Journal of Alloys and Compounds 509 (2011) 494–498

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis and microwave absorbing properties of FeCo alloy particles/graphite nanoflake composites

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ARTICLE INFO

Article history:
Received 31 March 2010
Received in revised form
12 September 2010
Accepted 18 September 2010
Available online 24 September 2010

Keywords:
FeCo alloy
Graphite nanoflake
Microwave absorption
Soft magnetism
Co-deposition

ABSTRACT

Exfoliated graphite was processed into nano-sized flakes by jet milling, ultrasonication and acid treatments, and then FeCo alloy particles were uniformly deposited onto the surface of the prepared graphite nanoflakes (GNFs) by a co-deposition and subsequent annealing process in reducing atmosphere. The FeCo-GNFs composites demonstrate good soft magnetic performance and effective microwave absorption, especially in the lower frequency range. The strongest absorption reaches −30.6 dB at 7.4 GHz with a coating thickness of 2 mm. Furthermore, effective microwave absorption at different frequency bands can be acquired by adjusting the coating thicknesses and filling ratios of FeCo-GNFs absorber. Considering the low cost and high efficiency, the FeCo-GNFs composites have great potential as microwave absorber for practical applications.

1. Introduction

The requirements for an ideal microwave absorbing material (MAM) include thin coating thickness, low density, broad absorbing band and strong absorption. The usual radar frequency band locates at 2–18 GHz and it is usually difficult to obtain an effective absorption in the lower frequency range, especially in 2–4 GHz with thin coating thickness. In this range, some kinds of ferrites and Fe-based materials have demonstrated great absorbing performance [1–7]. However, they still have some drawbacks, such as high density and requiring high mass filling percentages, which are usually over 60 wt%, or even 90 wt%. Compared to ferrites and Fe-based materials, graphite powder possesses much lower density and stronger electric loss. Furthermore, if graphite particles can be separated into nanoflakes with platelet shape, more effective absorption might be obtained due to the advantages of platelet-shaped materials than the rod-shaped and sphere-shaped ones in microwave absorption applications [8]. Therefore, GNFs are promising as one kind of low density electric loss absorber for MAMs. However, GNFs do not show the magnetic loss for microwave, which limits its applications in this field due to their thicker coatings and higher absorbing frequency band. For instance, Lee et al. [9] synthesized graphite nanoplates/epoxy composites and showed absorbing peaks around 15 GHz. However, the coating thicknesses were more than 7 mm. Fan et al. [10] treated flake graphite by ball milling and ultrasonic stirring in ethanol solution of phenol-formaldehyde cement (EFC). The coating thickness of flake graphite/EFC was only 2 mm and the absorption was less than −25 dB and the absorbing peak still located at higher frequency band (over 14 GHz). In order to obtain a thinner coating (e.g. 2 mm) with effective microwave absorption at the same time, it is necessary to functionalize the GNFs to enhance their magnetic properties. Depositing magnetic metal particles onto the surface of GNFs may be a feasible route. Fan et al. [11] coated graphite with Ni by an electroless plating method. The absorbing peaks located at frequency range of 8–18 GHz and the absorption was not very strong. Liu et al. [12] and Yang et al. [13] used the GIC method to synthesize Fe/graphite and FeNi/graphite materials respectively. The lower frequency absorption of graphite was improved remarkably. However the absorption was not strong enough (above −7 dB with 2 mm thickness) and the process was so complicated. We also synthesized FeCoNi/graphite absorber [14], which possessed the strongest absorption of −24 dB and the absorbing peak was still in higher frequency range (over 12.2 GHz).

