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Facile synthesis and electromagnetic wave absorption properties of magnetic carbon fiber coated with Fe–Co alloy by electroplating

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ABSTRACT

Magnetic carbon fiber coated with Fe–Co alloy was prepared by electroplating at 25 °C for 5 min. The obtained magnetic coatings show sheet-like morphology and the crystal structure of the uniform coating is Co_3Fe_7 with a thickness of about 0.5 μm. The saturation magnetization of the magnetic carbon fiber reaches 31.5 emu/g with a coercivity of 87.1 Oe. The complex permittivity and permeability of magnetic carbon fiber/paraffin (30 wt%) composite were measured in the 2–18 GHz frequency range. The reflection loss below −10 dB covers the whole frequency range while below −20 dB the absorption frequency bandwidth is 6.8 GHz, and the minimum value is −48.2 dB at a coating thickness of 1.7 mm. Magnetic carbon fiber exhibits excellent electromagnetic wave absorption properties.

1. Introduction

Electromagnetic wave absorption (EMA) materials are drawing extensive attention because of increasing electromagnetic pollution in daily life as well as military requirements for stealth weapon systems [1]. Due to low density, high strength and excellent electrical property, carbon materials are suitable candidates for EMA materials compared to conventional magnetic metal and ferrite. Among carbon materials, carbon fiber (CF) is a promising structural EMA material that can not only absorb EM but also bear loads [2]. Dielectric and magnetic loss are required for a desired EMA material. Therefore, chemical plating and reducing are usually adopted to prepare magnetic coatings on carbon materials such as carbon fiber [3], carbon nanofiber [4], carbon nanotube [5], etc. The drawbacks of these methods are time consuming, low yield and uncertain quality.

It is well known that iron-cobalt inter-metallic compounds exhibit the highest saturation magnetization among commercial magnetic materials. Besides, they have high Curie temperature and good permeability. Recently, many researchers have focused on the EMA properties of Fe–Co alloy nanoparticles [6,7] and FeCo/C nanocapsules [8], and the results were satisfying. Electroplating has been used to make carbon fiber coated with Ni [9], Cu [10], Fe [11], etc. However, to the best of our knowledge, there is no report on magnetic alloy coated carbon fiber by electroplating, while this method gives light to a simple and efficient way to the fabrication of EMA material with excellent magnetic properties. In this paper, a conventional electroplating method was used to obtain magnetic carbon fiber coated with Fe–Co alloy. The mechanism of the formation of coating morphology and electromagnetic wave absorption were also discussed.

2. Experimental

The CFs contained 12,000 filaments and the diameter of a single filament was about 7 μm. The CFs were firstly heated at 500 °C for 15 min in air and then immersed in nitric acid (50%, v/v) for 1 h at room temperature to remove the impurities and oxidize the surfaces to increase their specific surface areas. The electroplating of Fe–Co alloy was performed in an acid solution, containing 90 g/L cobalt sulfate heptahydrate, 90 g/L ferrous sulfate heptahydrate, 0.1 g/L sodium dodecyl sulfate as dispersing agent, and 40 g/L boric acid as buffering agent. The pH of the bath was regulated between 3 and 4 by the addition of dilute sulphuric acid (10 wt%). The pretreated continuous CFs worked as the cathode while a pure iron board (99.99%) functioned as the anode. The electric current was maintained at 0.5 A and the plating time was limited to 5 min. The electroplating temperature was kept at 25 °C by water bath, the corresponding sample was named M-CF.

Phase structure analysis of the prepared M-CF was performed by means of X-ray diffraction (XRD, Rigaku D/max-2500, with Cu Kα) and transmission electron microscopy (TEM, FEI Tecnai G2 F20). The morphology of the M-CF was characterized on a scanning electron microscope (SEM, Hitachi S-4800 and FEI sivion). Energy dispersive spectroscopy (EDS) attached with the SEM was used for elemental analysis. Static magnetic property was measured with a vibrating sample magnetometer (VSM, LDJ-9600) at room temperature. For microwave measurement, the M-CF was cut into 2–3 mm in length, and then mixed with paraffin (as binder matrix) with a mass fraction of 30%. The mixture was pressed to ring form of 7 mm outer and 3 mm inner diameter, and the thickness of the composite was about 2 mm. The complex permittivity $\varepsilon_r = \varepsilon' - j\varepsilon''$ and permeability $\mu_r = \mu' - j\mu''$ of the composite were measured in frequency range of 2–18 GHz over a vector network analyzer (Agilent E8363B).

