Microwave absorbing properties of Ag-coated Ni–Zn ferrite microspheres prepared by electroless plating

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ABSTRACT

This investigation presents an electromagnetic radiation absorptive composition comprising Ag-coated ferrite microspheres dispersed in a silicone rubber matrix for use as a thin microwave absorber in GHz frequencies. Ni–Zn ferrite microspheres with an average diameter of 50 μm were prepared by spray-drying and sintering at 1130 °C. A conductive Ag layer was coated on the ferrite spheres by electroless plating. Uniform Ag coating can be obtained using the plating solution with a high $AgNO_3$ concentration. For particle compacts of the conductive Ni–Zn ferrite spheres, electrical resistance is reduced to as low as 10^{-2} Ω. Rubber composites containing the Ag-plated ferrite spheres exhibit a high value of both real and imaginary parts of complex permittivity, while the complex permeability spectrum is not significantly changed with Ag plating. Due to the conductive and magnetic property of the microspheres, matching thickness can be reduced to as low as 2 mm at the frequency of 7.6 GHz, which is much thinner than non-coated ferrite absorbers.

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1. Introduction

There have been a number of proposed materials which are capable of absorbing electromagnetic radiation for the applications in electromagnetic compatibility (EMC) and stealth technology. Ferrites with spinel or hexagonal crystal structure are typical absorptive materials operated in microwave frequencies [1–5]. Offering chemical stability, corrosion resistance and high magnetic loss, ferrites are widely used in either tile or composites form for various EMC engineering practices, depending on the frequency of operation. Iron particles and other magnetic alloy particles are also used in many electronic devices, since they have the advantage of a high magnetic permeability (above Snoek's limit) resulting from high saturation magnetization [6–9].

In resonant absorbers of quarter wavelength, zero-reflection can be obtained by wave impedance matching at the surface of the absorbing layer. This method requires a proper combination of magnetic permeability and dielectric permittivity at a given thickness and frequency of interest [10,11]. A traditional method for controlling the material parameters has been to mix different kinds of absorbent fillers together. For instance, adding a conductive carbon or a metal powder to ferrite composites was an effective way to increase dielectric permittivity [12,13]. However, the addition of conductive fillers at the loading limit in powder composites reduces the magnetic permeability of the mixture.

The use of core–shell particles is another technique for controlling the material parameters. Typical examples of such techniques include metal coating on dielectric particles or fibers [14,15], ZnO or Ni–P coating on ferrite powders [16,17], and ferrite coating on metal nanopowders [18]. In single-layered microwave absorbers, this method allows for permittivity control through the conductive layer and permeability control through the magnetic core. This technique offers the particular advantage of high particle loading in the composites, since the intrinsic high-frequency properties can be controlled using small-volume shells or films (with a thickness below skin depth) on the cores.

This investigation presents an electromagnetic radiation absorptive composition comprising Ag-coated ferrite microspheres dispersed in a silicon rubber matrix for use as thin microwave absorbers. For uniform Ag coating by electroless plating, Ni–Zn ferrite microspheres were used as the core material. This investigation focuses on the effect of Ag coating on the material parameters (complex permittivity and permeability) and microwave absorbance (matching frequency and matching thickness) of the composite specimens.

2. Experimental procedure

For uniform Ag coating on ferrite particles, Ni–Zn ferrite microspheres (with composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$) with an average size of about 50 μm were prepared by spray drying and subsequent sintering at 1130 °C. The conductive layer was formed on the ferrite spheres by electroless Ag plating with variations in sensi-

