Percolation-induced low frequency plasmonic state in metal granular composite materials

Takanori Tsutaoka[1*], Herieta Massango[1], Teruhiro Kasagi[2]

[1]*Graduate School of Education, Hiroshima University, Higashi-Hiroshima, 739-8524, Japan*
[2]*National Institute of Technology, Tokuyama College, Shunan, 745-8585, Japan*

*Corresponding author

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Abstract

Low frequency plasmonic (LFP) state induced by the electrical percolation of metallic particles has been investigated for metal granular composite materials containing Cu, $Ni_{47}Fe_{53}$ and $Co_{50}Fe_{50}$ microparticles. In these composites, a conductivity jump due to electrical percolation takes place at different particle volume fraction φ; a conductive state is established above the percolation threshold φ_C. The φ_C is 0.16 for Cu, 0.61 for $Ni_{47}Fe_{53}$, and 0.76 for $Co_{50}Fe_{50}$ composites, respectively. In the Cu composite, the LFP state takes place in the conductive state just above φ_C. However, in the $Ni_{47}Fe_{53}$ composite, the LFP state is established at $\varphi = 0.90$; the LFP state couldn't be observed in the $Co_{50}Fe_{50}$ one. Hence, a non-plasmonic conductive state can exist in the percolated state; the LFP state can be established in the conductive state with about 1.0 S/cm of the conductivity value. Copyright © 2018 VBRI Press.

Keywords: Metal granular composite, low frequency plasmonic state, permittivity, conductivity.

Introduction

Electromagnetic metamaterials (EMMTMs) having the negative permittivity (ENG: Epsilon Negative) or permeability (MNG: Mu Negative) spectra in the microwave or photonic frequency range have been the subject of considerable interest in these days. The double negative (DNG) materials with both the ENG and MNG properties can have Left-Handed characteristics having the negative refraction of the EM waves or perfect EM absorbing [**1-4**]. The ENG and MNG properties have been realized by the artificial periodic structure of printed metal patterns or strip lines [**2**].

Meanwhile, the ENG and MNG properties of real materials have also been investigated using composite structures including metallic, magnetic or dielectric particles, and fibers in the host materials [**5-7**]. The MNG spectrum can be obtained by the magnetic resonance of ferromagnetic or ferrimagnetic materials but the ENG spectrum by the dielectric resonance in the ferroelectric materials does not exist in the microwave range. To realize the ENG characteristic in the RF to microwave range, electrically percolated state in the metal granular composite materials has been proposed and negative permittivity spectrum was realized [**5,6**]. In the granular composite metamaterials, the large MNG by the magnetic resonance of embedded ferromagnetic particles is difficult to be achieved due to the broadening of the permeability spectrum in the composite structure [**7**]. Hence, the tunable large ENG property of the composite materials is desired to compensate the magnetic response in the DNG metamaterials.

In this study, the electrical properties of the low frequency plasmonic state in the metal granular composite materials containing arborized anisotropic Cu and spherical metal particles ($Fe_{53}Ni_{47}$ and $Fe_{50}Co_{50}$) have been investigated from the RF to microwave range. It was found that the non-plasmonic state can exist in the conductive state above the percolation threshold φ_C. In this report, the experimental results of the complex permittivity as well as the ac conductivity for these metal granular composites will be presented and the condition of the onset of LFP state in the metal granular composite material will be discussed.

Experimental

As the embedded particles, commercially available ferromagnetic alloys ($Ni_{47}Fe_{53}$ and $Co_{50}Fe_{50}$) and Cu microparticles were used. The characteristics of these particles are presented in the previous papers [**6,9,10**]. The particle size and its distribution were examined by the scanning electron microscope (SEM); the obtained mean particle diameters of spherical particles are 7.07 μm for $Ni_{47}Fe_{53}$ and 2.08 μm for $Co_{50}Fe_{50}$ [**9,10**]. The size of the Cu particle is in the order of several 10 μm [**6**].

