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Investigation on magnetic and microwave behavior of magnetite nanoparticles coated carbon fibers composite

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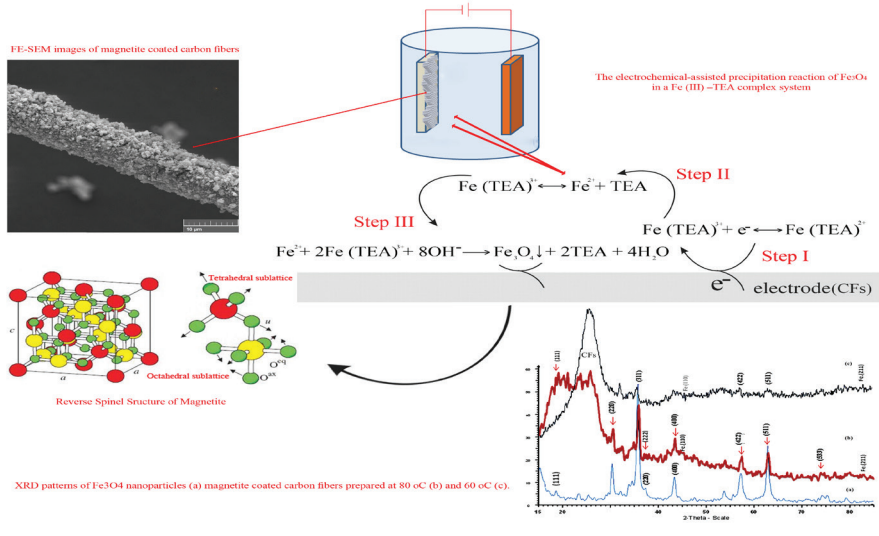
HIGHLIGHTS

- Fe_3O_4 nanoparticles were synthesized through a facile hydrothermal method.
- Nanomagnetite coated carbon fibers (MCCFs) were fabricated by electro-deposition method.
- The deposition time has a significant effect on reflection loss characteristics of MCCFs.
- The sequence of coating process is also an important parameter.
- A uniform deposition layer was observed after deposition in three steps of four minutes.

GRAPHICAL ABSTRACT



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ABSTRACT

Radar absorbing materials, i.e. magnetite (Fe_3O_4) coated carbon fibers (MCCFs) were fabricated by electro-deposition (ED) technique. Single spinel phase Fe_3O_4 nanoparticles were easily synthesized by hydrothermal method through the reduction of Fe (III) - Triethanolamine complex in an aqueous alkaline solution at 60-80°C. Uniform and compact Fe_3O_4 films were fabricated on nitric acid treated carbon fibers. A correlation between the magnetic and absorption properties of the specimens was made. It was found that the deposition time, and the sequences of the coating process have a significant effect on the reflection loss characteristics of the MCCFs. On the other hand, the temperature of the coating process strongly affected the composition of the thin film. MCCFs prepared at 80°C possesses a much higher loss factor than the one prepared at 60°C. The morphology, phases in the coating layer, magnetic properties and absorption behaviors of the MCCFs were examined using FE-SEM, XRD and permagraph, vector network analyzer (VNA), respectively. The highest reflection loss (−10 dB at 12.27 GHz) was observed for the sample deposited for four minutes. It was also found that a uniform deposition layer can be observed, when the sample deposited in three steps in which each step takes four minutes.