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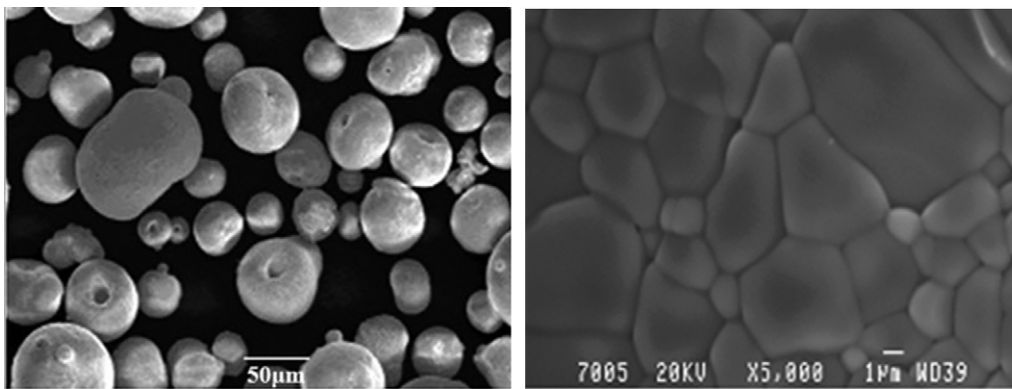E-mail address: sskim@chungbuk.ac.kr (S.-S. Kim).

Fig. 1. SEM observation of Ni–Zn ferrite microspheres and their surface morphology.

tizing condition, $AgNO_3$ concentration, amount of reducing agent and plating time. As pre-treatment for the Ag plating, the ferrite spheres were etched in HF solution for surface cleaning and surface roughening. Ag plating was carried out in a two-step operation: first, the surface of the microspheres was sensitized with $SnCl_2$, and then the salts of metals ($AgNO_3$) were chemically reduced using a mild reducing agent of fructose ($C_6H_{12}O_6$).

20 g of ferrite spheres were placed in a funnel with a catalyst solution of $SnCl_2 \cdot 2H_2O$ (8 g in 200 mL distilled water) and HCl (5 mL). This mixture was shaken at 60 °C for 10 min. The microspheres were then washed with distilled water, gravity filtered, and air dried at 60 °C. The sensitized ferrite spheres were placed in a mixture solution of 100 mL of plating solution containing 0.4–1.2 g of $AgNO_3$ and 100 mL of reducing agent solution of $C_6H_{12}O_6$, whose amount was proportional to $AgNO_3$ by a weight ratio of 1:12. The mixture was tumbled for 1 h, gravity filtered, washed with distilled water, and finally air dried at 60 °C.

The uniformity of the coating layer was identified by measuring apparent electrical resistance of the particle compacts and by directly observing the coating using a scanning electron microscope (SEM). Apparent electrical resistance was measured in a green compact of 1 g Ag-coated microspheres pressed slightly in an insulated cylinder mold of 10 mm inner diameter.
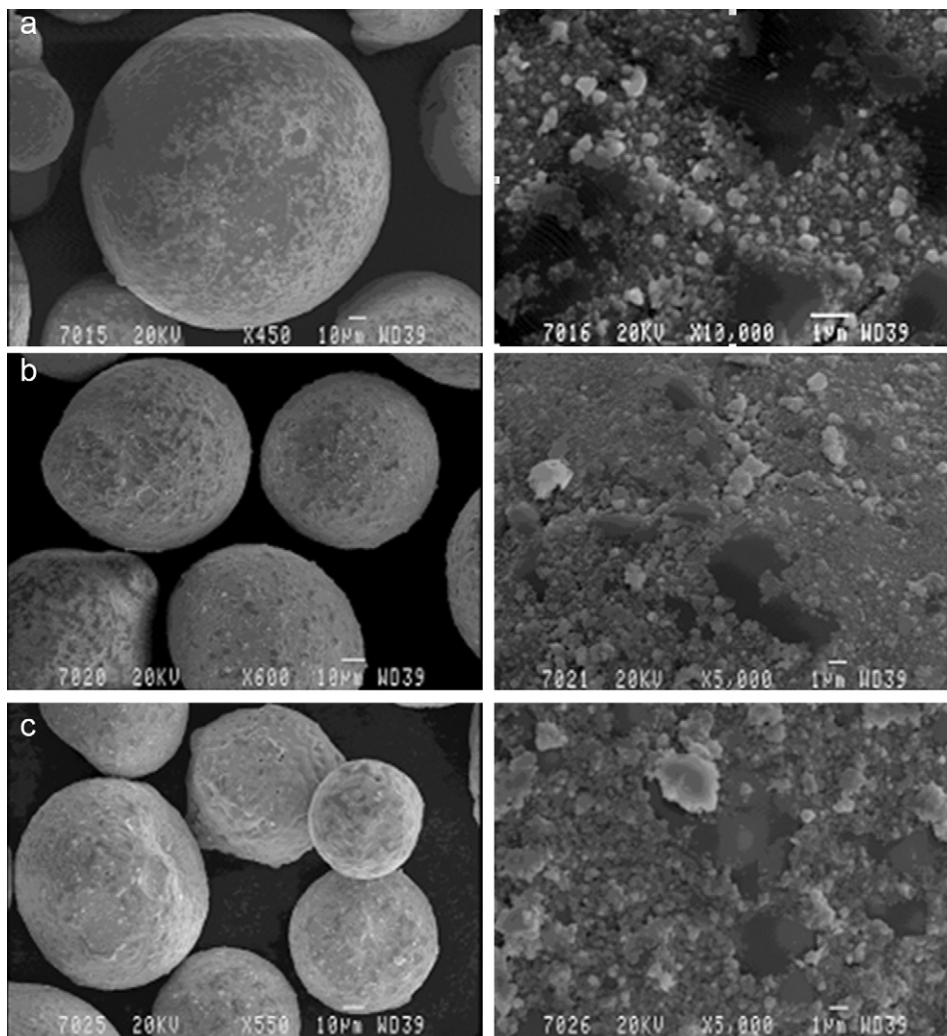

