Preparation and Microwave Absorption Properties of Iron Nanoparticles/Carbon Fiber/Epoxy Matrix Composites (Postprint)

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Abstract

Fe nanoparticles were prepared by direct current arc plasma method for use as microwave absorbers. The Fe nanoparticles were surface-modified with γ-aminopropyltriethoxysilane (KH550) and then uniformly mixed with epoxy resin at various ratios. Fe nanoparticle/carbon fiber/epoxy resin-based functional/structural integrated microwave absorbing composites were fabricated by adding carbon fibers to the mixture. The effects of absorber content and concentration gradient, carbon fibers, and plate structure on the microwave absorbing properties in the 2-18 GHz range were investigated. The results demonstrate that carbon fibers promote multiple reflection and absorption of electromagnetic waves within the structure, generating reflection loss peaks in the low-frequency band and enhancing microwave absorbing performance. As the Fe nanoparticle content increases, the absorbing capability gradually strengthens with the absorption peak shifting toward lower frequencies. During the epoxy resin curing process, gravity induces a gradient distribution of Fe nanoparticle concentration, causing differences in microwave absorbing performance between the front and back surfaces of the plate-shaped composite. This gradient distribution of absorber concentration facilitates the penetration and absorption of electromagnetic waves.

Full Text

Fabrication and Electromagnetic Microwave Absorbing Properties of Fe-Nanoparticles/Carbon Fibers/Epoxy Resin Based Composites

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Abstract: Fe-nanoparticles (NPs)/carbon fibers (CF)/epoxy resin (EP) based composites were designed and fabricated. The microwave absorbers Fe-NPs were prepared by the direct current (DC) arc-discharge plasma method and modified with silane coupling agent KH550. The reflection losses of composites were measured in the frequency range of 2-18 GHz and the effects of Fe-NPs, CF and the geometry feature of test plates on the microwave absorbing properties were investigated. Results show that reflection loss peaks appear at low frequency and the microwave absorbing properties are enhanced due to the addition of CF. With increasing mass fraction of Fe-NPs the microwave dissipation increases and the reflection loss peaks move towards the low frequency. The concentration gradient of Fe-NPs in EP matrix was caused by gravity during the preparation process and it causes reflection loss differences between the two surfaces of a plate, which is beneficial for microwave to enter the composite plate and be absorbed by properly setting the plate.

KEY WORDS: composite, reflection loss, Fe nanoparticles, carbon fiber

Introduction

With the development of various electronic devices, electromagnetic interference has become increasingly significant, while advances in radar technology demand better stealth performance for weapons and equipment. Consequently, the development of electromagnetic wave shielding and absorbing materials has grown increasingly important, attracting serious attention. Electromagnetic wave absorbing materials maximize the absorption and dissipation of incident waves and are divided into two categories: coating-type absorbing materials and structural absorbing materials. Coating-type absorbing materials offer advantages such as convenient application, flexibility, adjustability, and good absorbing performance, but suffer from poor weather resistance, easy peeling, and require heavy maintenance. Structural absorbing materials exhibit excellent absorbing performance and mechanical properties, can both bear loads and reduce radar cross-section (RCS), and offer the benefits of light weight and high strength [1].

In gradient structural absorbing materials, the absorber is distributed in a gradient pattern, which better satisfies impedance matching at the incident surface and achieves absorption of electromagnetic waves over a wider frequency band. Masahiro Itoh et al. [2] prepared coaxial samples with outer diameter 7.00 mm and inner diameter 3.04 mm using carbonyl iron and permalloy (Fe-47Ni) as absorbers via centrifugal mold technology, demonstrating that gradient distribution of absorbers provides better broadband absorbing performance than uniform distribution. Li Xiaomin et al. [3] prepared gradient absorbing composite plates using E-51 epoxy resin as matrix and Fe78Si13B9 powder as absorber, achieving reflection loss below -4 dB across 2.7-18 GHz when the absorber-to-epoxy mass ratio was 6:1. Guan Denggao et al. [4] prepared gradient electromagnetic shielding materials of nickel/nickel-zinc ferrite epoxy resin, which showed reflection loss reduced by an average of 6-8 dB and absorption loss increased by an average of 6-14 dB compared with non-gradient materials at frequencies below 1 GHz. Wang Zhihui et al. [5] prepared single-layer, double-layer, and triple-layer coating absorbing materials using nano-nickel ferrite composite cobalt powder and carbonyl iron powder as absorbers via electroless plating, finding that double-layer composite coatings showed significantly improved low-frequency absorbing performance compared with single-layer coatings, while triple-layer composite coatings exhibited even better performance.

