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Dielectric properties of Permalloy granular composite materials

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Abstract

Dielectric and electrical properties of Permalloy granular composite materials have been studied considering the application to left-handed meta-materials. Surface oxidized Permalloy particles have high surface electrical resistance; the eddy current effect in the composite structure is suppressed. The electrical conductivity of compacted Permalloy particles increases with increasing temperature and indicates the semiconductive layer formation on the particle. The low frequency ac electrical conductivity of Permalloy composite materials shows a drastic increase in the particle content between 50 and 60 vol.%. Electrical permittivity spectra of Permalloy composites show a non-metallic characteristic and the enhancement of permittivity is observed with increase of Permalloy particle content.
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1. Introduction

Left-handed meta-materials, which have simultaneously negative permeability and permittivity (DNG) in the microwave frequency range, have been the subject of considerable interest in these days. There are possibilities that the negative refraction of electromagnetic waves or breaking the limitation of antennas can be achieved.[1,2] A granular composite material composed of nanometer-sized magnetic metal particles has been theoretically investigated as a candidate of the left-handed media.[3] We have been studying the possibility of a left-handed meta-material using the frequency dispersion of the permeability in ferromagnetic metal composite materials combined with the permittivity spectrum of the metal wire array composite (WAC) structure.[4–7] Generally, though soft ferromagnetic metals have a large permeability in the low frequency region, the permeability rapidly decreases with increasing frequency due to the eddy current effect. On the other hand, ferromagnetic metal granular composites with the low particle content show a large electrical resistivity so that the relatively high permeability can be obtained in the GHz range.[8] Further, the high particle content Permalloy ($Ni_{45}Fe_{55}$) composite containing the surface oxidized particles has a negative permeability spectrum in the microwave frequency range.[4] However, the heat-treated particle composites also have a relatively large permittivity in the microwave range.

To establish the DNG property by the combination of the negative permeability of heat-treated particle composites and the negative permittivity materials such as the WAC, dielectric properties of the permeability negative (MNG) material have to be considered. Thus, in this work, the ac electrical conductivity and the permittivity spectra of Permalloy granular composite materials containing heat-treated particles have been investigated.

2. Experimental

A commercially available Permalloy powder ($Ni_{45}Fe_{55}$) was used for Permalloy composite materials. From the morphology examination by a scanning electron microscope (SEM), the particle shape is spherical and the mean particle diameter d_m is 2.53 μm. Permalloy particles were heat treated in air using an electric furnace at the temperature of 300 °C for 5 h to make the oxidized surface. Though the heat-treatment of particles at 300 °C does not affect the main crystal structure of Ni–Fe alloy, the saturation magnetization of the Permalloy particle shows a small decrease.[4]

Permalloy composite materials were prepared by mixing Permalloy powder with polyphenylene sulfide (PPS) resin powder, melting the resin at 300 °C and pressing the mixture at a

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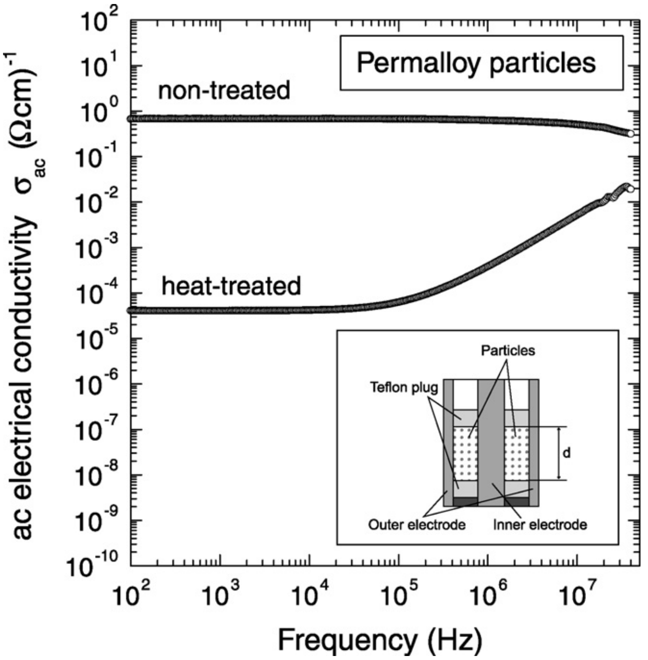

Fig. 1. The ac electrical conductivity σ_{ac} of heat-treated and non-treated Permalloy particles as a function of frequency at room temperature. The inset shows the coaxial electrode.

pressure of 624 MPa in the cooling process down to room temperature. Obtained samples were cut into a toroidal form (inner diameter is 3 mm, outer diameter is 7 mm). The thickness of samples is controlled about 1 mm in order to avoid the dimensional resonance of the electromagnetic wave in a coaxial line. The particle content was estimated using the density values of the sample, host resin and embedded particles, respectively.