Fig. 2. SEM observation of Ag-plated Ni–Zn ferrite microspheres and their surface morphology with variation of $AgNO_3$ concentration in plating solution: (a) 4 g/L $AgNO_3$, (b) 6 g/L $AgNO_3$, and (c) 10 g/L $AgNO_3$.
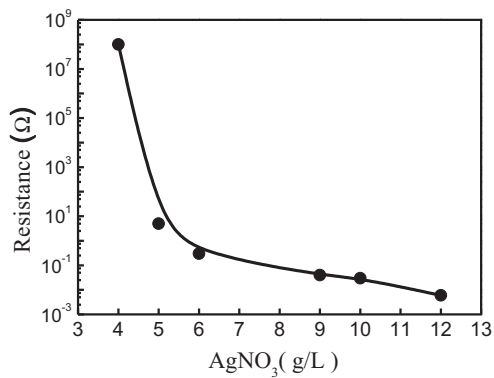
Fig. 3. The decrease of electrical resistance of green compacts of Ag-coated ferrite microspheres with increase of $AgNO_3$ concentration in plating solution.

The complex permeability and permittivity was measured in the composite specimens of the Ag-coated microspheres dispersed in the silicone rubber matrix. The mixing ratio of particles to rubber was 5:1 by weight. A toroid sample (inner diameter of 3 mm, outer diameter of 7 mm, and thickness of about 2 mm) was inserted in a standard coaxial sample holder (APC-7 beadless air line), and the reflection signal (S_{11} parameter) and transmission signal (S_{21} parameter) were measured by using HP 8722D network analyzer. The frequency range of the measurement was 0.05–18 GHz. The complex permittivity and permeability was calculated from the S_{11} and S_{21} parameters. Reflection loss was determined by measuring the S_{11} parameter after the rear face of the sample was terminated by metal.

3. Results and discussion

Fig. 1 shows the SEM observation of the non-coated ferrite microspheres and their surface structure. Nearly spherical particles with an average diameter of about 50 μm are observed. Most of the particles show a dense and polycrystalline structure.