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1. Introduction

The applications of electromagnetic (EM) waves are widely spread in all fields of human's life, and most of them (personal computers, communication, medical and analytic devices) work in the microwave frequency range. In order to provide a solution to electromagnetic interference (EMI) shielding and radar cross section (RCS) reduction, the microwave absorbing materials are intensively developed in the recent years [1–6]. In general, microwave absorbing materials can be divided into two types: magnetic materials and dielectric materials. The absorbing characteristics of the materials depend on the frequency, layer thickness, complex permittivity ($\varepsilon' - j\varepsilon''$) and complex permeability ($\mu' - j\mu''$). The conventional microwave absorption materials such as ferrites and metal powders produced a large electric or magnetic loss. However, their fatal disadvantages like high density, high electrical conductivity, difficulty of manufacturing and relatively narrow absorption bandwidth restricts their applications [7-10]. As an ideal EM wave absorber, it should possess low weight, high EM wave absorption, broad width, tunable absorption frequency and multi-functionality. One of the ways to solve the problem is to combine the magnetic absorption materials with low density substrates. Recently, carbon based composite materials have been developed for microwave absorption applications. The carbon fiber (CF) radar absorption materials are composites with high strength and modulus, good carrying capacity, low electrical resistivity (10^{-2} Ωcm) and low radar cross-section [11-19]. The electro-deposition technique is widely applied in the preparation of metal composites due to its low cost, simple process, high shielding efficiency of coating, excellent environment stability and other notable features [6,12-15]. Nanostructure materials might be one of the most promising materials to enhance the EM wave absorption ability, owing to their high surface area, multi-reflection and larger dielectric or/and magnetic loss. As an important magnetic material, Fe_3O_4 has been extensively studied because of its excellent microwave absorption property [2,6,12,15, 20]. Shibing and co-workers prepared Fe_3O_4–carbon sphere composite by a hydrothermal method [2,20]. Xianguang et al. fabricated magnetite (Fe_3O_4) coated carbon fibers by Electro-deposition method [6]. Chengwen et al. employed low-temperature wet chemical preparation method to prepare Fe_3O_4 covered carbon fibers [12]. Rui et al. coated carbon fiber with nickel and Fe_3O_4 nanoparticles (Fe_3O_4-NPs) by co-electroplating [15]. These carbon fiber based composites exhibited excellent microwave absorption performances.

Consideration of unique properties of CFs and Fe_3O_4, we tried to prepare Fe_3O_4 films on CFs, which are expected to exhibit good radar-absorbing property. During this investigation, magnetite (Fe_3O_4) coated carbon fibers (MCCFs) were successfully fabricated by an electro-deposition technique and the effect of temperature, deposition time and coating uniformity related to the sequence of coating on the absorption behaviors were studied.

2. Materials and methods

2-1.Sample preparation

Nano-Fe_3O_4 was deposited in an alkaline solution of $Fe_2(SO_4)_3.xH_2O$ (12357 Sigma-Aldrich) stabilized by Triethanolamine (TEA) (2922 13 10 Merck). NaOH (2815 11 00 Merck) was used as a sedimentary medium. All chemicals were used as received without further purification. In order to preparation of complex Fe^{3+}-TEA solution, Firstly, 100 mL of 0.1 M NaOH solution was mixed with 100 mL of 0.1 M TEA aqueous solution at 60°C. Then, 50 mL of 0.1 M Fe^{3+} aqueous solution was added dropwise to the previous solution under stirring conditions. ED coating of magnetite on the surface of PAN based carbon fibers was performed in the mentioned solution. Before the electro-deposition, the CFs were treated with nitric acid (65 wt.%) for 4 h at room temperature in order to enhance the interfacial adhesion between the nano-Fe_3O_4 films and CFs [23], and then washed thoroughly and dried for 24 h at 120°C. Pure iron (99.95%) sheets were polished and served as the anode. In order to investigate the influence of temperature and find the optimum deposition time, ED coating was conducted for 2, 4, 6, 8 and 10 min under a constant electric current of 1 A at different temperatures of 60°C (MCCFs-1) and 80°C (MCCFs-2). In addition, after finding the optimum coating time and temperature, in order to improve the quality of electrodeposited magnetite coating, a sample was deposited electrochemically in three steps at 80°C (MCCFs-III) for 4 minutes. At the end of each step, to remove loosely coated magnetite parts, MCCFs were immersed in the stirring (100 rpm) distilled water for 20 s, then dried at 80°C for 30 min. All the final products were dried in the heating oven at 80°C for 1 h.