This paper employs magnetic Fe nanoparticles as microwave absorbers, leveraging the superior properties of nanomaterials such as small size, high surface energy, quantum size effects [6], and the high Snoke limit [7] and high permeability of magnetic metals to fabricate Fe nanoparticles/carbon fibers/epoxy resin based functional/structural integrated composites and investigate their electromagnetic wave absorption properties and mechanisms. Fe nanoparticles possess excellent electromagnetic response characteristics and absorbing performance [8], while carbon fibers have strong reflection effects on electromagnetic waves [9].

1.1 Preparation and Surface Modification of Fe Nanoparticle Absorbers

Fe nanoparticle microwave absorbers were prepared by the DC arc plasma method [8], using a tungsten rod as cathode and bulk Fe material placed on a water-cooled copper seat as anode. After evacuating the generation chamber, 0.02 MPa argon and 0.02 MPa hydrogen were introduced as reaction gases, and DC arc plasma was used as heat source to evaporate the Fe block and prepare Fe nanoparticles.

The phase composition of the nanopowders was determined using an EMPYREAN X-ray diffractometer (XRD) with Cu Kα radiation (λ=0.154 nm) at 40 kV tube voltage, obtaining diffraction patterns in the range of 20°<2 <90°. The morphology of nanoparticles was observed using a TecnaiG220 S-Twin transmission electron microscope (TEM).

The Fe nanoparticles were surface-modified with γ-aminopropyltriethoxysilane (KH550) as follows: An appropriate amount of 10% (mass fraction) KH550 alcohol solution was poured into a beaker containing Fe nanoparticles at a mass ratio of mFe:mKH550=20:1. A small amount of deionized water was added and dilute hydrochloric acid was dropped in to adjust the mixed solution pH to 5, then the mixture was subjected to ultrasonic vibration and mechanical stirring in a 60°C water bath for 60 min. The mixture was then centrifuged and water-washed multiple times until the pH reached 7, and finally dried in a vacuum oven at 80°C for 12 h.

FT/IR-430 infrared spectrometer (FTIR) was used to analyze the Fourier infrared absorption spectra of Fe nanoparticles before and after modification and KH550 to confirm the modification effect.

1.2 Fabrication of Flat Fe Nanoparticles/Carbon Fibers/Epoxy Resin Based Composites

Using the modified Fe nanoparticles and 120 g epoxy resin E51 as baseline, curing agent methylhexahydrophthalic anhydride (MeHHPA) and accelerator (PPh3) were added at a ratio of mE51:mMeHHPA:mpph3=100:80:1 to prepare mixed solutions with Fe nanoparticle mass fractions of 0%, 20%, and 30%. As shown in the preparation flow chart [Figure 1: see original paper], a mold with inner dimensions of 20 cm$×20*cmwaspreheatedinadryingovento*110°*C*(*Fig.*1*a*);*halfofthemixedsolutionwaspo*
cm was placed horizontally in the mold, and the other half of the resin solution was quickly poured in (Figs. 1c and d); the mixed resin solution was cured following the process of 110°C/0.5 h + 123°C/1.5 h + 134°C/2 h. Figure 1e shows the schematic cross-section of the prepared sample, and Fig. 1f shows the top view of the actual sample. Table 1 lists the thicknesses of carbon fiber/epoxy resin based composite plates with different Fe nanoparticle contents.

To compare the effect of carbon fibers on the absorbing properties of composite plates, reference samples without carbon fiber fabric were prepared. The surface contacting air during curing was designated as the top surface, corresponding to the low Fe nanoparticle concentration side; the other surface contacting the mold was designated as the bottom surface, corresponding to the high Fe nanoparticle concentration side.

A Nova NanoSEM 450 field emission scanning electron microscope (SEM) was used for elemental line scan analysis of the composite cross-section.

1.3 Measurement of Microwave Absorbing Properties of Structural Nanocomposites

According to national standard GJB2093-94, the reflection losses of standard-size 20 cm$×$20 cm composites were measured in the 2-18 GHz range using the arch reflection method with an Agilent 8720B vector network analyzer in a microwave anechoic chamber. The sample stage and surrounding walls were covered with high-efficiency absorbing pyramid material with background reflection below -40 dB. Figure 2 [Figure 2: see original paper] shows the schematic diagram of the arch reflection testing system. To compare the difference in absorbing performance when electromagnetic waves were incident from the low-concentration side versus high-concentration side, reflection losses were measured with both the top and bottom surfaces as incident surfaces, while maintaining consistent carbon fiber orientation.