FeCo alloy is one kind of excellent soft magnetic material. Recently, the studies on synthesis and applications of FeCo alloy nanoparticles and nanowires have been initiated because

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doi:10.1016/j.jallcom.2010.09.078

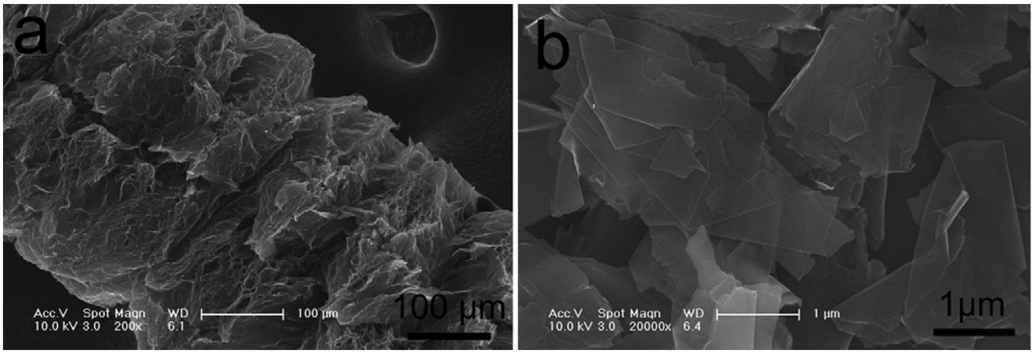

Fig. 1. SEM images of graphite samples. (a) Original exfoliated graphite with a worm-like structure, (b) as-prepared GNFs after a series of post-treatments.

of their microwave absorbing performance [6,7,15–19]. Nie et al. [6] synthesized FeCo alloy particle absorber by mechanical alloying process, which had an excellent absorption in 2–4 GHz. Yang et al. [7] synthesized FeCo nanoplates by reducing aqueous Fe^{2+} and Co^{2+} with hydrazine, and the absorber showed great absorption in different frequency range by controlling the coating thickness. These studies indicate that FeCo may be a good material to be deposited on GNFs. In the present work, a traditional co-deposition method, which is commonly used in synthesis of ferrite materials, has been improved. We use this simple and effective method to load FeCo alloy particles onto GNFs and design a novel microwave absorber, which can combine the excellent electric property of GNFs and magnetic property of FeCo alloys together, and may lead to an ideal microwave absorbing performance especially in the lower frequency range.

2. Experimental

2.1. Sample preparation

The exfoliated graphite was firstly treated by jet milling and then ultrasonic stirring in isopropanol for 2 h. After that, the sample was treated in a hot mixing acid solution (HNO_3:H_2SO_4 = 1:1) for 4 h. Subsequently, the as-treated exfoliated graphite was put into a solution containing different molar ratios of $FeSO_4$ and $CoSO_4$ (e.g. Fe:Co = 2:1, 1:1 or 1:2). The molar ratio of FeCo and GNFs is 1:1. NaOH solution was used to adjust the pH value of the solution to pH 12. The precipitate was separated and then annealed in reducing atmosphere (Ar/H_2) for 1 h at 300 °C, 450 °C and 600 °C, respectively. Finally, the products were cooled to room temperature in Ar ambient to obtain FeCo-GNFs samples. The pure FeCo alloy powder (Fe:Co = 2:1, 450 °C annealed) was also synthesized by the same method for comparison.

2.2. Characterization

X-ray diffraction (XRD, D/max-2500) was used for phase analysis. Scanning electron microscope (SEM, FEI SIRION 200) and transmission electron microscope (TEM,