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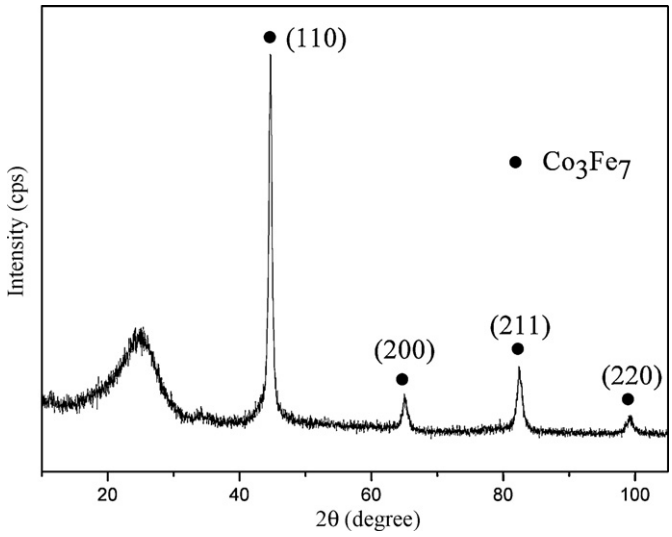

Fig. 1. XRD pattern of the M-CF.

3. Results and discussion

Fig. 1 shows the XRD pattern of the M-CF. All the diffraction peaks can be indexed as Co_3Fe_7 (JCPDS: 48-1816), and no oxide is observed. The discernible peaks are indexed to (1 1 0), (2 0 0), (2 1 1) and (2 2 0) planes of BCC structure. The broad peak around 25° is from carbon fiber. In the deposition of Fe–Co alloy during electroplating with the same sulfate concentration, the product of Co_3Fe_7 is a result of anomalous co-deposition. Due to the low solubility of carbon in iron and cobalt, Fe–Co alloy is deposited on CF by mechanical bonding, and chemical reactions do not take place in the interface between the alloy and CF.

Magnetic alloy coatings with sheet-like surfaces were obtained, as shown by SEM images in Fig. 2. The coatings on most of the CFs are dense and uniform (Fig. 2a). Fig. 2b and c shows that alloy sheets distribute on the surface of the coating. The thickness of each sheet is about 50 nm (Fig. 2d), and the thickness of the alloy coating is approximately 0.5 μm (Fig. 2e). In Fig. 2e sheets at the surface of the coating can be observed in the top left corner, so it is believed that the cross section of the M-CF consists of three layers: the CF in the center, the dense alloy coating in the middle and the alloy sheets on the surface.

The formation of the alloy coating morphology can be explained by the following procedure. At the beginning of the electroplating process, the atoms nucleate on the sites where the electric current density is higher, since the oxidized surfaces of the CFs are not smooth, small spots appear on the surfaces of the CFs. Then the atoms diffuse around and coatings are gradually formed [12]. During this process, two main factors are determined by electroplating temperature, the so-called ion transport speed in the bath and the atomic diffusion speed in the coating. Deposition speed is controlled mainly by the electric current. If these three speeds get a proper balance, smooth coatings can be obtained. When the temperature is limited to 25 °C, deposition speed becomes relatively faster, so atoms do not have enough time to fully diffuse. Soon after the beginning of deposition, small sheets are formed in a certain direction and then grow up, thus the three layers of the M-CF are obtained. Temperature plays a key role in controlling the morphology of the coating in electroplating, the similar conclusion was reported by Sahaym et al. [13]. It should be noted that coating with uniform sheet-like surface on CF has not been reported elsewhere. The underlying reasons for the formation of alloy sheets need further research.

EDS spectrum and electron diffraction pattern in Fig. 3 confirm the element composition and the crystal structure of the coatings, which are in good agreement with the XRD results. The EDS spectrum (Fig. 3a) shows that components of the material are C, O, Fe and Co, and O come from the pretreated process of the CFs.