2.1 Structure and Morphology of Fe Nanoparticle Absorbers

The X-ray diffraction pattern of unmodified Fe nanoparticles [Figure 3: see original paper] shows three main peaks corresponding to the standard diffraction pattern of α-Fe (b.c.c) with a lattice constant of 0.28664 nm. Using the Scherrer formula D=0.9λ/βcos (where D is particle size (nm), λ is X-ray wavelength, β is half-peak width, and   is diffraction angle), the Fe crystallite size was calculated to be approximately 65.7 nm.

The TEM image of unmodified Fe nanoparticles [Figure 3: see original paper] reveals spherical particles with a surface oxide layer several nanometers thick. During preparation, passivation was performed to reduce the surface activity of Fe nanoparticles, resulting in a thin oxide layer that did not appear in the XRD pattern.

2.2 Surface Modification of Fe Nanoparticles

Due to their large specific surface area, high surface energy, and high particle activity, nanoparticles easily agglomerate, are difficult to disperse, and have poor matrix bonding. Therefore, surface modification is necessary. The surface modification mechanism of Fe nanoparticles with KH550 is shown in [Figure 4: see original paper]. After modification, the Fe nanoparticle surfaces bear amino functional groups. After ionization, the amino groups maintain electrostatic repulsion between particles while enhancing steric hindrance, greatly improving the dispersion stability of Fe nanoparticles [10].

To visually demonstrate the modification effect, equal masses of unmodified and modified Fe nanoparticles were added to separate bottles A and B containing equal volumes of anhydrous ethanol. After ultrasonic vibration for 20 min, the dispersion was allowed to stand and the settling behavior was recorded. The photograph after 40 min of standing [Figure 6: see original paper] shows that unmodified Fe nanoparticles had significantly settled (Fig. 6A), while modified Fe nanoparticles remained dispersed in ethanol (Fig. 6B), indicating greatly improved dispersibility.

2.3 Compositional Analysis

Figure 5 [Figure 5: see original paper] presents the infrared spectra of surface modifier KH550 and Fe nanoparticles before and after modification. The peak near 2970 cm^{-1} corresponds to asymmetric stretching vibration of methyl groups, while peaks at 2920 cm^{-1} and 2900 cm^{-1} correspond to asymmetric and symmetric C-H stretching vibrations, respectively [11]. The peak at 1390 cm^{-1}

corresponds to C-Si-O [12], and the peak at 1050 cm^{-1} may be Si-O-Fe generated by the reaction between KH550 and hydroxyl groups on the Fe nanoparticle surface. The peak at 1080 cm^{-1} is the symmetric stretching vibration peak of Si-O-C [11].

Compared with unmodified Fe nanoparticles, new vibration peaks appear near 1050 cm^{-1}, 1080 cm^{-1}, 1390 cm^{-1}, and 2970 cm^{-1} in the spectrum of modified Fe nanoparticles. Comparison with the infrared spectrum of KH550 confirms that KH550 has been successfully grafted onto the Fe nanoparticle surface.

Figure 7 [Figure 7: see original paper] shows the SEM test results for the composite containing 20% Fe nanoparticles. Figure 7a shows the SEM line scan area, with the top surface being the top side. The red, green, and blue lines represent C, O, and Fe elements, respectively, where C shows continuous peaks at the carbon fiber fabric positions while O is uniformly distributed. Figure 7b shows the Fe element distribution, revealing that Fe concentration gradually increases from the top surface inward until reaching the carbon fiber. Due to gravity, Fe nanoparticles naturally settled during the epoxy resin curing process, resulting in a gradient distribution in the composite plate.

2.4 Microwave Absorbing Properties of Flat Fe Nanoparticles/Carbon Fibers/Epoxy Resin Based Composites

Using the top surface (low Fe nanoparticle concentration side) of composite plates as the incident surface, reflection losses were measured. The red and black curves correspond to composite plates with and without carbon fibers, respectively. Figures 8a-c [Figure 8: see original paper] present the microwave absorbing performance test results for composite plates with different Fe nanoparticle contents. The black curve in Fig. 8a shows the reflection loss of epoxy resin plate without Fe nanoparticles, with a reflection loss value of 0, indicating that epoxy resin has no loss for electromagnetic waves and is an excellent wave-transparent material. The reflection loss of carbon fiber/epoxy resin composite plates generally decreases with increasing frequency, with minimum values greater than -9 dB, demonstrating that carbon fibers as a reflective layer also possess certain electromagnetic wave loss capability that strengthens with frequency.