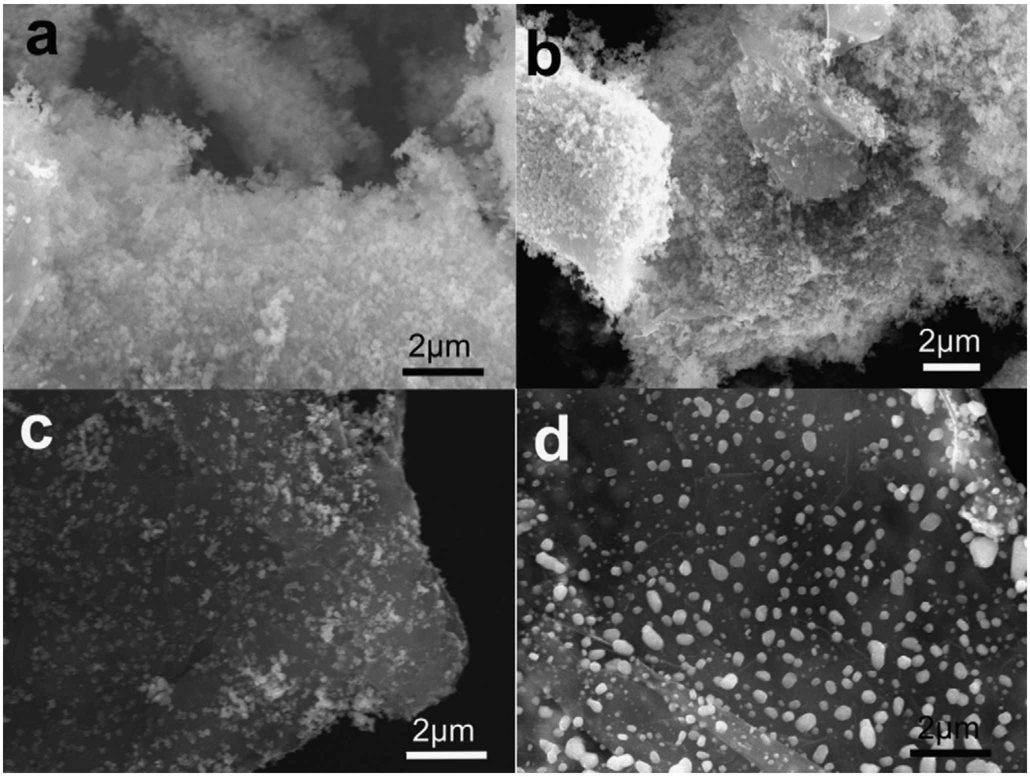

Fig. 2. SEM images of the different FeCo-GNFs samples with the ratio of Fe:Co = 2:1. (a) Untreated sample and samples annealed at (b) 300 °C (c) 450 °C (d) 600 °C in H_2 atmosphere, respectively.

FEI TECNAI G^2 F20) were further applied to examine the structures and the morphologies. A vibrating sample magnetometer (VSM, Lake Shore 730T) was used to study the magnetostatic properties. Electromagnetic (EM) parameters were measured by a vector network analyzer (HP8722ES), in which the FeCo-GNFs samples were mixed with paraffin at certain mass filling ratios (30 wt% and 50 wt%) and compressed to standard ring shapes (outer diameter: 7 mm, inner diameter: 3 mm, thickness: 2 mm).

3. Results and discussion

3.1. Characterization of the structure

The SEM image of original exfoliated graphite is shown in Fig. 1(a). It can be seen that the original exfoliated graphite possesses worm-like structure. However, after a series of post-treatments, the worm-like structure was destroyed and the graphite could be effectively separated into very thin flakes, as shown in Fig. 1(b). The thickness of these flakes is about tens of nanometers. Compared with the worm-like structure, the as-prepared GNFs show more obvious anisotropy and nano-size effect, which will be beneficial to microwave absorption. Meanwhile, the acid treatment can increase surface defects of flaky graphite, which will facilitate the deposition of FeCo alloy particles onto the flakes.

Fig. 2 shows SEM images of the FeCo-GNFs samples with the molar ratio of Fe:Co = 2:1. In the cases of FeCo-GNFs samples untreated and annealed at 300 °C, the products are in fluffy morphology, as shown in Fig. 2(a) and (b). However, for the samples annealed at 450 °C or 600 °C, the FeCo deposits have grown into nanoparticles and are well-dispersed on the surface of graphite flakes, as shown in Fig. 2(c) and (d). These are further supported by XRD results, as shown in Fig. 3. Both the untreated sample and that annealed at 300 °C show complex diffraction peaks. XRD analysis reveals that the sample annealed at 300 °C contains a lot of $CoFe_2O_4$,

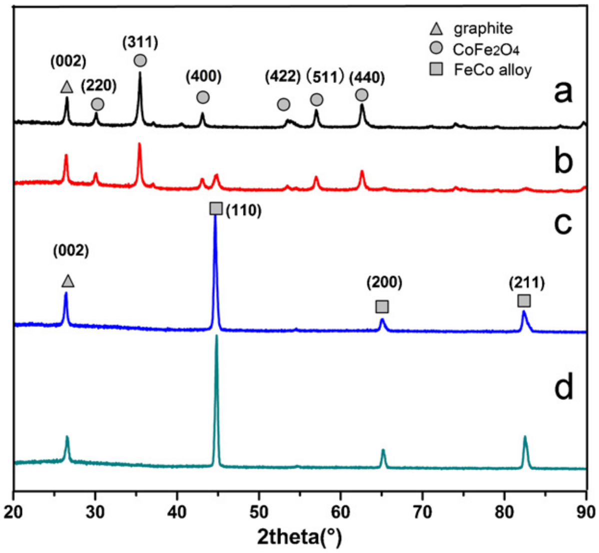

Fig. 3. XRD patterns of different FeCo-GNFs samples with the ratio of Fe:Co = 2:1. (a) Untreated sample and samples annealed at (b) 300 °C (c) 450 °C (d) 600 °C in H_2 atmosphere.