Composite materials were prepared by mixing the metal powders with Polyphenylene Sulfide (PPS) resin powder, melting the resin at 300ºC and pressing the mixture at a pressure of 623.9 MPa in the cooling process down to room temperature. Relative complex permittivity (ε_r = ε_r' - $j\varepsilon_r$'') was measured by the conventional *S*-parameter method using a coaxial transmission line and a network analyzer from 100 MHz to 10 GHz; the ac electrical conductivity σ_{ac} was obtained from the electrical resistivity measurement by the two-terminal method with an impedance analyzer from 100 Hz to 40 MHz [**6,10**].

The SEM images of Cu and $Ni_{47}Fe_{53}$ granular composites are shown in **Fig. 1**. The volume fractions of these particles are 0.20 for Cu composite and 0.65 for $Ni_{47}Fe_{53}$ one, respectively. From the **Fig. 1(a)**, the coagulated Cu particles are randomly dispersed in the host resin; the particles are connected each other in this particle content. Meanwhile, spherical $Ni_{47}Fe_{53}$ particles have almost the same particle connection as that of Cu particles at φ = 0.65 as shown in **Fig. 1(b)**. As is well known that the electrical percolation threshold is affected much by the embedded particle's shape and geometry; the anisotropic particle system tends to have a lower percolation threshold φ_C. Thus the Cu composite can have the lower percolation threshold than that of the $Ni_{47}Fe_{53}$ composite.

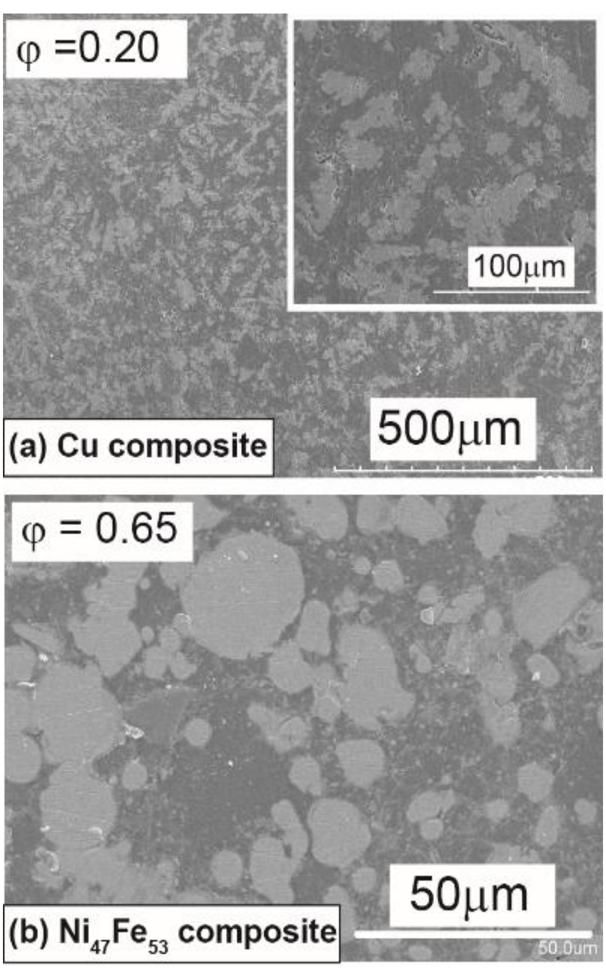

Fig.1. Scanning Electron Microscope (SEM) images of the polished surface of Cu and $Fe_{53}Ni_{47}$ composites ((a) Cu: φ =0.20, (b) $Fe_{53}Ni_{47}$: φ =0.65) [**6**, **9**]