Fig. 2 shows the microstructure of the ferrite microspheres coated with Ag films by electroless plating. The growing morphology of the Ag film is sensitive to the $AgNO_3$ concentration in plating solution. In the case with the low concentration of $AgNO_3$ (4 g/L $AgNO_3$ per 20 g ferrite spheres), Ag film formed only on the surface of small grains and in the grain boundary region of the Ni–Zn ferrite microspheres, as shown in Fig. 2(a). The Ag grains are isolated (showing island structure) due to low concentration of $AgNO_3$. At the concentration of 6 g/L $AgNO_3$, nearly uniform Ag coating was obtained, as shown Fig. 2(b). However, complete coating was not observed in the large grains or irregular surface regions. At the concentration above 10 g/L $AgNO_3$, the Ag film is completely coated, as shown in Fig. 2(c).

The electrical resistance of green compacts of Ag-coated ferrite microspheres is very sensitive to the grain structure of the Ag film, which is in turn controlled by the $AgNO_3$ concentration, as shown in Fig. 3. The non-coated Ni–Zn ferrite microspheres have a high electrical resistance (above $10^8\ \Omega$) due to their intrinsic insulating property. For the Ag-coated ferrite microspheres plated in 4 g/L $AgNO_3$ solution, the electrical resistance is still high ($\sim 10^8\ \Omega$) due to the island grain structure of the Ag film (shown in Fig. 2(a)). However, the electrical resistance rapidly diminishes with a uniform or thicker coating of Ag film, due to the increased concentration of $AgNO_3$. In the solution of 5 g/L $AgNO_3$ concentration, the electrical resistance is reduced to about 5 Ω, indicating that the electrical connection between the plated Ag grains is the most important factor for obtaining a highly conductive coating on ferrite microspheres. Further increase in $AgNO_3$ concentration (12 g/L) reduces the electrical resistance to as low as $10^{-2}\ \Omega$.

Fig. 4 shows the frequency dispersion of complex permeability ($\mu_r = \mu_r' - j\mu_r''$) and complex permittivity ($\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$) of rubber composites containing Ag-coated ferrite microspheres. For non-coated Ni–Zn ferrite spheres (Fig. 4(a)), a typical ferromagnetic resonance is observed at 0.4 GHz with a rapid decrease in μ_r' and
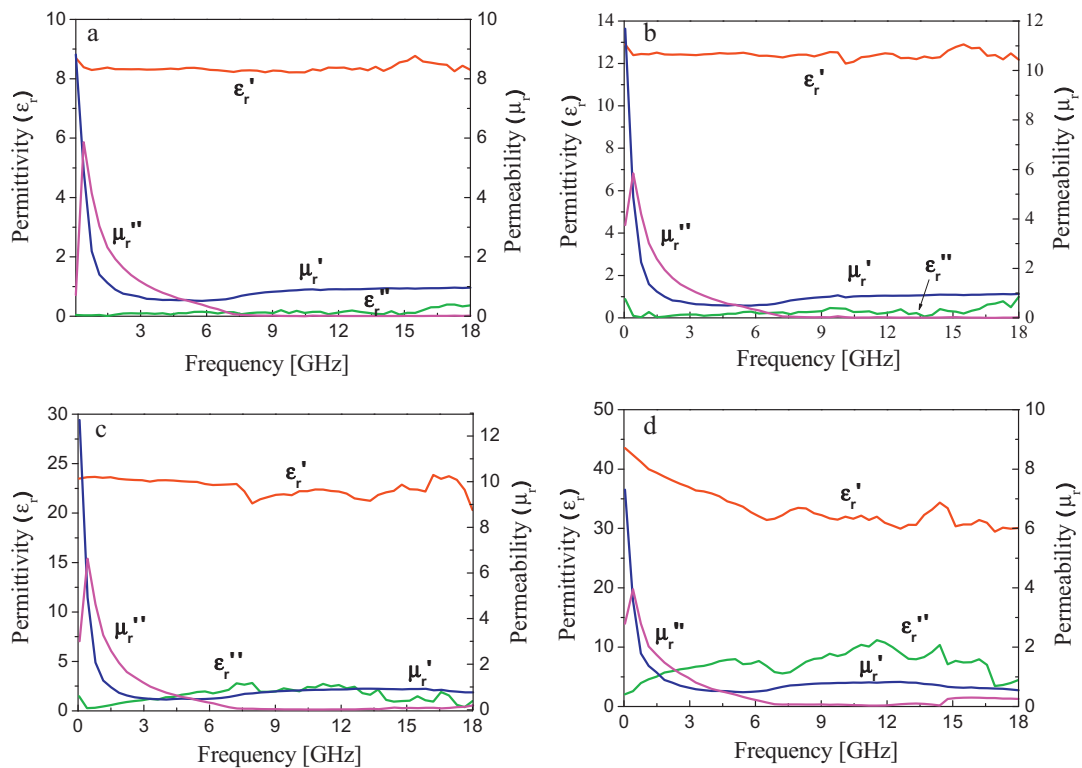

