High Microwave Magnetic Permeability of Composites with Submicron Iron Flakes

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Abstract. An effective method for the development of magnetic materials with high microwave permeability on the basis of carbonyl iron powders has been proposed. This method consists in the modification of particle morphology from the spherical shape into flaky one with subsequent silica coating of the flakes by sol-gel method. Composites with submicron flaky iron powders (thickness < 1 µm) exhibit remarkable improvement in the microwave magnetic spectra compared to the spherical powder based composites. Even a thin silica overlayer provides a sufficient insulation of the metal particle and decreases the permittivity values.

1. Introduction
The development of magnetic composite materials utilized in various microwave devices has attracted intensive research interest in recent years. Such composites are made by embedding magnetic particles into nonmagnetic polymer resins. Among different magnetic fillers, carbonyl iron powders have received much attention due to the high values of relative complex permeability in GHz range, high saturation magnetization \(4\pi M_s\) and high Curie temperature [1–3]. Produced by the thermal decomposition of iron pentacarbonyl, carbonyl iron powders contain more than 96 % of iron, along with carbon, oxygen and nitrogen. However, depending on the manufacturing conditions, carbonyl iron powders of the various types are classified into two groups with different microstructural properties of their particles [4, 5].

Primary carbonyl iron powders are characterized by onion microstructure of their particles and by the presence of the impurities which leads to the formation of iron carbide (Fe₃C), iron nitride (Fe₄N) and iron oxide (Fe₂O₃) phases [4, 6]. In contrast to the primary powders, carbonyl iron powders reduced with hydrogen are extremely pure, mechanically soft, and onion microstructure is replaced by the polycrystalline one [4, 5]. In terms of magnetic properties it leads to the intensification of domain wall motion and higher values of permeability. However, eddy current losses decrease the values of permeability at high frequencies. In its turn, eddy current losses in composite materials with spherical inclusions are given by

\[ P_{\text{eddy current}} = 0.2\pi^2 \frac{d^2\mu_p}{\rho} \mu_m 10^{-9} \] (1)

where \(d\) is the particle diameter, \(\rho\) is the resistivity of the particle, \(\rho_p\) is the loading factor, and \(\mu_m\) is the initial permeability of the composite material [6]. Generally, it is better to use particles with the sizes

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not exceeding the skin depth, in order to decrease eddy current losses. The skin depth \( \delta \) is defined as follows
\[
\delta = \frac{2}{\sqrt{\omega \mu \sigma}}
\]
where \( \omega \) is the angular frequency, \( \mu \) is the intrinsic permeability, and \( \sigma \) is the conductivity [7]. For pure iron the skin depth does not strongly depend on the frequency starting from 5 GHz, and is about 1 – 2 \( \mu m \) in the frequency range above 5– 6 GHz. Therefore, the ideal particle size should be within 1 – 2 \( \mu m \).

Eddy current losses can be further reduced by modifying the shape of the particles from spherical one to flaky [8, 9]. For high frequency applications, the optimum thickness of the flakes should be less than the skin depth (around 1 \( \mu m \)) with aspect ratios from 10 to 100 [10]. However, despite the increasing values of permeability at high frequencies, flaky composites possess high values of permittivity, which is undesirable for some microwave devices. In order to avoid permittivity enhancement, a good insulation of the particles should be provided by coating process.

In this work, we studied the effect of particle morphology, as well as the influence of silica coating of iron particles on the changes in electromagnetic properties of iron composites. For this purpose, the reduced carbonyl iron powder having the smallest available particle size was chosen as a starting material.

2. Experimental results and discussion

Reduced carbonyl iron powder SM (median particle size from 2.8 to 3.5 \( \mu m \)) characterized by spherical particle shape and polycrystalline structure of the particles (BASF, Germany) was used as a starting material. The purity of SM carbonyl iron powder was above 99 % containing carbon < 0.1%, nitrogen < 0.1%, and oxygen < 0.55 %. A commercially available silicone elastomer (SYLGARD 184, Dow Corning, USA) was used as a polymer matrix material. Tetraethyl orthosilicate (TEOS) (95%, Sigma-Aldrich) and absolute ethanol (200 proof, Fisher Scientific Co) were used for silica coating. Ammonium hydroxide solution (NH\(_4\)OH, 28–30 % NH\(_3\) basis, Sigma-Aldrich) was used as a catalyst for a sol-gel reaction of TEOS.

