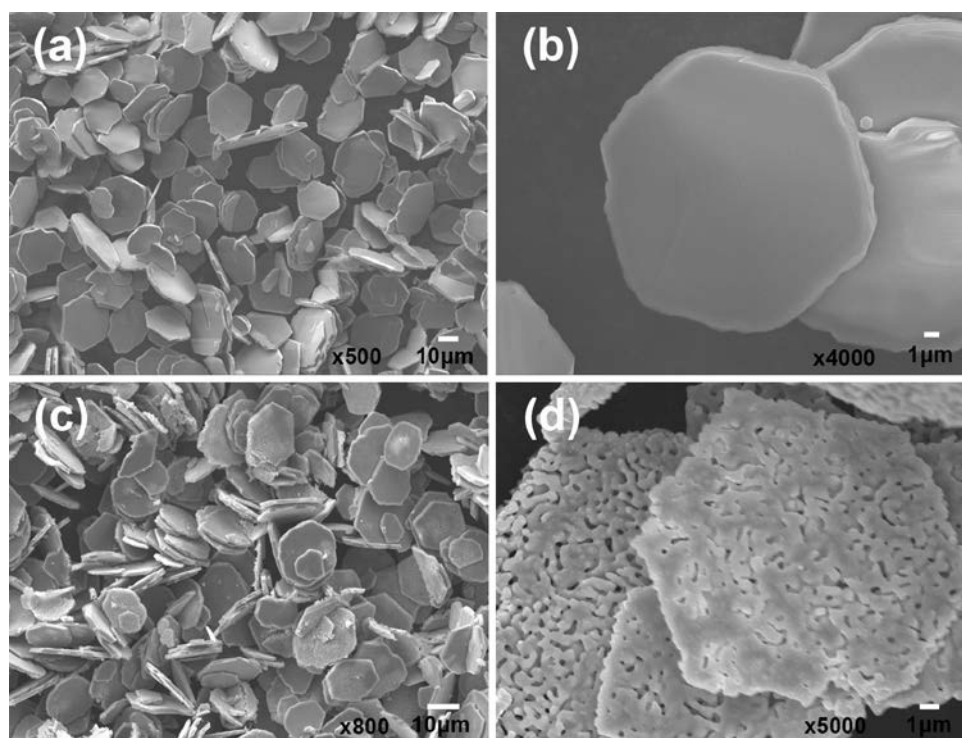
Results and Discussions

Fig. 1 SEM images of (a) α-Fe$_2$O$_3$ precursor. (b) partial enlarged detail of (a). (c) reduced porous Fe flakes. (d) partial enlarged detail of (c).

The morphologies of the prepared precursor and the H_2 annealed particles are shown in Fig. 1 (a, b) and Fig. 1(c, d), respectively. The planar sizes of both particles mostly fall into the range of 10-23 μm. And the thicknesses mostly fall into the range of 208-375nm. Obviously, the surfaces of the precursors are smooth, after H_2 annealing, many porous with bore diameter about 100-200 nm formed on the surfaces. After annealing, the surface area increases while the apparent density decreases. In addition, according to the width and thickness values, the aspect ratio is larger than 10 which could caused strong shape anisortropy.

The XRD patterns of the precursor and the H_2 annealed particles are shown in Fig. 2. The crystal structure for the particles of each type is a single pure phase. For the precursor, most of the diffraction peaks which are marked by the rhombus are related to the α-Fe_2O_3 phase (JCPDS No. 33-0664), while for the H_2 annealed particles, the several trilateral-marked peaks are related to α-Fe phase (JCPDS No. 05-0696). According to the Scherrer's equation [12], the grain sizes of α-Fe_2O_3 and α-Fe phase are 386.3 nm and 160.1nm, respectively.

As seen from the hysteresis loop in Fig. 3(a), the α-Fe_2O_3 precursor is magnetic. the magnetization is very small but the coercivity (H_c) values gets a very high value, 1293.4 Oe. Seen from Fig. 3(b), the saturation magnetization (σ_s) and coercivity (H_c) values of the porous Fe flakes are 224 emu/g and 53 Oe, respectively. The results indicate that the porous Fe flakes have good soft magnetic properties. So much high saturation magnetization value would lead to large permeability values. Besides, the variations of coercivity values could be owing to the different grain size of the each magnetic phase [13].
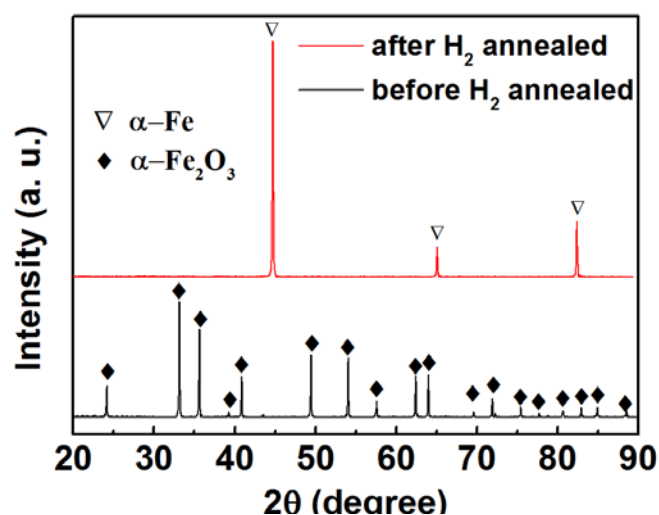

Fig. 2 XRD patterns of α-Fe_2O_3 precursor before and after H_2 annealed.