The ac electrical resistivity ρ_{ac} of compacted Permalloy particles was measured in the frequency range from 100 Hz to 100 MHz at various temperatures up to 373 °C by a two-terminal method using a coaxial electrode and an impedance analyzer. In the process of the ρ_{ac} measurement, Permalloy particles were set between the two Teflon plugs in a coaxial electrode which has the inner diameter of 3 mm and the outer diameter of 7 mm as shown in the inset of Fig. 1. The compacted particles were made by pressing with the 156 MPa load. Complex permittivity spectra in the frequency range from 1 kHz to 40 MHz were obtained by measuring the conductance G and the susceptance B difference between the empty and the sample inserted coaxial capacitance using the impedance analyzer. Complex permittivity spectra in the microwave range were measured by the S-parameter method in the frequency range from 100 MHz to 10 GHz using a network analyzer.

3. Results and discussion

Fig. 1 shows the ac electrical conductivity σ_{ac} of compacted Permalloy particles at room temperature as a function of frequency. In the non-treated particles, σ_{ac} is constant about 0.8 $\Omega\,cm^{-1}$ up to 40 MHz and slightly decreases above it. On the other hand, the σ_{ac} of the heat-treated particles shows the low conductivity value about $4.1 \times 10^{-5}\,\Omega\,cm^{-1}$ up to 10 kHz and

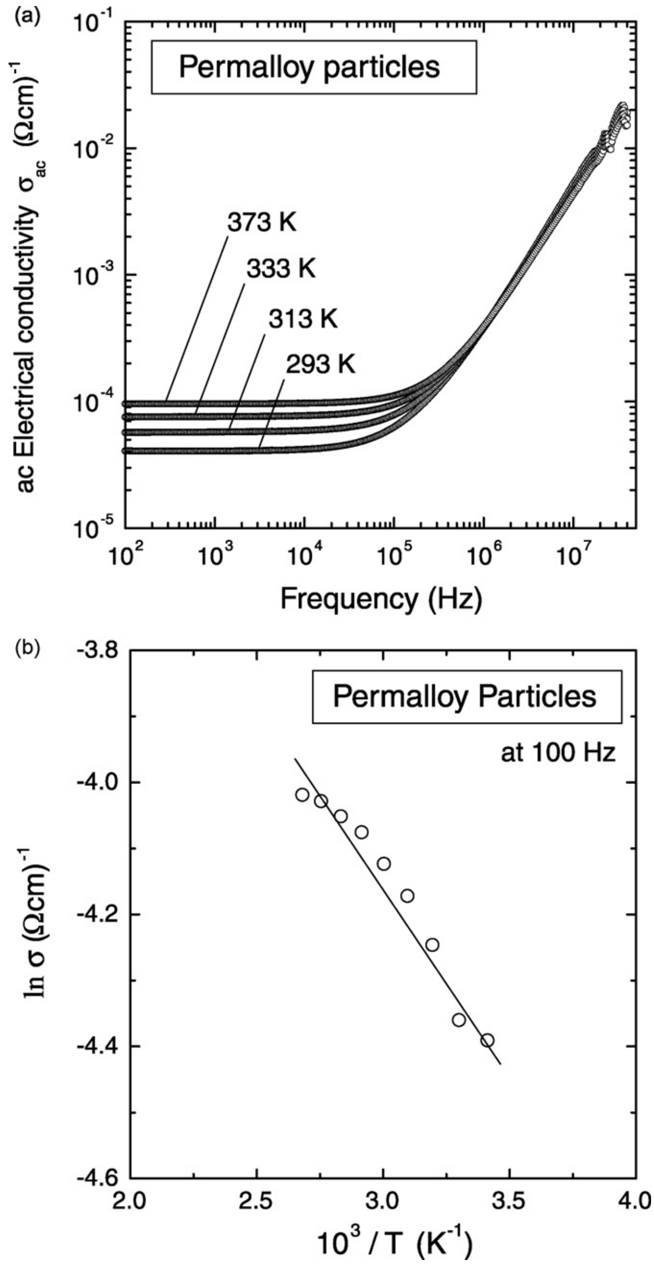

Fig. 2. Electrical conductivity σ_{ac} as a function of frequency at several temperatures (a) and the $\log \sigma_{ac}$ at 100 Hz vs. $1/T$ plot (b) for compacted Permalloy particles.