Results and discussion

The ac conductivity σ_{ac} measured at 1 kHz are shown in **Fig. 2** as a function of the particle volume fraction φ. In the Cu composite materials, the σ_{ac} is in the order of 10^{-9} to 10^{-7} S/cm in the low particle content range up to φ = 0.1. A huge conductivity jump is observed at about φ = 0.16; the σ_{ac} becomes more than 10^{-1} S/cm. After that the σ_{ac} gradually increases with φ. Meanwhile, the spherical magnetic particle composites show a large conductivity jump in the higher particle content. The electrical percolation threshold φ_C was defined as 0.16 for Cu, 0.61 for $Ni_{47}Fe_{53}$, and 0.76 for $Co_{50}Fe_{50}$ composites from this variation of conductivity with volume fraction [**6,9,10**]. Above φ_C, the composite materials are in the electrically conductive (metallic) state; a conductive loss appears in the complex permittivity spectrum [**5**]. The conductivity of $Ni_{47}Fe_{53}$, and $Co_{50}Fe_{50}$ composites increases with φ after the percolation; the σ_{ac} of the $Ni_{47}Fe_{53}$ composite reaches the same order as that of the Cu composite at about 0.9. However, the σ_{ac} of the $Co_{50}Fe_{50}$ composite show lower conductivity value of the order of 10^{-3} S/cm in the entire volume fraction. The increase of σ_{ac} in the percolated state is attributed to the decrease of the contact resistance between metallic particles. The gradated area above dashed line indicates the LFP state in these composite materials which is discussed later.

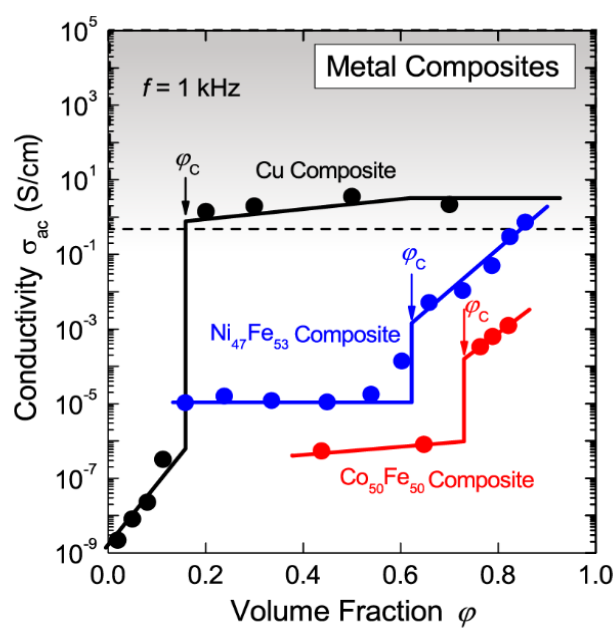

Fig.2. Electrical conductivity σ_{ac} of metal granular composite materials as a function of the volume fraction of particles. The dashed line indicates the boundary between non plasmonic and plasmonic state.

The real part of relative complex permittivity ε_r' spectra of Cu composite materials are shown in **Fig. 3**. From φ = 0.068 to 0.15, a typical dielectric permittivity spectrum with positive ε_r' was observed; no frequency dispersion of ε_r' was recognized up to 10 GHz. The ε_r'

increases with particle content; ε_r' value reaches 50 at 100 MHz in the fraction of 0.15. This variation is attributed to the dielectric polarization induced in the isolated Cu particle or particle clusters. In this particle content range, the dielectric loss is almost zero.

Meanwhile, at φ = 0.16, the Cu composite show a plasmonic permittivity dispersion with a large negative ε_r' value about -10000 at 100 MHz; the ε_r' becomes positive in the high frequency range. With the increase of φ, the negative permittivity is enhanced; the ε_r' value reaches about -10^5 at 220 MHz.

As is shown in **Fig. 3**, the permittivity spectrum can be separated into two types in the Cu composite materials. The first one shows the dielectric frequency dispersion with the positive permittivity value.