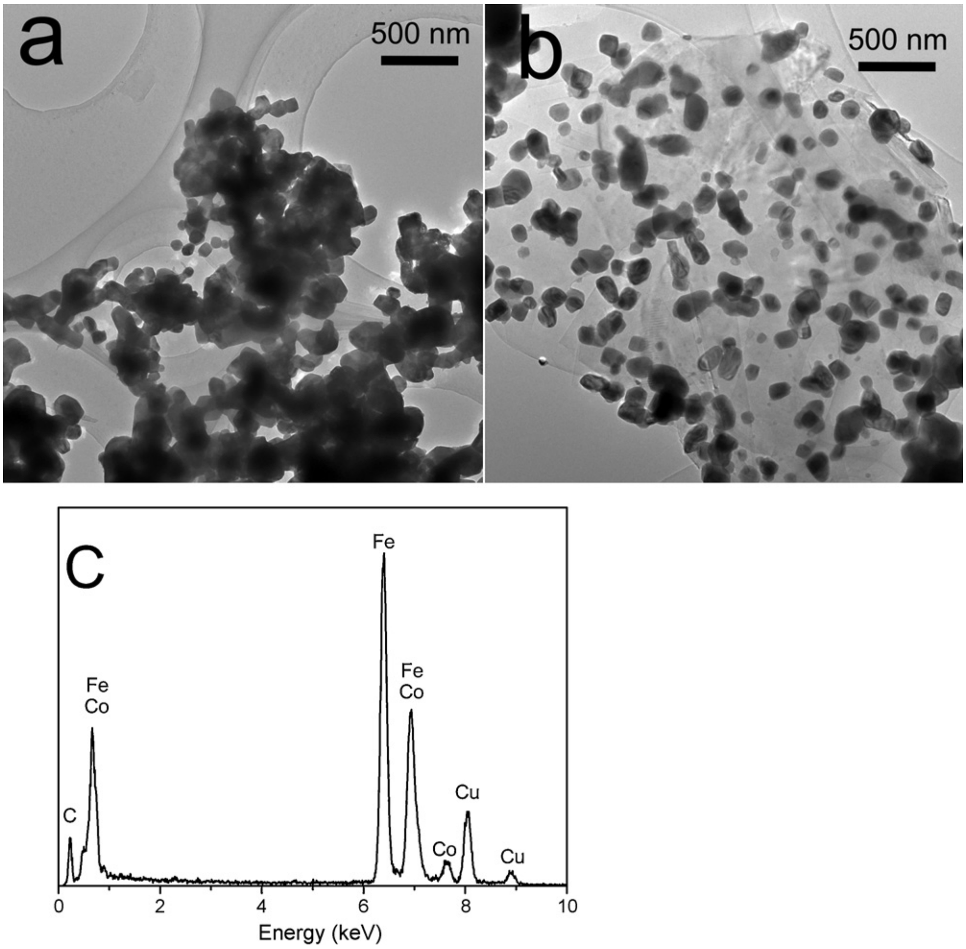

Fig. 4. TEM photos and energy dispersion spectrum of different samples. (a) Unsupported FeCo alloy powder (Fe:Co = 2:1, annealed at 450 °C), (b) FeCo-GNFs (Fe:Co = 2:1, annealed at 450 °C), (c) energy dispersion spectrum of (b), the Cu signals derive from the TEM sample holder.