2.2.Sample characterization

The structure and morphology of the Fe_3O_4 nano-powders and MCCFs were characterized by X-ray diffraction (XRD) and scanning electron microscopy (FE-SEM (MIRA3 FEG-SEM, Tescan, Czech)). XRD measurements were made by X-ray diffraction (Siemens D5000 X-Ray diffractometer) using Cu-Kα radiation (λ = 1.5405 Å) from 15° to 85°. The magnetic properties of MCCFs were investigated with a permagraph (C300) at room temperature. The microwave absorption properties and reflection loss (RL) of MCCFs were measured over the frequency range of 8–12 GHz by a vector network analyzer (VNA model HP) at room temperature. For microwave absorption measurements, the MCCFs were cut into short fragments (2–3 mm in length) and mixed with epoxy resin through ultrasonic agitation. The mixtures poured into a rectangular homemade mold (with width and length 10mm× 21mm respectively). The weight fraction of MCCFs was 33.3% for single step coated samples (i.e. MCCFs-1 and MCCFs-2) and 60% for three steps coated samples (i.e. MCCFs-III). Thickness of the absorption layer was 1.7 mm in all samples.

3. Results and discussion

3.1. Composition of MCCFs and nano-powders

Figure 1 shows the typical XRD patterns for nano-powders, MCCFs-2 and MCCFs-1. Peaks dealing with Fe_3O_4, Fe and graphite are observed. In samples 1a and 1b the most peaks can be indexed as face centered cubic Fe_3O_4 with a lattice constant a=8.391 Å, which is in a good agreement with JCPDS, No. 19-0629. From, as it can be seen in the Figure 1a, the synthesized powder is pure Fe_3O_4. The corresponding peaks of Fe_3O_4 crystalline structure are (111), (220), (311), (222), (400), (422), (511), (440) and (533). In the Figure 1b, peaks due to Fe_3O_4 and graphite from CFs substrate are obvious. The peaks between 2θ =10° and 25° are due to the carbon fiber substrate. Nine diffraction peaks at 2θ = 18.96, 29.24, 36.66, 37.54, 44.84, 53.92, 57.4, 63.34 and 73.93° can be assigned to scattering from the (111), (220), (311), (222), (400), (422), (511), (440) and (533) planes of the Fe_3O_4 crystal lattice. Strong and sharp peaks suggests that the as-synthesized products are well crystallized. The Fe_3O_4 prepared by electro-deposition in this experiment is better than that previously reported [6, 21, 22]. Besides, Fe (JCPDS Card No. 06-0696) was also found in both patterns. The ratios of the first-strong peak intensities of Fe_3O_4 (311) and Fe (110) reflections (IM (311) /IFe (110)) are 1.13 and 2.1corresponding to MCCFs-1 and MCCFs-2, respectively. This indicates that Fe is inclined to be generated at lower temperature. The XRD patterns suggest that the temperature has an obvious influence on the composition of MCCFs.

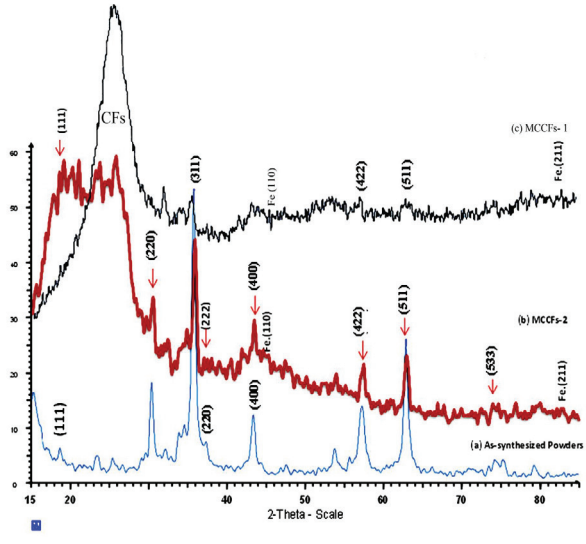

Fig. 1. XRD patterns of Fe_3O_4 nanoparticles (a) magnetite coated carbon fibers prepared at 80°C (b) and 60°C (c).