The magnetic property of the M-CF is manifested in the M–H loop acquired by VSM measurement, as shown in Fig. 4. It can be seen that the M-CF exhibits typical soft ferromagnetism. The saturation magnetization (Ms) and coercivity (Hc) are 31.5 emu/g and 87 Oe, respectively. The magnetic property of the M-CF is from the alloy coating because carbon fiber shows paramagnetism [4,14].

For an EMA material, complex dielectric permittivity and magnetic permeability play a significant role in determining the absorption characteristics [15]. The complex permittivity $\varepsilon_r = \varepsilon' - j\varepsilon''$ and permeability $\mu_r = \mu' - j\mu''$ of the M-CF/paraffin composite were measured in frequency range of 2–18 GHz. As shown in Fig. 5a, with fluctuation during increase of frequency, the real (ε') part of the complex permittivity declines from 20.2 to 12.6 while the imaginary (ε'') part increases from 4.3 to 9.7. Fig 5b shows the real (μ') and imaginary (μ'') part of complex permeability observed as a function of frequency. It can be seen that the former is between 0.9 and 1.1; the latter is close to 0 in frequency range of 2–13 GHz and then declines at higher frequencies. The low μ' and μ'' values can be related to the smaller magnetization of the M-CF as compared to that of pure Fe–Co alloy.

The tangent of dielectric and magnetic loss of the M-CF/paraffin composite are calculated as $\tan\delta_e = \varepsilon''/\varepsilon'$ and $\tan\delta_m = \mu''/\mu'$, respectively. Fig. 6a shows the plots of dielectric and magnetic loss versus frequency. In frequency range of 2–9 GHz, the values of $\tan\delta_e$ and $\tan\delta_m$ change a little, while in the rest of the frequency range, a clear increase and decline tendency occur for dielectric and magnetic loss, respectively. The electromagnetic wave absorption of the M-CF composite results mainly from dielectric loss rather than magnetic loss because the value of $\tan\delta_e$ is much higher than that of $\tan\delta_m$. The similar phenomenon was reported by Han et al. who studied the electromagnetic properties of FeCo/C nanocapsules [8]. Polarization and interfacial polarization are two major reasons for the dielectric loss of composite in microwave frequency range, the interfaces between the CF and alloy coating can introduce more interfacial polarization. The magnetic loss mainly comes from the magnetic eddy current loss and natural resonance at microwave band. The eddy current loss is related to the thickness (d) and the electric conductivity (σ), which can be expressed as $\mu'' = 2\pi\mu_0(\mu')^2 d^2 f\sigma$. Where μ_0 is the permeability of vacuum and f is the applied frequency. If the magnetic loss only results from the eddy current loss, the values of $f^{-1}(\mu')^{-2}\mu''$ should be a constant. Fig. 6b represents the values of $f^{-1}(\mu')^{-2}\mu''$ versus frequency, it can be seen that the values of $f^{-1}(\mu')^{-2}\mu''$ show a decreasing trend generally with the increasing of frequency. Therefore, the eddy current loss could be excluded, and the natural resonance is the main magnetic loss for the M-CF.

The reflection loss (RL) of a microwave absorbing layer backed by a perfect conductor was calculated by the following equations [16].

$$\mathrm{RL(dB)} = 20\log_{10}\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \quad (1)$$

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

where RL is a ratio of reflected power to incident power in dB, Z_{in} is the normalized input impedance relative to the impedance in free space, d is the thickness of the absorber, and f and c are the frequency of microwave and the velocity of light, respectively. The RL value versus frequency can be evaluated at a specified thickness by knowing four parameters ε', ε'', μ' and μ''.

