Microwave electromagnetic characteristics of polymeric composite materials containing carbonyl iron and MWCNT/Ferrites

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Abstract. Microwave electromagnetic characteristics of radiomaterials based on carbonyl iron with the addition of multi-walled carbon nanotubes or ferrites were investigated. On the basis of the obtained measurement results, the frequency dependences of the reflection coefficients for the samples of composite materials were calculated. Comparison of calculations with the results of the experiment is presented. Adding 2 wt.% multi-walled carbon nanotubes to a composite with 40 wt.% carbonyl iron is equivalent to increasing the concentration of carbonyl iron to 60 wt.%, which significantly reduces the consumption of materials and the weight of the composite. The results obtained make it possible to characterize the materials under study as effective absorbers of electromagnetic radiation in the microwave frequency range.

1. Introduction
Every year there are more and more modern wireless devices that operate in the microwave frequency range. This leads to a number of problems. Such problems include the threat to biological objects (electromagnetic ecology), protection against interception of transmitted information (electromagnetic safety), ensuring electromagnetic compatibility, etc. To solve the above problems, it is reasonable to use shielding or absorbing coatings. They can be used to ensure the electromagnetic compatibility of devices and the matching of the receiving-transmitting path, to protect biological resources and objects from exposure to electromagnetic radiation, to protect computer information processing systems from unauthorized access and to reduce the radar visibility of military and civilian objects. To date, there is no single-component material with high absorbing and low reflectivity in a wide frequency band of the microwave range. Therefore, the use of composites as a basis for radio absorbers is becoming increasingly important. The use of such materials is of particular interest due to the fact that by mixing materials we can achieve properties that the components of the composite do not possess separately from each other. It is quite convenient to work with composite materials, since various polymers (paints, varnishes, plastics, epoxy resins, polyethylene structures, silicone, etc.) can be used as a binder (matrix) [1]. They can be easily processed and applied to a particular surface. As fillers for modern high-frequency radio composites various ferromagnets and ferrimagnets [2 – 4], carbon materials (carbon black, graphene, nanodiamonds, single-wall and multi-walled nanotubes, onion structures) [5...
‐7], ultrafine metal powders (most often carbonyl iron) [8, 9] and microwires [10] are most often used. Fillers are used both separately and together [11, 12].

Thus, the development and study of materials and coatings based on carbonyl iron with multiwalled carbon nanotubes and ferrites are of great interest and also have great practical significance.

2. Materials and Methods
The structure of the materials was determined by X-ray analysis. Images were obtained on X-Ray Diffractometer Shimadzu XRD 6000 with copper radiation (CuKα) and Wavelength Dispersive X-Ray Fluorescence Spectrometer XRF-1800. Powder samples and composites samples were studied. Tube voltage of 40 kV, anode current of 30 mA, goniometer speed when shooting is 2 deg/min, X-ray diffraction is 2θ=(20÷60)°.

The structure of material was studied by optical microscope and by scanning electron microscopy. Electron-microscopic measurements were carried out with a scanning electron microscope with a focused ion beam QUANTA 3D.

2.1. Materials
The choice of binder depends on the purpose of the composite coatings. As the resin base may be: silicone sealants, plastics, paints, varnishes, epoxy resins, natural and synthetic rubbers. In our case an EDP-20 grade epoxy resin with a hardener of polyethylene polyamine (PEPA) was chosen.

Powders of various radio materials were used as fillers. The main component of the radio composite was an industrially manufactured carbonyl iron (CI) of mark P-100. Additionally, a ferrimagnet (Fer) and multiwalled carbon nanotubes (MWCNT) were used. The obtained images of the microstructure of ferrite and MWCNT are shown in figure 1.

![Figure 1. TEM images of the powders of ferrite (a) and MWCNT (b).](image)

Ferrite is a magnetite spinel structure with the chemical formula Fe₃O₄. It was manufactured by the method of self-propagating high-temperature synthesis and contained up to 96 wt.% of the main phase. Later it was pressed and ground into a powder with a particle size of less than 250 microns. Used MWCNTs were synthesized by catalytic gas-phase deposition of ethylene in the presence of a FeCo catalyst at a temperature of 680 °C [13]. They have a high degree of purity and content of the main phase (Table 1). Metal impurities are the residue of the catalyst encapsulated inside the nanotubes.