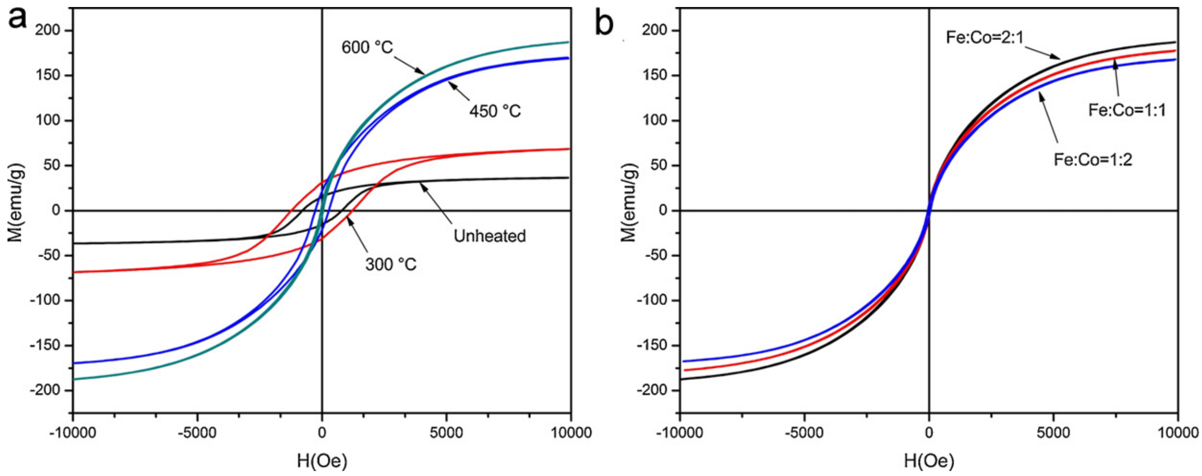

Fig. 5. Hysteresis loops of different FeCo-GNFs samples. (a) Fe:Co = 2:1 samples annealed at different temperatures, (b) FeCo-GNFs samples with different Fe:Co ratios annealed at 450 °C.

which indicates that H_2 reducing reaction was not yet completed. However, after annealing treatment at 450 °C or 600 °C, the samples show obvious BCC structures of FeCo alloy, as shown in Fig. 3(c) and (d). In addition, it is also found that the annealing temperatures may affect the size of deposited FeCo alloy particles. From Fig. 2(c) and (d), it can be clearly seen that the sample annealed at 600 °C possesses larger particle size (about 200 nm) than that treated at 450 °C. Using the Scherrer formula, it can be calculated from Fig. 3 that the average crystalline size of the FeCo alloy annealed at 450 °C is 22.6 nm, while that annealed at 600 °C is 31.0 nm.

FeCo alloy particles deposited on GNFs demonstrate different features to that of unsupported FeCo alloys, as shown in Fig. 4(a) and (b). The aggregation of FeCo particles deposited on GNFs (Fig. 4(b)) can be more effectively avoided than that of unsupported ones, which aggregate easily due to the high surface energy of nanoparticles (Fig. 4(a)). After being treated by mixing acid, many defects on the surface of GNFs could be created, where FeCo alloy would nucleate preferentially during annealing treatment. As a result, well-dispersed FeCo particles on graphite could be obtained. This also in turn provides an effective route to solve the aggregation problem of nano-sized powders. From the energy dispersion spectrum of the sample deposited on graphite (Fe:Co = 2:1, annealed at 450 °C), as shown in Fig. 4(c), it can be seen that no oxygen element is detected, which indicates that the particles were completely reduced and form FeCo alloys.

3.2. Magnetostatic properties

Magnetostatic properties of FeCo-GNFs (Fe:Co = 2:1) samples annealed at different temperatures are shown in Fig. 5(a). Obviously, the sample annealed at 600 °C has the best soft magnetic performance. The saturated magnetization (M_s) is 187.2 emu/g and the coercitive force (H_c) is 44.2 Oe. M_s of the sample annealed at 450 °C is 169.7 emu/g, which is similar to the one annealed at 600 °C. However, H_c of the sample annealed at 450 °C is 271.8 Oe, which is much larger than that annealed at 600 °C. This can be attributed to that higher annealing temperature may improve the growth of FeCo alloy grains, which leads to lower H_c values. Soft magnetic properties of the samples untreated and annealed at 300 °C are worse because of the negative effect of those incompletely reduced components among them. Fig. 5(b) shows magnetic properties of FeCo-GNFs samples with different Fe:Co ratios annealed at 450 °C. The sample with Fe:Co = 2:1 possesses the best soft magnetic performance, and the other two samples are similar to it, which indicates that the effect of Fe:Co ratios is not so significant as annealing temperature.