SM powder was milled in a PM 400 Retsch planetary ball mill at 100 rpm. The starting powder was loaded into a jar with steel milling balls of 5 mm in diameter. The ball to powder ratio was 10:1. The jar was filled with ethanol to avoid agglomeration. The mechanical milling was performed for 8, 12 and 16 hours. SM flakes were dried at 70°C for 15 hours. As-milled carbonyl iron flakes were named SM-8, SM-12, and SM-16 respectively. The morphology of raw material and powders milled for 8, 12, and 16 hours was studied by JEOL JSM-6340F field emission scanning electron microscope as shown in Figure 1. With increasing ball milling time, spherical particles deform into flaky ones, where after 8 hours of ball milling spherical particles still exist, after 12 hours no spherical particles can be found and the thickness of flakes is about 1\( \mu m \), after 16 hours the thickness of flakes is below 1\( \mu m \).

Silica coating of carbonyl iron particles was performed by the hydrolysis of tetraethyl orthosilicate (TEOS) via conventional sol-gel method [11]. The alkoxide solution was obtained by mixing TEOS and ethanol. In the other beaker we mixed ethanol and water with ammonium hydroxide stock solution in order to get the catalyst solution. Then the catalyst solution was poured into the alkoxide solution and stirred. Eventually, we mixed all solutions in glass vessel; the sol-gel process was initiated. The mixture was stirred with 300 rpm at 70°C. After 2 hours of stirring, coated carbonyl iron particles were filtered off, washed with ethanol and dried. Core-shell structure with the thickness of the shell about 10-15 nm was revealed by TEM image. The existence of a \( \text{SiO}_2 \) nanoshell can be also confirmed indirectly by permittivity measurements.

Composite fabrication procedure involved preparation of the composites with spherical inclusions (SM powder) and flakes (SM-8, SM-12, and SM-16). The volume concentrations of the filler in composite materials were calculated using the densities of the carbonyl iron and silicone elastomer, 7.8 g cm\(^{-3}\) and 1.05 g cm\(^{-3}\) respectively.
The static magnetic properties of iron powders were measured by a Vibrating Sample Magnetometer (VSM, EV9, ADE Magnetics, USA) with a maximum magnetic field of 20 kOe. The saturation magnetization of iron powders increases with ball milling time (Figure 2, left).

![Fig. 1. SEM images of iron powders for different milling times: (a) 0 h, (b) 8 h, (c) 12 h, (d) 16 h.](image)

![Fig. 2. Magnetization curve of SM, SM-8, SM-12, and SM-16 powders measured on pressed powder samples (left) and complex permeability spectra of composites containing 40 vol. % of powders with various milling time (right).](image)

The relative complex permeability \( \mu^* = \mu' - j\mu'' \) and permittivity \( \varepsilon^* = \varepsilon' - j\varepsilon'' \) of the specimens were obtained by 7 mm coaxial line method. Toroidal samples with inner diameter of 3.04 mm and outer diameter of 7 mm were inserted into a coaxial line and the scattering parameters (reflection coefficient \( S_{11} \), transmission coefficient \( S_{21} \)) were measured in the frequency range from 50 MHz to 18 GHz by a Vector Network Analyzer (VNA), Agilent N5230A. The complex permeability and permittivity were calculated from the scattering parameters.