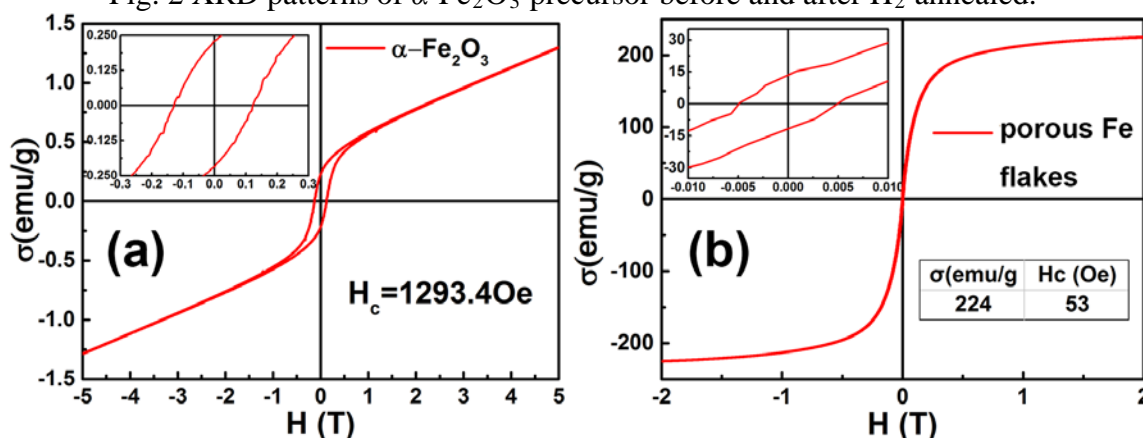
Fig. 3 The magnetic hysteresis loops of (a) α-Fe_2O_3 precursor. (b) porous Fe flakes. The insets are the enlarged zone of the loops and the listed σ_s and H_c values.

The measured microwave permeability spectra of composites containing Fe microflakes are shown in Fig. 4. The real part (μ'_s) and imaginary part (μ''_s) of effective permeability at 0.5 GHz are about 3.5 and 1.5, respectively. The frequency dependence of imaginary part of permeability reveals a

superposition of two resonance peaks. Generally speaking, the resonance peaks are related to nature resonance in GHz range [6]. And according to our previous work [7], the origins of wide magnetic loss peaks is that the inhomogeneity of composites system will result in the distribution of magnetic anisotropy fields, which will give rise to the distribution of natural resonances of spins rotation. In this case, the porous structure causes inhomogeneity of the shape anisortropy. Therefore, the two wide magnetic loss peaks could be understood. Moreover, it implies that the composites with porous Fe microflakes can be used for the purpose of electromagnetic noise attenuation over a wide frequency range.
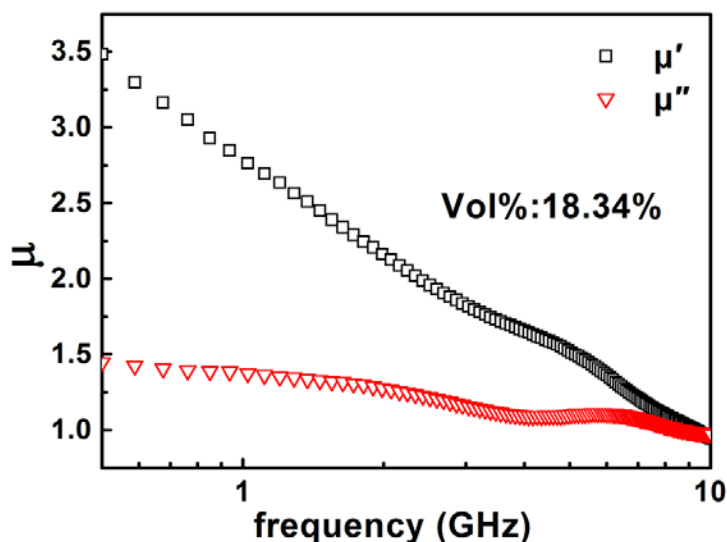

Fig. 4 permeability of the composites containing the porous Fe flakes. The insert is the volume fraction of the porous Fe flakes in the composites.

Acknowledgment

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