3.3. Microwave absorbing performance

By using electromagnetic parameters, the reflection loss of samples can be calculated by the formulas as below,

$$R = 20\lg\left|\frac{Z_{in}-Z_0}{Z_{in}+Z_0}\right| \tag{1}$$

$$Z_{in} = Z_0\sqrt{\frac{\mu}{\varepsilon}}\tanh\left(i\left(\frac{2\pi fd}{c}\right)\sqrt{\mu\varepsilon}\right) \tag{2}$$

Here Z_0 is the wave impedance of free space and a constant, Z_{in} is the input impedance, R is the reflection loss, f is the frequency, d is the coating thickness and c is the velocity of light. ε and μ are the measured relative complex permittivity and permeability, respectively. The reflection loss-frequency (R-F) curves can be used to determine microwave performance of different samples, as shown in Figs. 6 and 7.

Fig. 6 shows the R-F curves of the FeCo-GNFs samples with the ratio of Fe:Co = 2:1. The mass percentages of FeCo-GNFs in all

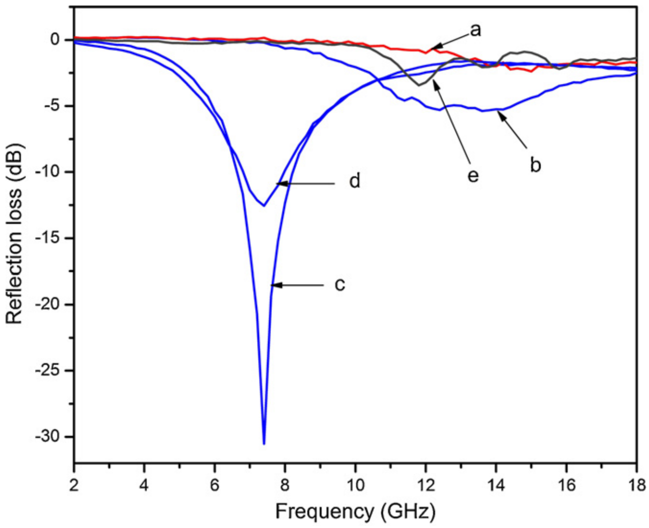

Fig. 6. Microwave reflection loss of the different FeCo-GNFs samples with Fe:Co = 2:1 (30 wt%, d = 2 mm). (a) Untreated sample, (b) annealed at 300 °C, (c) annealed at 450 °C, (d) annealed at 600 °C, (e) unsupported FeCo alloy powders (Fe:Co = 2:1, annealed at 450 °C).