| Characteristic value                        | Material | CNT content | Average diameter of nanotubes (diameter range) | Metal impurities | Outer specific surface | Number of layers CNT (wall thickness) |
|--------------------------------------------|----------|-------------|-----------------------------------------------|------------------|------------------------|--------------------------------------|
|                                            | MWCNT    | More than 97.5 wt.% | 9.4 nm (4 – 21 nm)                           | < 1.7 wt.% (FeCo, Al₂O₃) | 320 m²/g                | 7-9 layers (4.0 nm)                      |
2.2. Obtaining experimental samples
Manufactured samples are plane-parallel washers for measurement in a coaxial cell. Sample sizes: outer diameter \(d_{\text{out}} = 7\) mm, internal diameter \(d_{\text{in}} = 3\) mm, thickness \(h = 2.25\) mm. The sample preparation scheme is shown in figure 2. For the production of the samples a thorough weighing of their component parts (filler and binder) was produced on a Shimadzu AUX-320 scales (error \(\approx 0.5\) mg). Thereafter, the composite components were mixed in the appropriate parts (by weight). Then the mixture was blended until homogeneous state (using an ultrasonic disperser and magnetic stirrer). Ultrasonic treatment was carried out for 3 minutes at a power of 80 watts. Manufactured mixture was placed in a special form. The final composite sample is of a toroidal shape with various thickness. Polymerization of the finished product was carried out for several hours at room temperature.

![Figure 2. Production of samples of composite materials.](image)

Thus, 9 experimental samples of composites for measurements were made. Their main characteristics are presented in table 2.

| Sample No. | Content of epoxy resin, wt.% | Content of the filler, wt.% | Carbonyl iron | MWCNT | Ferrite |
|------------|------------------------------|----------------------------|---------------|-------|--------|
| 1          | 60                           | 40                         | –             | –     | –      |
| 2          | 50                           | 50                         | –             | –     | –      |
| 3          | 40                           | 60                         | –             | –     | –      |
| 4          | 30                           | 70                         | –             | –     | –      |
| 5          | 20                           | 80                         | –             | –     | –      |
| 6          | 59                           | 40                         | 1             | –     | –      |
| 7          | 58                           | 40                         | 2             | –     | –      |
| 8          | 40                           | 40                         | –             | 20    | –      |
| 9          | 20                           | 40                         | –             | 40    | –      |

2.3. Measuring equipment
The waveguide method using a coaxial measuring cell was used to study the behavior of electromagnetic characteristics. As the instrumental basis of the experimental setup, the vector network analyzer P4M-18 produced by the company “Micran” was used. This device allows measurements in the frequency range from 0.01 to 18.00 GHz. The experimental study was carried out according to the measurement scheme “for pass” and “for reflection” (figure 3).

The “pass” scheme (figure 3a) is used to measure the scattering matrix coefficients \(S_{11}, S_{12}, S_{21}\) и \(S_{22}\), in other words, to measure the transmission and reflection coefficients of a wave through a sample placed in a coaxial cell, while the wave passes in one direction and in the opposite. On the
basis of the S-parameters obtained, taking into account the change in their phase, it is possible to calculate the spectra of the complex magnetic and the dielectric constant. For this purpose, the Becker-Jarvis technique [14] was used. On the basis of the obtained spectra of the complex magnetic and dielectric constant in the plane-wave approximation, the reflection coefficient from the layer of magnetodielectric located on the reflecting surface (metal surface) is calculated.

![Figure 3. Schematic diagrams of measurements: a) “on pass”; b) “on reflection”](image)

The “reflection” scheme (figure 1b) allows to directly measure the frequency dependence of the electromagnetic response on samples of composites that are placed in a coaxial cell with a short-circuit at the end. This method characterizes the absorbing properties of a sample located on a metal surface. The measurements allowed us to obtain the values of the reflection coefficient ($R$) from the layer of composites on the metal in the frequency range from 10 MHz to 18 GHz.

3. Results and discussion
Figure 4 presents the frequency dependences of the complex magnetic and dielectric constant for composite materials containing various concentrations of carbonyl iron.

![Figure 4. Frequency dependences of permeability (a) and permittivity (b) for a composite containing various concentrations of carbonyl iron.](image)

The concentration of carbonyl iron varies from 40 wt.% to 80 wt.% in 10% increments. With an increase in the concentration of carbonyl iron, an increase in the value of the complex permeability is observed. This is especially noticeable for the real part of the permeability at low frequencies. In the range of 1-2 GHz, composites containing carbonyl iron show a sharp decline in the real part of permeability, as well as a maximum in the imaginary part of permeability, which corresponds to the phenomenon of natural ferromagnetic resonance. Spectra of complex dielectric constant are presented.
With an increase in the mass fraction of carbonyl iron, an almost linear increase in the values of the real part of permittivity from 4 to 9 relative units is observed. The imaginary part changes slightly, only at frequencies above 7 GHz and at a maximum concentration of carbonyl iron $\varepsilon''$ reaches 0.6 relative units. Such behavior of the complex permittivity is caused solely by the polarization characteristics of the filler.