3.2. Morphology of Fe_3O_4 films and nanoparticles

Figure 2 shows the FE-SEM micrograph of as-synthesized Fe_3O_4 powder with an average crystalline size much smaller than 100 nm. Some Fe_3O_4 particles with the approximate size of 30 nm have been recognized in FE-SEM image. The other illustration of this figure is the tendency of particles to be agglomerated, accumulatively. High surface area occupied by surface charges is a reason for agglomeration of nano-powders. The electrochemical-assisted precipitation reaction of Fe_3O_4 in a Fe^{3+}–TEA system can be simplified by three consecutive steps: (1) electrochemical reduction of Fe^{3+}–TEA complex to produce Fe^{2+}-TEA, (2) the ligand dissociation of Fe^{2+}-TEA, and (3) the precipitation of Fe_3O_4 as outlined in Eqs. (1) – (3) [6,21].

$$Fe(TEA)^{3+} + e^- \rightleftharpoons Fe(TEA)^{2+} \quad (1)$$

$$Fe(TEA)^{2+} \rightleftharpoons Fe^{2+} + TEA \quad (2)$$

$$Fe^{2+} + 2Fe(TEA)^{3+} + 8OH^- \rightarrow Fe_3O_4 \downarrow + 2TEA + 4H_2O \quad (3)$$

The surface morphology of the MCCFs specimens deposited for 2, 4, 8, 12 and MCCFs-III are shown in Figure 3(a-e). As can be seen in the specimen deposited for 2 minutes (Figure 3a), the fibers are not thoroughly coated. By increasing the deposition period to 4 minutes (Figure 3b), a uniform coating layer is formed on the CFs, but still some discontinuities can be observed. In the samples deposited for 8 and 12 minute (3c and 3d respectively), a significant amount of agglomerations occurred, resulting in a significant amount of uncoated regions on the CFs. The MCCFs-III revealed a thick, continuous and uniform coating layer on the CFs (Figure 3e). This is identified as the most suitable deposition process.

3.3. Magnetic properties of MCCFs

The hysteresis loops of the CFs samples, coated in a single stage for 4 minutes (MCCFs-1 and MCCFs-2), and MCCFs-III are shown in Figure 4. The saturation magnetization (Js), coercivity (Hc) and residual magnetization (Br) values were 10 G, 243 Oe and 10 G for MCCFs-1, 150 G, 248 Oe and 30 G for MCCFs-2, and 230 G, 151 Oe and 40 G for MCCFs-III respectively. These results indicate that with the increase of deposition process temperature from 60 to 80°C, amount of deposited ferri-magnetic phase (Fe_3O_4) on the carbon fibers was increased, where these outcomes are in complete agreement with X-ray diffraction patterns (Figure 1). The Js values in the samples coated at 80°C for 2, 4, 8 and 12 minutes, were 40, 150, 120 and 110 G, respectively. Thus, by increasing the deposition time (up to 4 minutes) Js increased and then the Js values decreased. This is attributed to the initiation of cracks and failure in the coating layer [13-15], thus reducing the Fe_3O_4 ferri-magnetic phase in the coating layer.