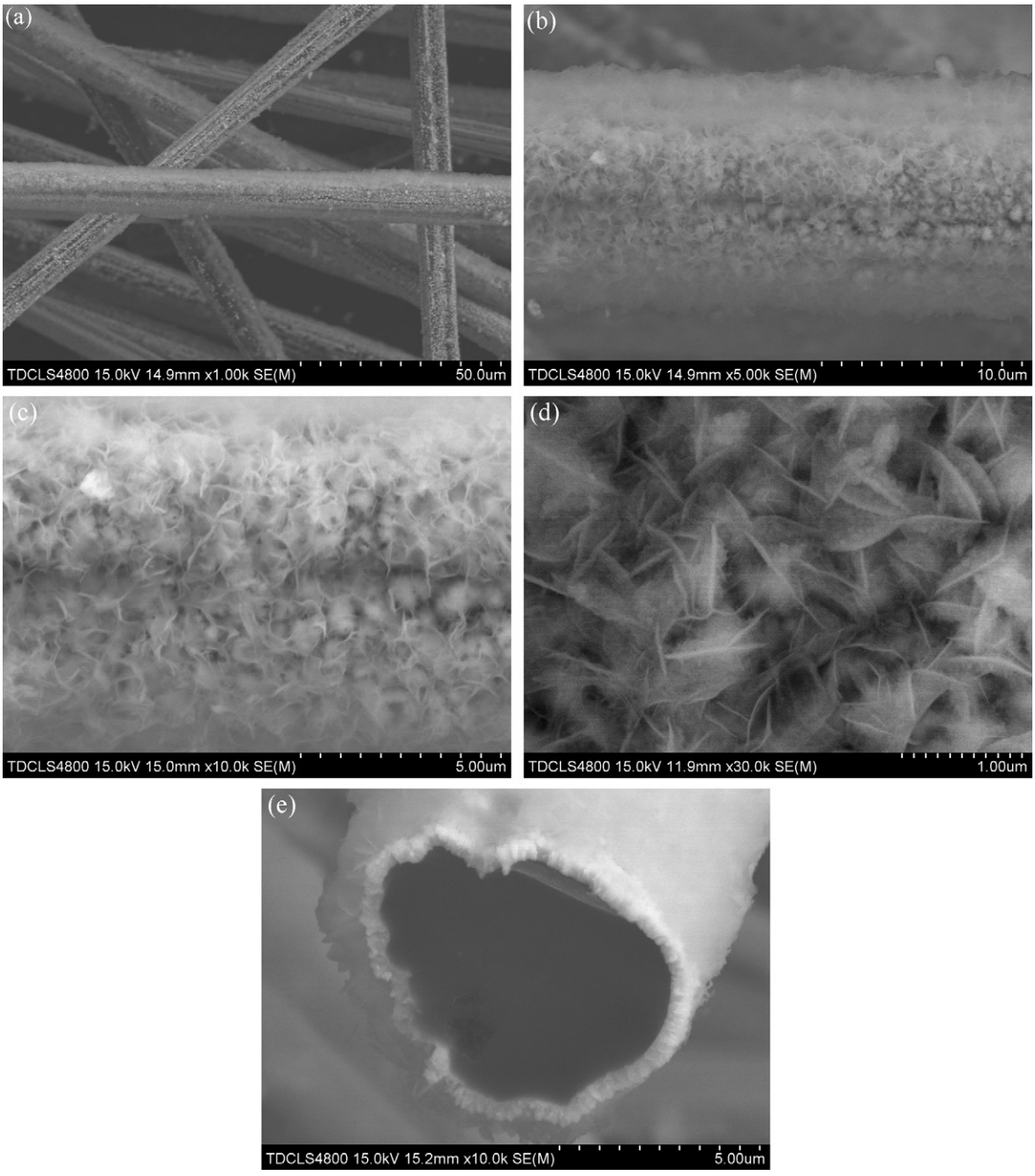

Fig. 2. SEM images (a–d) and the cross section SEM image (e) of the M-CF.

Table 1
Electromagnetic wave absorption properties of some recent reports, including the method, the absorption frequency range (GHz) of RL < −10 dB (and −20 dB), the minimum RL (dB) and the corresponding thickness (mm).

Specimen	Method	RL < −10	RL < −20	Minimum RL		Ref.
				Value	Thickness	
Carbon/Fe–Cu hybrids	Sol–gel/reduction	2–18	11–14	−21	7.5	[20]
FeCo nanoplates	Chemical reduction	3–13	4–11	−43	1.8	[7]
Fe_3Al/Al_2O_3	Mechano-chemical	5–18	7.2–17.4	−45	2.2	[21]
CuO/Co/carbon fiber	Electroless plating	8.7–18	12–13	−42.7	2	[22]
Fe_3O_4/carbon fiber	Electroless plating	3.5–10	5.5–7.8	−35	4.1	[23]
Fe–Co/carbon fiber	Electroplating	2–18	5.7–12.5	−48.2	1.7	This work