Figure 2 (right) shows the real and imaginary parts of complex permeability for the composites containing 40 vol. % powders. The initial values of \( \mu' \) increase from 5.76 to 7.46, 8.58 and 9.52 SM, SM-8, SM-12 and SM-16 powders respectively. The peak value of the \( \mu'' \) increases from 1.8 to 3.0, 3.5 and 3.7 with increasing of ball milling time. It is caused by the reduction of eddy current losses and demagnetizing features of the flaky particles. It is known that the permeability values also decreases by the demagnetization field depending on the shape of the magnetic inclusion. The demagnetizing field is determined by the following equation

\[
H = H_0 - NM
\]
where $H_0$ is the external applied field, $N$ is the demagnetizing factor and $M$ is the magnetization. For spherical particles, $N$ is equal to 1/3, while for flaky particles $N$ is smaller than 1/3 along the elongated directions. Based on these, higher magnetic permeability can be obtained in flaky composites.

However, a disadvantage of flaky composites consists in the enhancement of permittivity values with ball milling time. It is caused by the enhancement of space-charge polarization between metallic particles with increase of surface area and is undesirable for some microwave applications. In order to avoid permittivity enhancement, a good insulation of the particles should be provided by coating process. In this work we performed silica coating of iron particles by sol-gel method (Figure 3).

![TEM image of the SiO2 coated flake.](image)

Fig. 3. TEM image of the SiO2 coated flake.

It results in the slight decrease of permittivity of the composites filled with coated flakes while permeability values remain the same (Figure 4).

![Permeability and permittivity spectra for composites with 40 vol. % of SM-16 without and with SiO2 coating.](image)

Fig. 4. Permeability and permittivity spectra for composites with 40 vol. % of SM-16 without and with SiO2 coating.

Microwave losses in magnetic composite materials are attributed to hysteresis, domain wall resonance, natural ferromagnetic resonance and eddy current losses. The domain wall resonance usually occurs in frequency range from 1 to 100 MHz. Hysteresis loss originates from the time lag of magnetization vector behind the external magnetic field vector and is negligible in weak fields. In the GHz frequency range neither hysteresis loss no domain wall resonance contributes to the magnetic losses. The eddy current loss contribution to the imaginary part of permeability can be expressed as follows

$$
\mu'' = \frac{2}{3} \pi \mu_0 (\mu')^2 d^2 f \sigma
$$

(4)

where $\mu_0$ is permeability of vacuum, $\sigma$ - electrical conductivity. This equation can be transformed to

$$
\mu'' (\mu')^{-2} f^{-1} = \frac{2}{3} \pi \mu_0 d^2 \sigma
$$

(5)
If the magnetic loss originates only from eddy current loss, the values of left-hand side of this equation will remain constant with frequency changes [12]. Figure 5 shows the value of $\mu''(\mu')^{-2}f^{-1}$ of composites filled with spherical and flaky iron particles. As it can be seen, the values for spherical particles are close to each other at frequencies above 1 GHz, while in the case of flaky filled composites they increase with the frequency increasing. Therefore, it means that magnetic losses in composites with spherical inclusions are mainly caused by the eddy current loss over 1–18 GHz, whereas in the flaky composites by natural resonance. Moreover, the natural resonance peak broadens which can be explained by the decreasing of crystallite size with ball-milling time increasing (Figure 2, right).

Fig. 5. Values of $\mu''(\mu')^{-2}f^{-1}$ for composites with spherical (SM) and flaky (SM-16) iron powders versus frequency.

3. Conclusions

Comparative analysis of the electromagnetic parameters of magnetic composites filled with iron powders differ in their morphology was carried out. It was shown that the changes in the morphology of the particles have the crucial effect on the values and the character of electromagnetic spectra. Iron flakes were prepared by the high-energy planetary ball milling of the starting material with different milling time (8, 12, and 16 hours). The value of initial permeability and the peak value of imaginary part increases with the increasing of ball milling time. In order to avoid permittivity enhancement, silica coating of the particles was performed. It results in slight decrease of permittivity of the composite materials filled with coated flakes while permeability values remain the same. It was established that magnetic losses in composites with spherical inclusions are mainly caused by the eddy current losses over 1-18 GHz, whereas in the flaky composites by natural resonance.

From the practical point of view, composites on the basis of submicron silica coated flakes can be considered as candidates for producing high magnetic performance materials in microwave absorber design, electromagnetic interference (EMI) shielding.

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