Figure 5 shows the frequency dependences of the complex magnetic and dielectric constant for composite materials containing a fixed concentration of carbonyl iron with the addition of MWCNT and ferrite.

![Figure 5](image-url)

**Figure 5.** Frequency dependences of permeability (a) and permittivity (b) for a composite containing a fixed concentration of carbonyl iron with the addition of MWCNT and ferrite.

From the above dependences it can be seen that the addition of carbon nanotubes does not affect the value of magnetic permeability, since MWCNTs do not contain magnetic atoms (with the exception of an insignificant amount of metallic impurities) and do not possess magnetic properties. The addition of ferrite significantly increased the value of both the real and imaginary parts of permeability, but only at frequencies below 1 GHz. This indicates that the selected ferrite of the spinel structure has low-frequency magnetic properties.

Analyzing the frequency dependences of the dielectric constant, it can be seen that with the addition of multi-walled carbon nanotubes to the composite containing 40 wt.% CI, a significant increase in real part of permittivity (from 4.5 to 9.5 rel. units) and imaginary part of permittivity (from 0.2 to 1.4 rel. units) happens. However, at frequencies above 5 GHz, a slight decrease in the real part of the permittivity can be seen. This behavior is associated with both the polarization characteristics of carbon nanotubes and the significant conductive properties of this substance (decrease in dielectric constant with increasing frequency). The addition of ferrite has a less pronounced effect on the real part of permittivity $\varepsilon$. In this case, the real part of permittivity practically does not depend on the frequency and almost linearly increases with increasing ferrite concentration (from 4.5 to 6.5 relative units). The imaginary part varies little. This behavior of the complex permittivity is caused solely by polarization characteristics of the filler.

Below are the results of measurements of the electromagnetic response from composite materials located on the metal. In addition to studying the experimentally obtained dependencies, the method of calculating the electromagnetic response from the magnetodielectric layer was used, based on the calculated spectra of complex dielectric and magnetic constant, which allowed us to obtain the frequency dependence of the reflection coefficient in the plane-wave approximation.

Figure 6 shows the frequency dependences of the reflection coefficients from experimental samples of composite materials containing carbonyl iron, multi-walled carbon nanotubes, and ferrites. With
increasing concentration of carbonyl iron, the reflection coefficient decreases significantly, reaching values exceeding $R = -10$ dB, which corresponds to a decrease in reflected power by 10 times. The peak reflectance minimum is shifted to a low frequency region. The peak attenuation of $-15$ dB is attained at the frequency of 10.8 GHz.

![Figure 6](image)

**Figure 6.** The frequency dependence of the reflection coefficient of the material on the metal for samples containing different concentrations of carbonyl iron (a) and samples containing a fixed concentration of carbonyl iron with the addition of MWCNT and ferrite (b).

On the frequency dependence presented in figure 6b, a weakening of the reflection coefficient is observed when MWCNT and ferrite are added to the carbonyl iron. Adding a few percent (1% and 2%) of MWCNT is almost equivalent to adding a few tens of percent (20% and 40%) of ferrite. The addition of 2 wt.% MWCNTs led to a decrease in the reflection coefficient by about 8 times, while the absorption peak also shifts to lower frequencies. The addition of ferrite allows to decrease the reflection coefficient from -0.4 dB to $-2.5$ dB at frequencies from 1 to 4 GHz.

The dependences obtained make it possible to characterize a composite material based on epoxy resin with the addition of carbonyl iron, multi-walled carbon nanotubes and ferrites as an effective absorber of electromagnetic radiation.

Comparing the results obtained using modeling, it can be noted that this model agrees quite well with the experimentally obtained dependencies. And this model can be used to calculate the reflection coefficient of an electromagnetic wave from an absorbing coating located on a reflecting surface, if the spectra of complex permittivity and permeability are known.

### 4. Conclusions

A comparison of the measured and calculated values of the reflection coefficient from the composite layer on the metal is done. They showed a good match. So using the composite with 80 wt.% CI will reduce the reflection coefficient by more than 10 times in the frequency range from 5.5 to 9.5 GHz, the composite from 70 wt.% CI - in the range from 7.5 to 11.5 GHz, and the composite from 40 wt.% CI and 2 wt.% MWCNTs range from 9.5 to 12 GHz. Adding 2 wt.% MWCNTs to 40 wt.% CI is equivalent to increasing the concentration of carbonyl iron from 40 to 60 wt.%. Which significantly reduces the consumption of materials and the mass of the composite.

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