Epoxy resin based composite plates containing 20% Fe nanoparticles show some absorbing performance at high frequencies, but the loss capability is not optimal. With increasing Fe nanoparticle concentration, the absorbing capability gradually strengthens and the absorption peak shifts to lower frequencies. This result is consistent with the reflection pattern shown in Fig. 8.

Comparative analysis of Figs. 8a-c reveals that the absorbing performance of composite plates without carbon fiber fabric is closely related to Fe nanoparticle content, with improved high-frequency performance as Fe nanoparticle addition increases. Previous research indicates that as Fe nanoparticle concentration increases, both the real and imaginary parts of complex permittivity and complex permeability of Fe nanoparticles/paraffin composite samples increase to some extent [13]. According to the Bruggeman equation [14], as Fe nanoparticle concentration increases, the complex permittivity and complex permeability of epoxy resin based composites increase. When Fe nanoparticle concentration reaches a certain value, a network structure forms in the epoxy resin, enhancing electromagnetic wave scattering and reflection and strengthening the composite’ s absorption capability. Composite plates with added carbon fibers show significantly improved absorbing performance, with peak frequencies shifting to lower frequencies. As shown in Fig. 8a, carbon fibers possess certain electromagnetic wave loss capability and can promote multiple reflections of electromagnetic waves within the composite plate, increasing the electromagnetic absorption probability and loss efficiency of the absorber.

Composite plates with the same composition but added carbon fiber fabric show a reflection loss peak at 8.2 GHz with a minimum value of -9.3 dB [Figure 8: see original paper]. This result indicates that carbon fiber addition significantly changes the frequency characteristics of composite plate absorption, shifting the absorption peak to lower frequencies without substantially changing the absorption value. Figure 8c shows that epoxy resin based composite plates containing 30% Fe nanoparticles exhibit gradually enhanced absorbing capability. After adding carbon fibers, the reflection loss shows a peak at 6 GHz with a minimum value of -17.3 dB, demonstrating significantly improved absorbing performance.

To investigate the effect of Fe nanoparticle concentration gradient on composite plate absorbing performance, reflection losses were measured using the bottom surface (high Fe nanoparticle concentration side) as the incident surface and compared with top surface results. Figure 9 [Figure 9: see original paper] shows that the bottom surface reflection losses of Fe nanoparticles/carbon fibers/epoxy resin composite plates exhibit two absorption peaks across 2-18 GHz. The peak values shift to lower frequencies as Fe nanoparticle concentration increases, consistent with the top surface reflection pattern.

Table 2 lists the reflection loss values and corresponding frequency ranges for the top and bottom surfaces of Fe nanoparticles/carbon fibers/epoxy resin composite plates. The bottom surface shows reflection loss values below -5 dB (microwave absorption rate >68.4%) across a large frequency range. For the composite plate containing 20% Fe nanoparticles, the frequency ranges are 4.3-8.6 GHz and 13.5-18 GHz, corresponding to C-band and Ku-band, respectively. For the composite plate containing 30% Fe nanoparticles, the frequency range is 2.9-17.1 GHz, covering most of C-band, X-band, S-band, and Ku-band, essentially covering the full band. This indicates that using the high Fe nanoparticle concentration side as the incident surface provides better absorbing performance. The difference between top and bottom surface reflection loss curves is greater for the 30% Fe nanoparticles composite plate because gravity creates a larger concentration distribution gradient at higher Fe nanoparticle concentrations.

According to the formula fm=nc/(4tm| r r|) (where fm is matching frequency, tm is matching thickness, c is speed of light in vacuum, r and r represent relative permittivity and relative permeability of the sample, and n=1, 3, 5, 7, 9,

···), absorption frequency is affected by electromagnetic parameters and plate thickness. Based on the Bruggeman equation [14], as Fe nanoparticle content increases, the relative permittivity and relative permeability of carbon fiber/epoxy resin composites gradually increase. This is the primary reason for the absorption frequency shifting to lower frequencies as absorber content increases. Table 1 lists the thicknesses of carbon fiber/epoxy resin based composite plates with different Fe nanoparticle contents, showing that plate thickness increases with absorber content for equal amounts of epoxy resin, which is a secondary cause of low-frequency shifting. Comparison also reveals that it is difficult to add larger proportions of Fe nanoparticles to epoxy resin alone for further performance improvement, while carbon fiber addition can enhance absorbing performance.