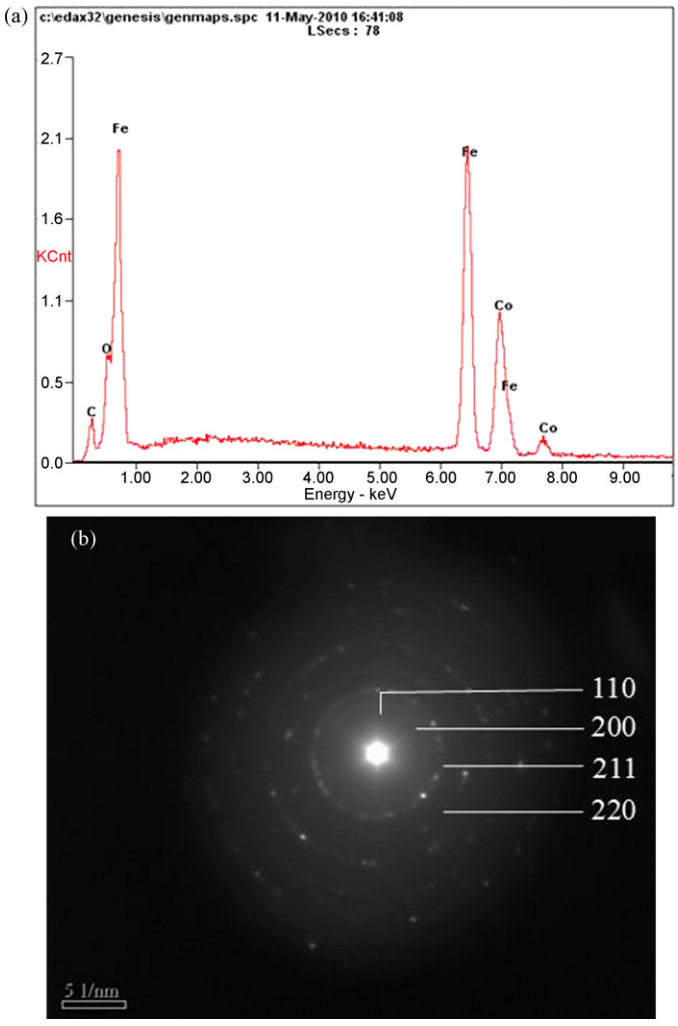

Fig. 3. EDS spectrum (a) and electron diffraction pattern (b) of the M-CF.

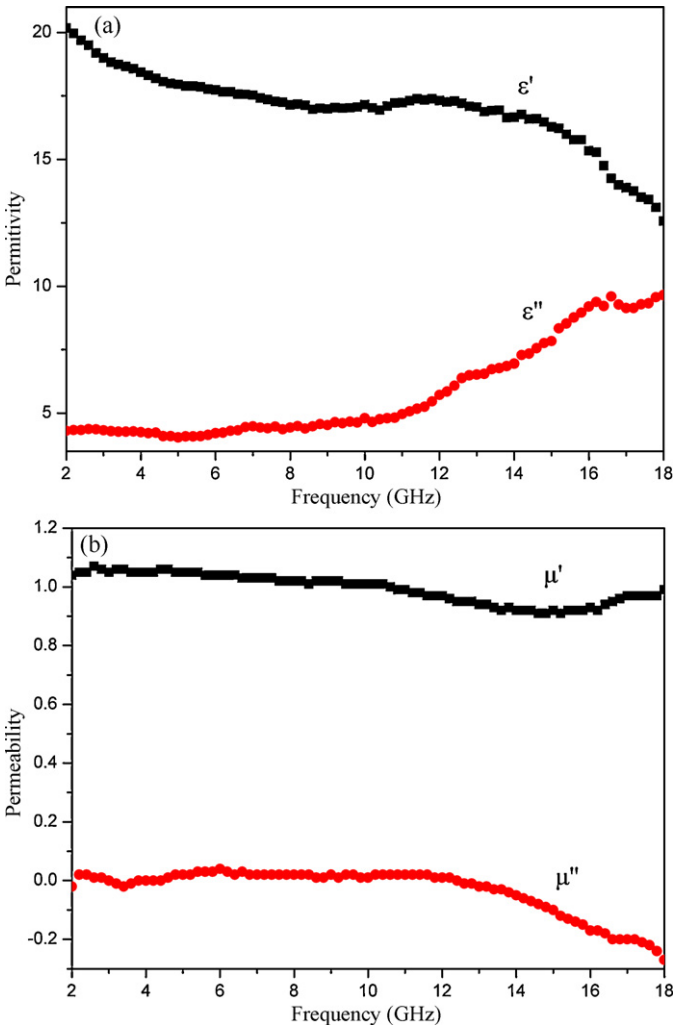

Fig. 5. Frequency dependence of the complex permittivity (a) and complex permeability (b) of the M-CF/paraffin composite.