σ_{ac} increases with increasing frequency above it, reaches about $2.0 \times 10^{-2}\,\Omega\,cm^{-1}$ at 40 MHz. This indicates that the Permalloy particle surface is oxidized by the heat-treatment and the contact electrical resistance among particles increases. The linear frequency variation of σ_{ac} can be explained by the power-law exponent in percolating clusters.[9,10]

Fig. 2(a) shows the ac electrical conductivity σ_{ac} of the compacted Permalloy particles, which are heat-treated, as a function of frequency. At each temperature, the σ_{ac} shows a constant value up to several 10 kHz and then increases with increasing frequency. The low frequency σ_{ac} increases with increasing temperature. Fig. 2(b) shows $\log \sigma_{ac}$ at 100 Hz vs. $1/T$ plot for compacted Permalloy particles. The variation of the σ_{ac} shows

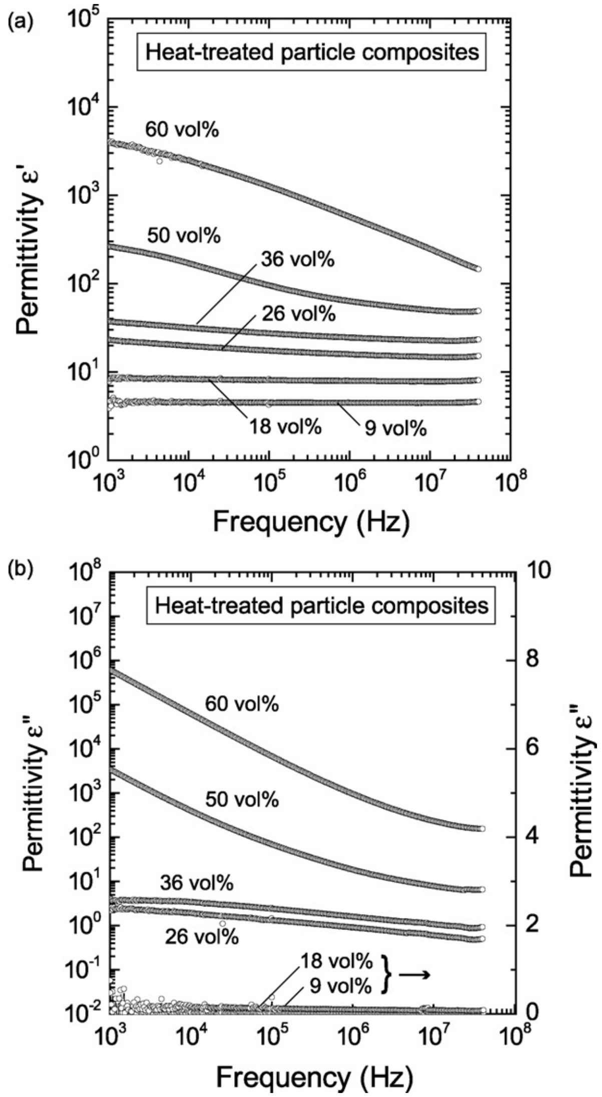

Fig. 3. The complex permittivity spectra ((a) real and (b) imaginary parts) of the Permalloy composite materials containing heat-treated particles in the frequency range from 10 kHz to 40 MHz.