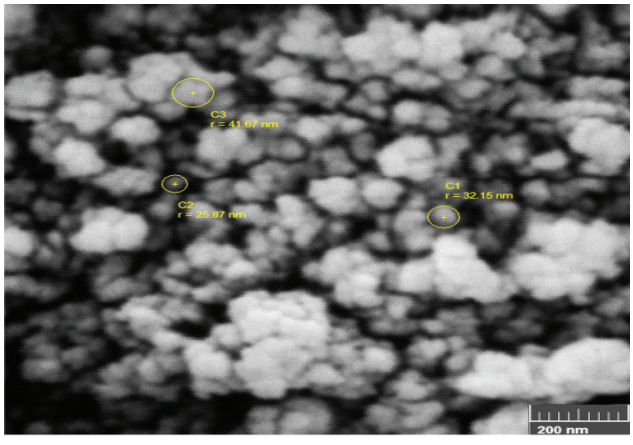

Fig. 2. FE-SEM image of the as- synthesized Fe_3O_4 nanoparticles

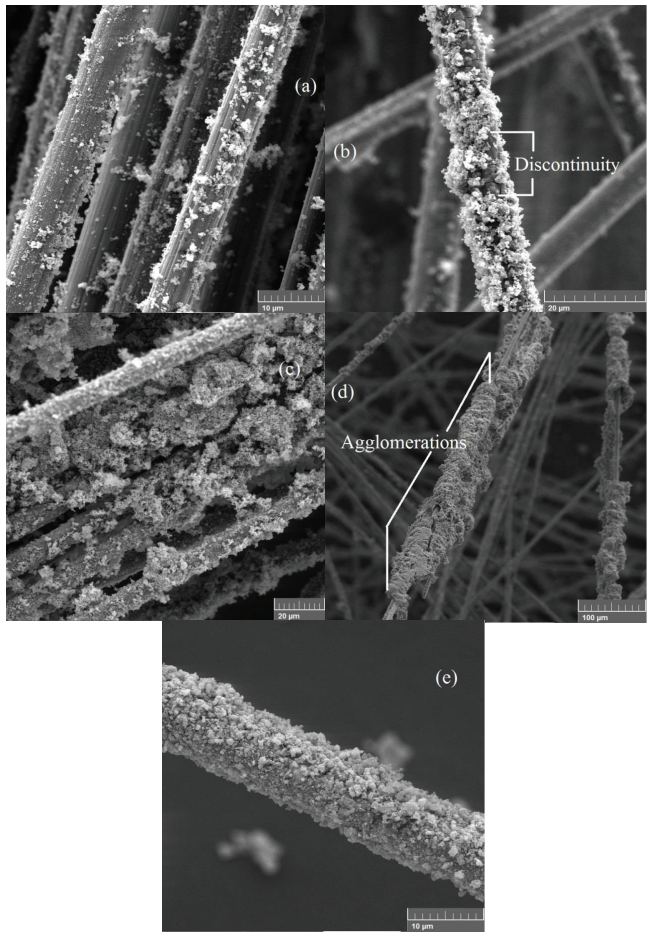

Fig. 3. FE-SEM images of magnetite coated carbon fibers coated in 2 (a) 4 (b) 8 (c) and 12 minutes (d) and prepared with a three step deposition process (e).

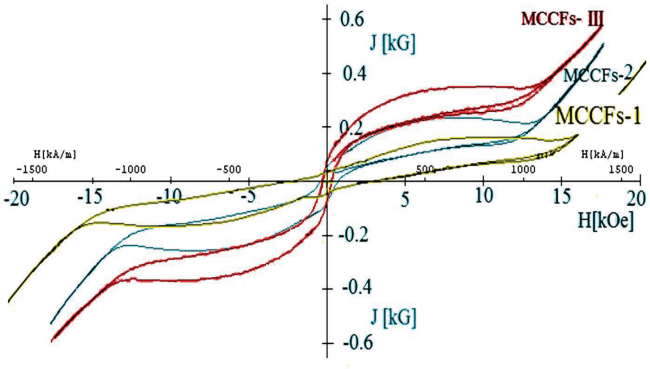

Fig. 4. The magnetic hysteretic loops of magnetite coated carbon fibers prepared at 80°C (MCCFs-2), 60°C (MCCFs-1) and prepared with a three step deposition process (MCCFs-III).

3.4. Microwave absorption properties of MCCFs

As previously described, in order to find the appropriate deposition time, four deposition times, i.e. 2, 4, 8 and 12 min were studied. Figure 5 shows the reflection loss (RL) for the specimens of (a-e) according to figure 4 and MCCFs-1 for a layer of 1.7 mm thickness. As we can see here the strongest RL of −10 dB at 12.27 GHz occurred in the sample deposited for 4 min (i.e. at MCCFs-2 coated for 4 min) where this result is in good agreement with SEM graph and magnetic behavior of MCCFs-2 coated for 4 min.