Fig. 4. Frequency dispersion of complex permeability and permittivity determined in the composites containing Ag-coated Ni–Zn ferrite microspheres plated with solution: (a) 0 g/L $AgNO_3$ (non-plated), (b) 5 g/L $AgNO_3$, (c) 6 g/L $AgNO_3$, and (d) 10 g/L $AgNO_3$.

a high magnetic loss peak of $\mu_r'' = 6$. The real part of complex permittivity is $\varepsilon_r' = 8.3$ and imaginary part is negligibly small ($\varepsilon_r'' \approx 0$). In the composite of ferrite microspheres plated with 4 g/L AgNO$_3$ solution, nearly the same frequency dispersion of complex permeability and permittivity is observed due to its high electrical resistance ($\sim 10^8\,\Omega$) caused by the island Ag grain structure. Further increase in AgNO$_3$ concentration increases the real and imaginary parts of complex permittivity, as shown in Fig. 4(b)–(d). In the case of ferrite microspheres plated with a high concentration of AgNO$_3$ (10 g/L), both the real and imaginary parts of complex permittivity increase to large values ($\varepsilon_r' \approx 34$, $\varepsilon_r'' \approx 7$), as shown in Fig. 4(d). The space charge polarization between the adjacent conductive particles (which are separated by an insulating rubber matrix) results in high values of dielectric constant and dielectric loss. The complex permittivity increases as the electrical resistance of the film decreases, due to the enhanced polarization.

Meanwhile, the magnetic permeability spectrum of the composites did not change greatly. Ferromagnetic resonance frequency and loss peak is virtually identical with the plating of Ag film on the ferrite spheres, which can be attributed to the small volume of Ag film relative to the ferrite microspheres. Nevertheless, the thin layer of Ag film is sufficient to enhance the space charge polarization in the polymer matrix.

For a microwave absorbing layer terminated by a metal plate, the input impedance at the absorber surface (Z_{in}) is given by:

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left[\frac{j2\pi d}{\lambda}\sqrt{\varepsilon_r \mu_r}\right] \qquad (1)$$

where Z_0 is the wave impedance of free space (377 Ω), λ is the wavelength in free space, and d is the layer thickness. Since the reflection coefficient (Γ) is proportional to the difference between Z_{in} and Z_0 as expressed in:

$$\Gamma = \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \qquad (2)$$

reflection loss can be calculated from the measured material parameters (μ_r and ε_r) as a function of frequency and thickness. A proper combination of μ_r and ε_r satisfying $Z_{in} = Z_0$ at the given frequency and thickness produces the zero reflection condition (impedance matching).

Fig. 5 shows the contour of frequency (f) and thickness (d) satisfying the impedance matching at the given material parameters in the range of $fd = 3$–33 GHz mm. The frequency dispersion value of $\mu_r' - \mu_r''$ and the dielectric constant ε_r' of the composite specimens are plotted in the maps which was constructed at a given dielectric loss tangent ($\tan\delta = \varepsilon_r''/\varepsilon_r'$). The matching frequency and matching thickness can then be determined from the crossing point of the complex permeability and the dielectric constant, as described in detail in the previous study [19]. For the specimen of non-coated ferrite spheres, impedance matching is satisfied at two frequencies: 0.7 GHz (1st matching) and 6.5 GHz (2nd matching), as shown in Fig. 5(a). Corresponding matching thickness is estimated to be 12 mm and 5 mm from the fd [GHz mm] values of 9 and 33 in the maps. Increasing the dielectric constant for the Ag-coated ferrite spheres causes the 1st matching frequency to decrease and the 2nd matching frequency to increase, while the corresponding matching thicknesses are diminished, as shown in Fig. 5(b) and (c). For instance, for the ferrite spheres plated at 6 g/L AgNO$_3$, the matching frequency is 0.5 GHz and 7.0 GHz, and corresponding matching thickness is estimated to be 11 mm and 3 mm.