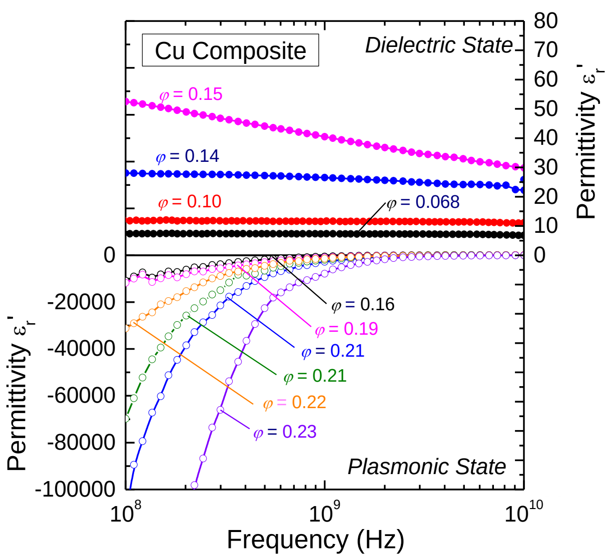

Fig.3. Real part of permittivity for Cu composite materials at φ as a function of frequency.

The second one is the plasmonic permittivity dispersion with the negative ε_r' below a characteristic frequency f_0 which is associated to the plasma frequency f_p of the oscillation of conduction electrons. The plasma frequency f_p is given by

$$f_p = \frac{1}{2\pi}\sqrt{\frac{n_0 q^2}{m\varepsilon_0}} \tag{1}$$

where m, q and n_0 are the mass, charge and the number density of conduction electron, respectively. The frequency dispersion of permittivity in metallic materials having the conductive loss can be described by the following formula using the Drude model [**11**],

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 - j\Gamma_e\omega}, \tag{2}$$

where Γ_e is a damping constant, ω is the angular frequency of the electric field ($\omega = 2\pi f$). The ω_p is the plasma angular frequency denoted by (1). In the percolated composite structure, the electric current flows along the percolated metallic particle chains; the plasmonic oscillation of the conduction electron is induced in the metal particle cluster chains. Since the plasma oscillation in the percolated composite is produced by the conduction electrons moving along the percolated chain only, the low carrier density state can be established in metal granular composites. In this state, the plasma frequency f_p can be decreased by the small n_0 value in the formula (1). This is the same concept of the negative permittivity in the Metal Wire Array (MWA) periodic structure [**2,12**]. From the formula (2), the characteristic frequency f_0 at which the permittivity ε_r' crosses zero from negative to positive becomes different from the f_p due to the effect of damping. The characteristic frequency is given by

$$f_0 = \frac{1}{2\pi}\sqrt{\omega_p^2 - \Gamma_e^2} \quad . \tag{3}$$

From formula (3) the characteristic frequency decreases with increasing damping factor which is associated with the relaxation time of the conduction electron motion.

The real part of relative complex permittivity ε_r' spectra of $Ni_{47}Fe_{53}$ composites are shown in **Fig. 4**. In contrast to the Cu composites, the $Ni_{47}Fe_{53}$ composite shows a dielectric property up to φ = 0.85; the LFP state was observed at φ = 0.90. At the φ = 0.40 and 0.60, the dielectric property with the permittivity value of about 100 was observed. As is shown in **Fig. 2**, the electrical percolation takes place at φ_C = 0.61 in the $Ni_{47}Fe_{53}$ composite from the conductivity data. Hence, the composites at φ = 0.75 and 0.85 are in the percolated conductive state. However, the LFP state is not established in these particle content. This result suggests that the enough current flow to make the LFP state may not be realized in these content range due to the high resistive particle surface condition. Since the dielectric state is maintained in the high particle content, a relatively large dielectric permittivity can be obtained in the microwave range by the $Ni_{47}Fe_{53}$ composite materials.