As previously observed in the samples coated in the single stage coating process, discontinued layer had formed along the carbon fiber's surface so the samples reflection loss behavior were weak. The RL of the MCCFs-III was found to be under -5 dB in whole range of X-band frequencies. Additionally, when the reflectivity is about -5 dB, the reflection loss of a microwave absorber will reach 69%.

4.Conclusions

Fe_3O_4 nanoparticles were successfully deposited on the carbon fibers by electro-deposition method at 80 ^oC. The results confirmed the significant influence of temperature on the composition and morphology of MCCFs. Fe_3O_4 films prepared at 80^oC (MCCFs-2) were uniform, dense and composed of numerous rectangle shape or faceted grains. As a component, Fe is inclined to be generated at lower temperatures (e.g. 60^oC). MCCFs-1 and MCCFs-2 exhibit a totally different microwave absorption behavior in 8–12 GHz frequency range. MCCFs-1 almost has no absorption properties. It's observed that Js value increased by increasing the deposition time (up to 4 minutes) and then its value decreased, dramatically. This could be due to the crack initiation and failure in the coating layer, followed by reduction of Fe_3O_4 ferri-magnetic phase. The optimum deposition time was found to be 4 minutes. Furthermore, it was found that coating with three deposition steps resulted in a uniform layer with an enhanced reflection loss in the whole X band (8-12 GHz). This simple trick makes it possible to separate the agglomerated parts of the coating and let the surface to be smooth and dense.

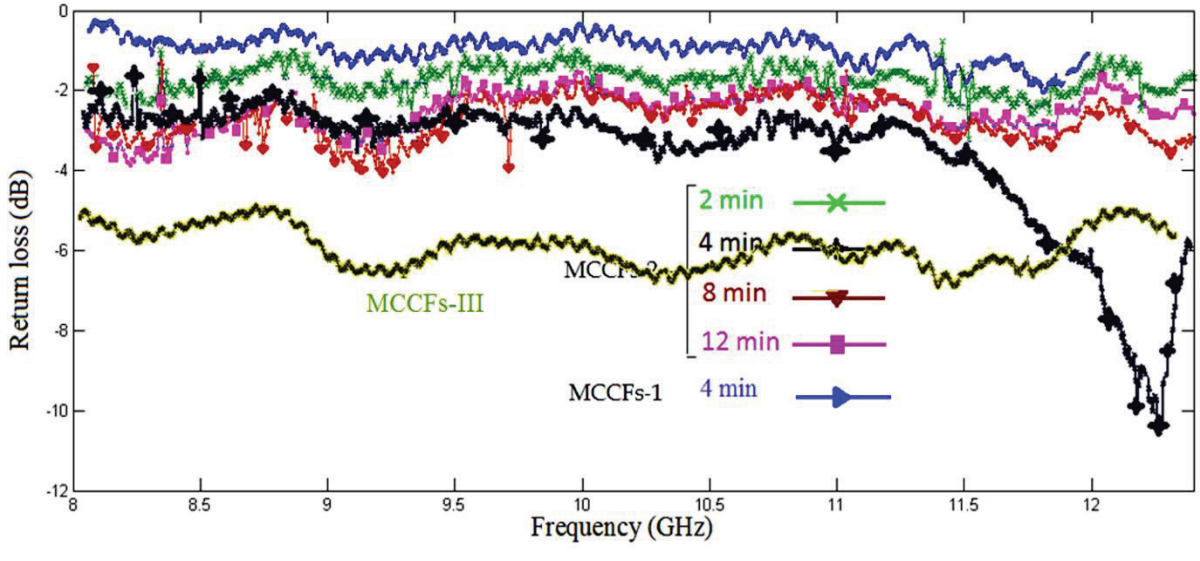

Fig. 5. Reflectivity curves of samples coated in 2-12 min and MCCFs-III.

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