This prediction coincides well with the reflection loss determined at the 1st and 2nd matching thickness, as shown in Fig. 6. An increase in the AgNO$_3$ concentration (increase of dielectric constant) leads to a considerable decrease in matching thickness. The
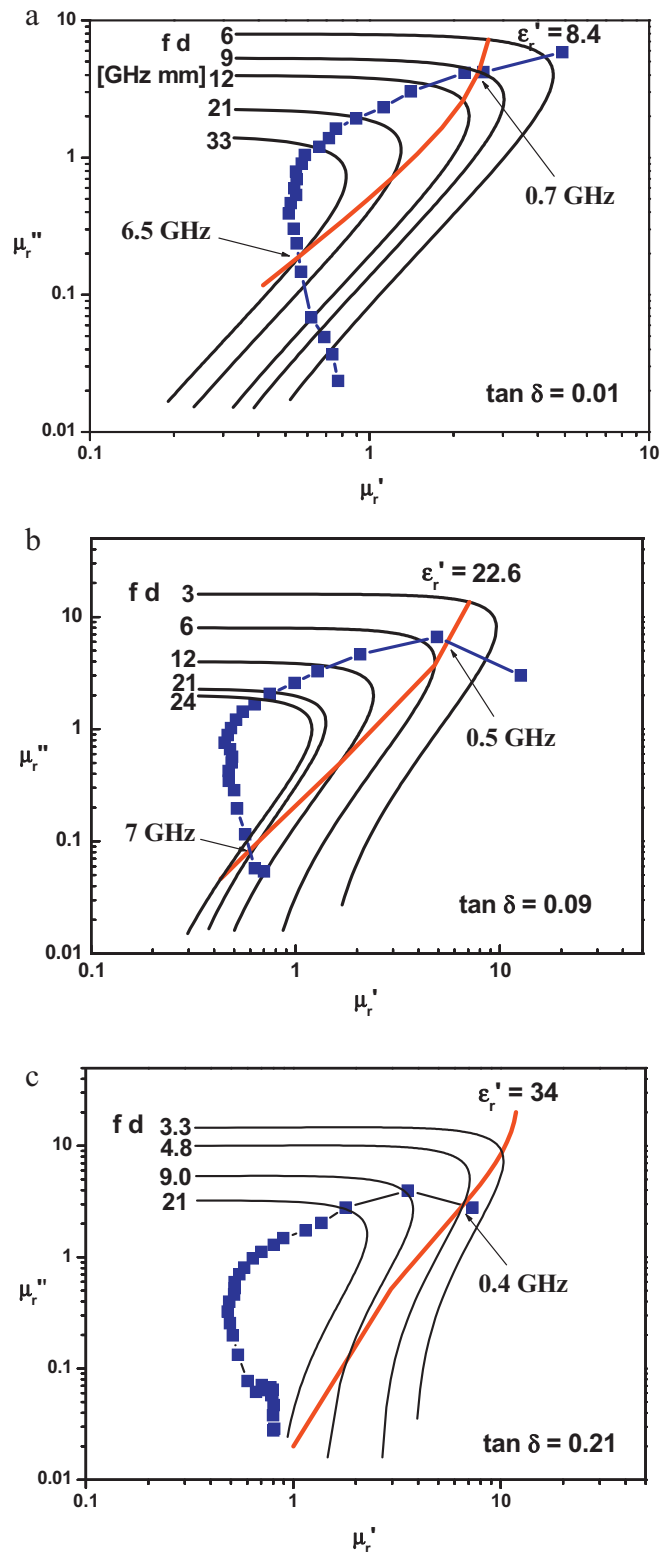