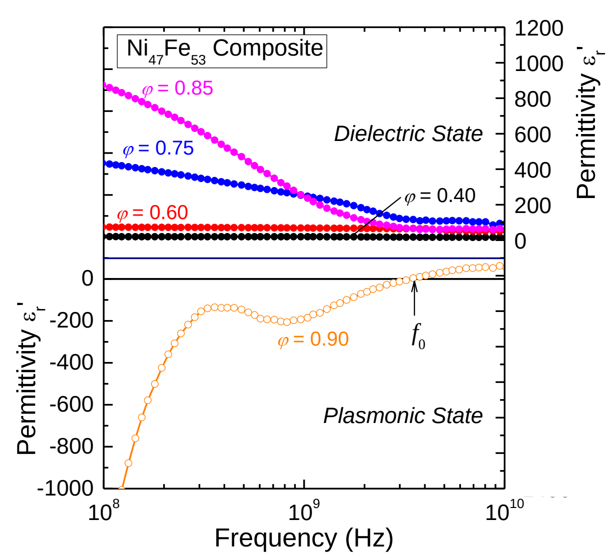

Fig.4. Real part of permittivity for $Ni_{47}Fe_{53}$ composites at various φ as a function of frequency. The f_0 indicates the characteristic frequency in the plasmonic state.

In the LFP state at the volume fraction φ = 0.90, a negative permittivity spectrum with the characteristic frequency of 4.7 GHz was observed. From the conductivity data in **Fig.2**, the σ_{ac} value at φ = 0.90 is 0.75 S/cm at 1 kHz; this is the same as that of the Cu composite in the LFP state. Generally, since the ac conductivity in the low frequency range can be regarded as the dc conductivity, it can be concluded that the relatively high electrical conductivity about 1.0 S/cm is required to establish the LFP state in the metal granular composite materials.

In this ε_r' spectrum, the frequency dispersion is different from that in the Cu composite; a broad maximum was observed at about 360 MHz as shown in **Fig. 4**. This characteristic can be attributed to the dielectric resonance of the electric polarization ***P*** which is induced in the isolated metal particle clusters [**8,12**]. The frequency dispersion of permittivity for the dielectric resonance of ***P*** can be described by the Lorentz type formula which have been used in the analysis of the dielectric resonance of Metal Fiber Array (MFA) periodic structures as well [**11,14**]. The dielectric resonance frequency and the damping constant can be estimated by the numerical fitting of the measured permittivity spectrum [**14**].

Fig. 5 shows the real part of relative complex permittivity ε_r' spectra of $Co_{50}Fe_{50}$ composites in the high particle content range up to φ = 0.82. The permittivity spectra of $Co_{50}Fe_{50}$ composites indicate the typical dielectric response; the ε_r' value is almost constant up to several GHz. Though the ε_r' increases with increasing particle content, the ε_r' value becomes at most 60 at φ = 0.82. The percolated state in the metal granular composite has a large dielectric polarization by the induced charges on the metal particle; a frequency dispersion of permittivity accompanying a large conductive loss was observed [**13**]. However, above mentioned results show that the $Co_{50}Fe_{50}$ composite indicates an insulating property in the percolated state.

In the permittivity spectrum of 0.76 and 0.82 volume fractions, a relaxation or resonance type small frequency dispersion is observed at several GHz. This characteristic may be caused by the dielectric resonance of the embedded particle clusters which was discussed above.

From the electrical conductivity results in **Fig. 2**, the σ_{ac} value of $Co_{50}Fe_{50}$ composite at 1 kHz is in the order of 10^{-3} S/cm at the volume fraction of 0.82. Since the percolation threshold is located at φ_C = 0.76, the non-plasmonic conductive state exists above φ_C in the $Co_{50}Fe_{50}$ composite particles, too. The high percolation threshold and the non-plasmonic state implies that the $Co_{50}Fe_{50}$ surface has a large contact resistance which is caused by the oxidation, etc.

To estimate the onset of the LFP state in the metal granular composites, the real part of permittivity of Cu and $Ni_{47}Fe_{53}$ composites at several frequencies is plotted as a function of the volume fraction φ in **Fig. 6**. In the Cu composite materials, the onset volume fraction of the LFP state indicated by the dashed line is almost the same as the percolation threshold φ_C. Dielectric state is located below φ_C; the LFP state exist above it. On the other hand, in the $Ni_{47}Fe_{53}$ composite, the percolation threshold is located at φ_C = 0.61; the LFP state takes place at about φ = 0.85 indicated by the dash-dotted line. Hence the non-plasmonic conductive state exists between boundaries. A large negative permittivity value can be obtained in the low frequency range such as 10 MHz or 100 MHz; high frequency permittivity at 10 GHz is positive in the entire volume fraction for both composites.