According to Eqs (1) and (2), and using the specific parameters of the composite, the relationship between RL and frequency for the M-CF/paraffin composite is obtained and shown in Fig. 7. The relationship between the thickness of the composite (d) and frequency (f) is expressed by $f = nc/(4d\sqrt{|\varepsilon|\,|\mu|})(n = 1, 3, 5, 7, 9\ldots)$. So in Fig. 7 with increasing thickness, the value of RL shifts to lower frequency, suggesting that the range of absorption frequency can be easily tuned by adjusting the thickness of the composite. It can also be seen that the minimum RL value reaches −48.2 dB at 10.8 GHz with thickness of 1.7 mm. As illustrated in Fig. 7, over 90% microwave absorption (below −10 dB) can be achieved in the whole 2–18 GHz frequency range with thickness from 1.3 to 6 mm. When the thickness is between 1.5 and 3 mm, the minimum RL value reaches −20 dB, corresponding to 99% of electromagnetic wave attenuation which can be considered to be effective for practical applications.

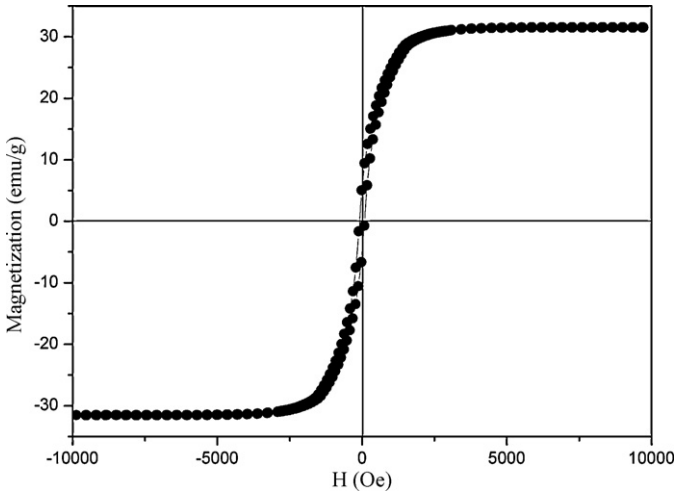

Fig. 4. M–H loop of the M-CF at room temperature.

Electromagnetic wave absorption is mainly due to dielectric and magnetic loss in this paper. When an electromagnetic wave travels through the M-CF/paraffin composite, the M-CF works as dipoles and generates an inductive current to cause current loss and energy dissipation. The EMA performance is also determined by matching relations between ε_r and μ_r [17]. It is necessary to point out that impedance matching plays an active effect on the strong and wide absorption since the dielectric and magnetic loss of the M-CF/paraffin composite are not high compared to other reported absorbers [18,19]. Moreover, there are many interfaces between the M-CF, the magnetic alloy coating and alloy sheets, so interfacial multipoles can contribute to the absorption of the composite.