Conclusions

1. After modification with KH550, the dispersibility of Fe nanoparticles was greatly improved.
2. Fe nanoparticles/epoxy resin composite plates without carbon fiber fabric showed poor absorbing performance, with some improvement in high-frequency performance as Fe nanoparticle content increased.
3. After adding carbon fiber fabric, Fe nanoparticles/carbon fibers/epoxy resin composite plates exhibited absorption peaks at low frequencies with significantly improved absorbing capability. In the coexisting system of Fe nanoparticles and carbon fibers, carbon fibers can promote multiple reflections of electromagnetic waves, increasing the electromagnetic absorption probability and loss efficiency of the absorber. The composite plate with 30% Fe nanoparticles achieved absorption greater than 98% at 6 GHz. The improvement in low-frequency performance stems from increased absorber content and corresponding increased composite plate thickness.
4. In Fe nanoparticles/carbon fibers/epoxy resin based composites, the gradient distribution of absorber concentration is an important factor affecting absorbing performance.

References

1. LIU Shunhua, LIU Junmin, DONG Xinglong, *Electromagnetic Shielding and Absorbing Materials* (Beijing, Chemical Industry Press, 2006) p.255
2. I. Masahiro, T. Masao, S. Fumiyoshi, M. Ken-ichi, Broadband electromagnetic wave absorbers prepared by grading magnetic powder density, *Journal of Applied Physics*, 108, 063911 (2010)
3. LI Xiaomin, ZHU Zhenghou, ZHENG Xialian, LIU Jilei, HUO Jia, Study on the SMC molding technology and absorbing properties of new-type absorbing composite, *Journal of Functional Materials*, 3(44), 337 (2013)
4. GUAN Denggao, HUANG Wanxia, MAO Jian, JIANG Yu, CHEN Jiazhao, TU Mingjing, Study on shielding functionally gradient materials

with lower reflection loss and high absorption loss for electromagnetic wave, *Journal of Functional Materials*, 6(34), 676 (2003)

5. WANG Zhihui, LUO Wu, XIA Zhidong, HU Chuanxin, Study on multilayer radar wave absorbing coatings, *Ordnance Material Science and Engineering*, 29(1), 61 (2006)
6. CAO Guozhong, WANG Yingzhu, Translated by DONG Xinglong, *Nanostructures and Nanomaterials: Synthesis, Properties and Applications* (Beijing, Higher Education Press, 2012) p.14, p.329
7. J. L. Snoke, *New Developments in Ferromagnetic Materials* (Amsterdam, Elsevier, 1947) p.25
8. B. Lv, X. L. Dong, H. Huang, X. F. Zhang, X. G. Zhu, J. P. Lei, J. P. Sun, Microwave absorption properties of the core/shell-type iron and nickel nanoparticles, *Journal of Magnetism and Magnetic Materials*, 320, 1106 (2008)
9. C. K. Po, G. L. Dai, Composite sandwich constructions for absorbing the electromagnetic waves, *Composite Structures*, 87, 161 (2009)
10. MA Chengyin, WU Yuanxiong, TANG Pingsheng, MENG Jie, Preparation and surface modification of nano-SnO2, *Chinese Journal of Applied Chemistry*, 26(2), 198 (2009)
11. I. J. Bruce, T. Sen, Surface modification of magnetic nanoparticles with alkoxysilanes and their application in magnetic bioseparations, *Langmuir*, 21, 7029 (2005)
12. B. G. Wei, Q. Chang, C. X. Bao, L. Dai, G. Z. Zhang, F. P. Wu, Surface modification of filter medium particles with silane coupling agent KH550, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 434, 276 (2013)
13. SHI Mengshi, *The Fabrication and Properties of Fe/epoxy Nanocomposites*, Master Dissertation, Dalian University of Technology (2012)
14. A. Berthault, D. Rousselle, G. Zerah, Magnetic properties of permalloy microparticles, *Journal of Magnetism and Magnetic Materials*, 112, 477 (1992)

Note: Figure translations are in progress. See original paper for figures.