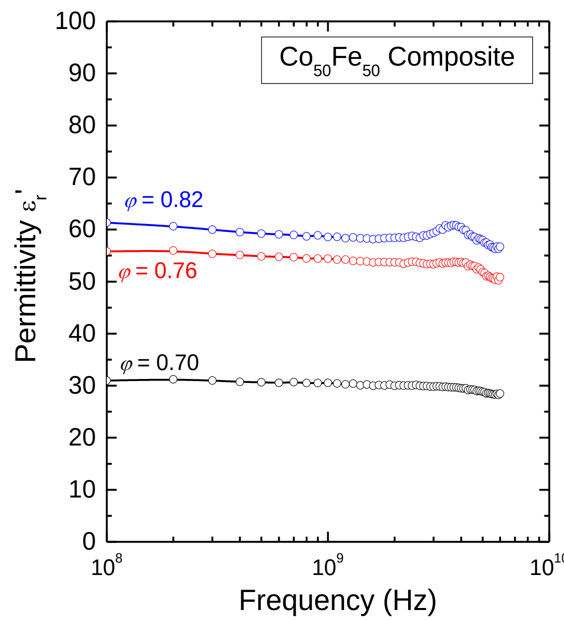

Fig. 5. Real part of permittivity for $Co_{50}Fe_{50}$ composites at various φ as a function of frequency.

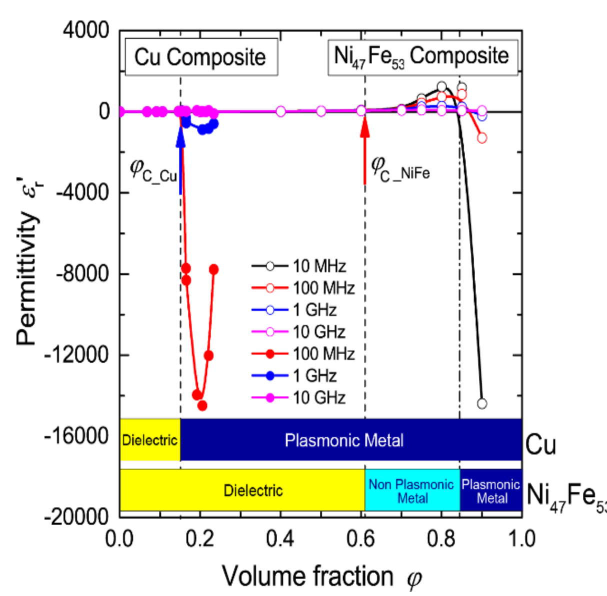

Fig. 6. Real part of permittivity ε_r' for the Cu and $Ni_{47}Fe_{53}$ composites as a function of the particle volume fraction φ. The φ_C denotes electrical percolation threshold.

Conclusions

Electrical properties of the percolation-induced low frequency plasmonic state in the metal granular composite materials have been investigated by the complex permittivity and ac conductivity measurements. It was found that the non-plasmonic state can exist in the electrically percolated state; the relatively high conductivity about 1.0 S/cm is required to establish the LFP state in the metal granular composite materials. In the non-plasmonic conductive state, the permittivity spectrum shows a dielectric frequency dispersion; relatively high dielectric constant value can be obtained in the microwave range. It is considered that the low frequency plasmonic state can be produced by the electric current flow with the low conduction electron density along the percolated cluster chains in the percolated state of the metal granular composite.

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Author's contributions

Conceived the plan: TT; Performed the expeirments: HM, TK; Data analysis: HM, TK, TT; Wrote the paper: TT, HM,TK. Authors have no competing financial interests.

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