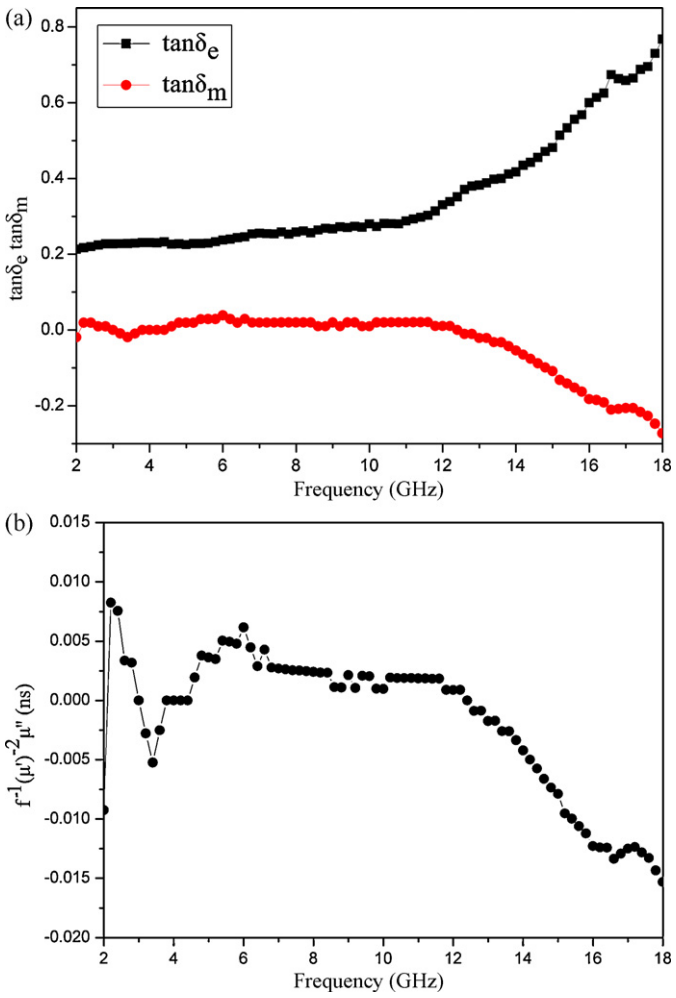

Fig. 6. Frequency dependence of the dielectric loss and magnetic loss of the M-CF/paraffin composite (a). Values of $f^{-1}(\mu')^{-2}\mu''$ versus frequency for the M-CF/paraffin composite (b).

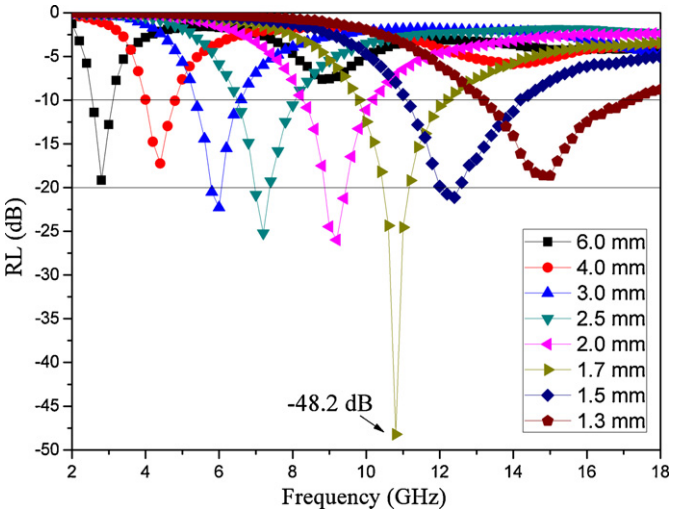

Fig. 7. Frequency dependence of reflection loss (RL) of the M-CF/paraffin composite at different thickness.

Table 1 shows EMA properties of some recent reports. It can be seen that the RL below −10 dB and −20 dB of this work are outstanding with a broad absorption frequency range. The minimum RL reaches −48.2 dB when the thickness is only 1.7 mm, which exhibit the strongest absorption with the thinnest thickness. The small mass fraction (30%) of the M-CF/paraffin composite makes it a light absorber. What is more, the electroplating method used in this work is simple, at low temperature, time saving and without using any toxic reductant or solvent, which are very important for practical production.

4. Conclusion

A facile conventional electroplating method was employed to prepare magnetic carbon fiber coated with Fe–Co alloy. The M-CF is covered with dense and uniform Co_3Fe_7 coatings with sheet-like surfaces and the coating thickness is about 0.5 μm. The saturation magnetization and coercivity of the magnetic carbon fiber are 31.5 emu/g and 87.1 Oe, respectively. The electromagnetic wave absorption of the M-CF/paraffin composite is mainly attributed to both dielectric and magnetic loss. The reflection loss below −10 dB covers the whole 2–18 GHz frequency range, and the bandwidth of absorption frequency below −20 dB reaches 6.8 GHz. The minimum reflection loss is −48.2 dB when the thickness of the composite is 1.7 mm. Fe–Co alloy coated carbon fiber by electroplating seems very attractive for a thin, light and easy for production EMA material with strong and wide absorption.

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