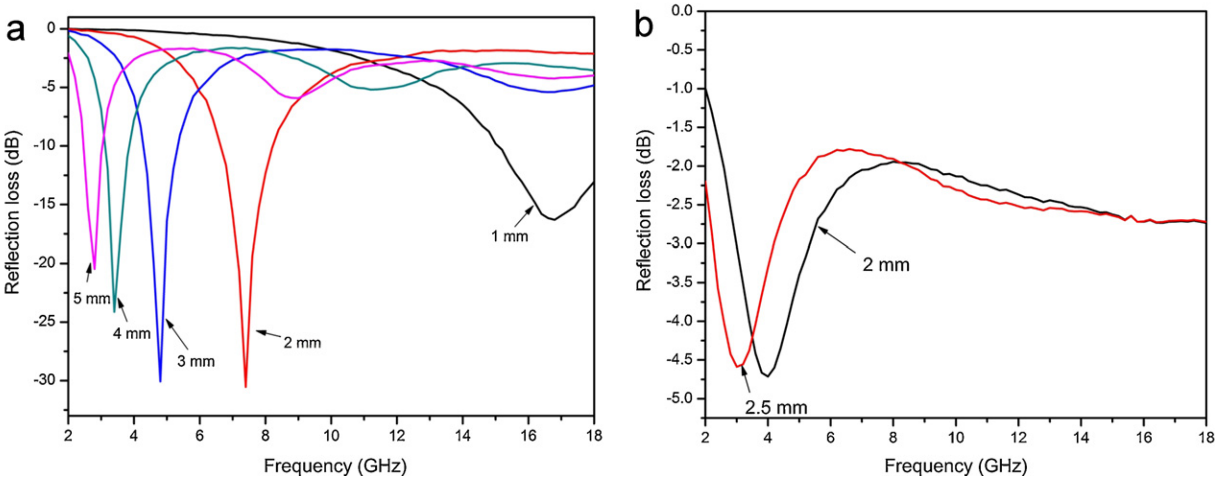

Fig. 7. Reflection loss of FeCo-GNFs samples (Fe:Co = 2:1, annealed at 450 °C) at different coating thicknesses. (a) With 30 wt% FeCo-GNFs filling ratio; (b) with 50 wt% FeCo-GNFs filling ratio.

microwave absorption samples are 30 wt% and the thicknesses of coatings are all 2 mm. It can be seen that the samples untreated and annealed at 300 °C demonstrate poor absorptions. However, the performance of FeCo-GNFs annealed at 450 °C and 600 °C are much better, especially the one at 450 °C, which shows the reflection loss of −30.6 dB at 7.4 GHz. More importantly, this absorbing peak locates in the lower frequency band (2–8 GHz) and the maximum absorption is much stronger than that in the similar studies as reported previously [11–14]. According to the SEM and TEM results, the size of FeCo particles in the sample annealed at 450 °C is much smaller than in the one annealed at 600 °C. The average particle size of the sample with ratio of Fe:Co = 2:1 annealed at 450 °C is about 100 nm, while that of the sample annealed at 600 °C is over 200 nm. Larger grains are favorable to the enhancement of soft magnetic property. However, the small grains show strong nano-size effects, which facilitate the absorbing ability. In the case of unsupported FeCo alloy powders (Fig. 6(e)), very poor absorbing performance was obtained due to the negative effects of aggregation and oversized particles, which may lead to the mismatch of impedance.

Changing the coating thickness and mass percentages of absorbers could also be used to improve the absorbing properties. Fig. 7(a) shows the R-F curves of the 30 wt% FeCo-GNFs samples annealed at 450 °C with different thicknesses (from 1 mm to 5 mm). It can be seen that the absorbing peak moves to lower frequency band by increasing the coating thicknesses. When the thickness is 5 mm, an excellent absorption at lower frequency can be obtained, which shows a maximum absorption of −20.6 dB at 2.8 GHz. Moreover, by increasing the mass percentage of the samples to 50 wt%, obvious absorption appears in 2–4 GHz band as shown in Fig. 7(b). When the thickness is 2 mm, the maximum absorbing is −4.9 dB at 3.9 GHz. The absorbing peak moves to 3 GHz with the absorption of −4.6 dB when thickness increases to 2.5 mm. Although this absorption is much weaker than 30 wt% samples, it is still competitive in present absorbers for 2–4 GHz band with such a thin coating thickness.

4. Conclusions

Exfoliated graphite was processed into GNFs by jet milling, ultrasonic stirring in isopropanol solution and acid treatment, and then magnetic FeCo alloy nanoparticles were successfully deposited on the surface of GNFs by a simple co-deposition and annealing process. This novel FeCo-GNFs structure demonstrates excellent microwave absorption performance, especially in lower frequency band. With 30 wt% filling, the FeCo-GNFs sample annealed at 450 °C shows a strong absorption of −30.6 dB at 7.4 GHz with a coating thickness of 2.0 mm. By increasing the thickness or filling percentage, the FeCo-GNFs absorber can provide better absorption at lower frequency. When the coating thickness is increased to 5 mm, the FeCo-GNFs sample demonstrates a maximum absorption of −20.6 dB at 2.8 GHz with 30 wt% filling. This kind of FeCo-GNFs nanostructure may provide a meaningful way to solve the problem of microwave absorption in lower frequency range and has a great potential to be used as a novel effective microwave absorber.

Acknowledgements

The authors are grateful to the financial support from National Natural Science Foundation of China under the Grant Nos. 50572047 and 50902080.

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