Fig. 5. Matching frequency and matching thickness determined in the composites containing Ag-coated Ni–Zn ferrite microspheres plated with solution: (a) 0 g/L AgNO$_3$ (non-plated), (b) 6 g/L AgNO$_3$, and (c) 10 g/L AgNO$_3$.

most significant effect of Ag coating is reduction of the absorber thickness, which can be attributed to the high dielectric constant of the composites maintaining a high permeability value nearly equal to that of non-coated ferrite microspheres. However, the bandwidth is quite narrow (about 1 GHz with respect to −10 dB
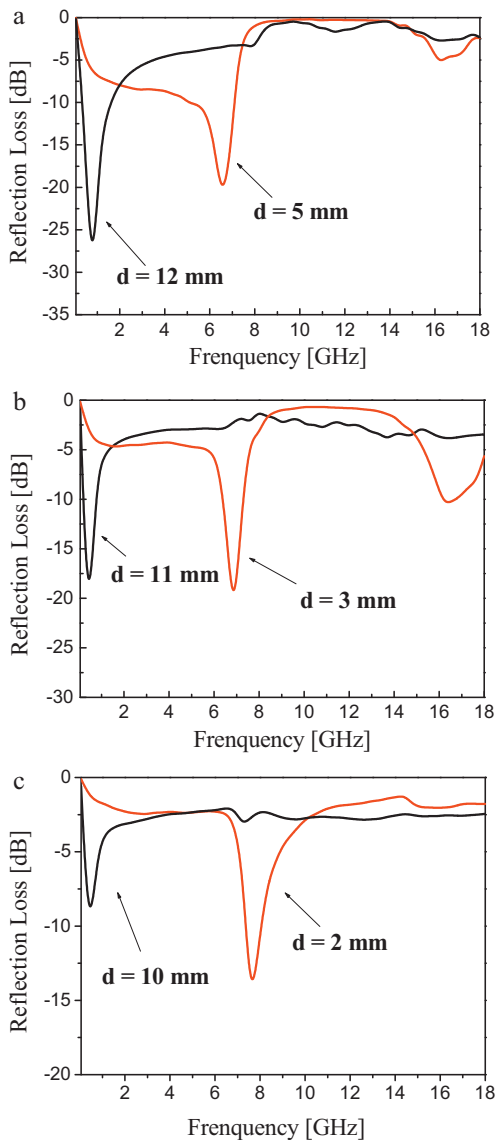
Fig. 6. Reflection loss determined in the composites containing Ag-coated Ni–Zn ferrite microspheres plated with solution: (a) 0 g/L $AgNO_3$ (non-plated), (b) 6 g/L $AgNO_3$, and (c) 10 g/L $AgNO_3$.

reflection loss) in comparison with previous results (about 3–4 GHz in polymer composites of NiZn ferrite or NiCuZn ferrite) [2,3]. In general, the bandwidth is reduced when the dielectric constant increases [20].

4. Conclusion

The most significant result of this study is that microwave absorbers with a reduced matching thickness can be designed with conductive Ni–Zn ferrite microspheres fabricated by Ag plating. The uniform coating of Ag films on the microspheres, which was identified by the low value of the electrical resistance and by direct observation by SEM, requires a high level of $AgNO_3$ concentration in the plating solution. The rubber composites containing the Ag-coated ferrite particles exhibit high dielectric constants and dielectric loss due to the enhanced space charge polarization between the conductive particles in the insulating matrix. Ag plating does not cause a substantial change in the magnetic permeability or magnetic loss, because the coating layer is too thin in comparison with the ferrite particle size. The conductive property of the magnetic spheres reduces the matching thickness of the composites as low as 2 mm at the frequency of 7.6 GHz, which is much thinner than conventional ferrite absorbers.

Acknowledgements

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