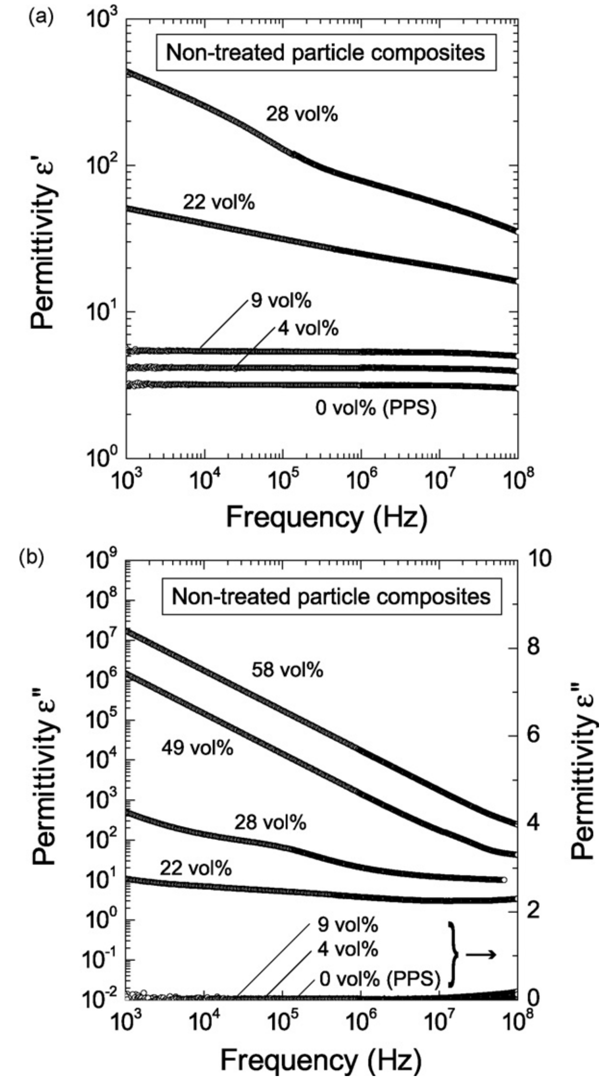

Fig. 4. The complex permittivity spectra ((a) real and (b) imaginary parts) of the Permalloy composite materials containing non-treated particles in the frequency range from 10 kHz to 100 MHz.

the almost linear decrease with increasing 1/*T*. This can be originated by that the oxidized Permalloy surface has a semiconducting property and electrical transport properties can be modified in the percolated particles. The solid line indicates the least mean square fitting result of the σ_{ac} plotted; the activation energy obtained from the slope of the solid line is 0.11 eV. As the semiconductive oxides, NiO and FeO (or Fe_3O_4) can be considered. The ac electrical conduction in percolated particles having a semiconductive surface can be described by the variable range hopping which was introduced for amorphous semiconductors.[9,10]

The low frequency complex permittivity spectra ($\varepsilon^* = \varepsilon' - i\varepsilon''$) for the Permalloy composite materials containing heat-treated particles are shown in Fig. 3 as a function of frequency. For the 9 and 18 vol.% composites, the ε' is almost constant and the ε'' is zero up to 40 MHz indicating the non-metallic property. On the other hand, a small frequency dispersion is observed in the 26 and 36 vol.% composites, but in higher frequency region, the ε' and ε'' approach to a constant value and zero, respectively. For the 50 and 60 vol.% composites, the ε' and ε'' strongly depend on frequency and decreases with increasing frequency.

In the previous study, we reported that the electrical percolation of the conductivity takes place about 40 vol.% in non-treated Permalloy particle composite,[8] and a transition from metallic to insulating state occurs at the electrical percolation limit ϕ_c. Fig. 4 shows the complex permittivity spectra of non-treated Permalloy composites in the frequency range from 1 kHz to 100 MHz. In the low particle content (0, 4 and 9 vol.%), the ε' is almost constant and ε'' is zero. On the other hand, in the 49 and 58 vol.% composites, low frequency ε'' have enormous value and is inversely proportional to the frequency indicating a metallic conduction. Further, ε' cannot be determined due to the current flow in the composite. In general, the complex permittivity ε^* of metallic materials can be described by the following formula:

$$\varepsilon^* = 1 + i\frac{4\pi}{\omega}\sigma^*. \tag{1}$$

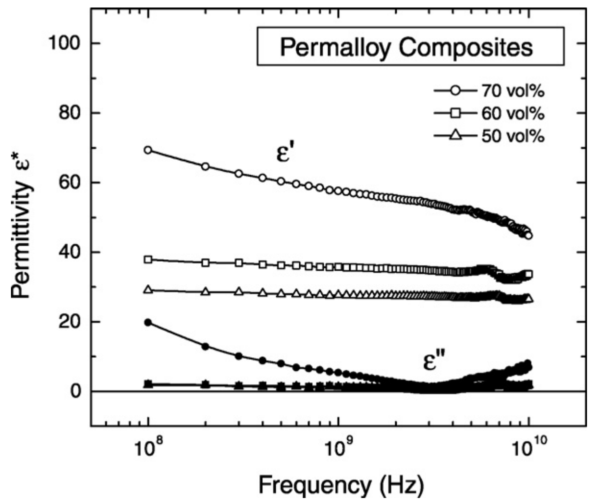

Fig. 5. The complex permittivity spectra ((a) real and (b) imaginary parts) of the Permalloy composite materials containing heat-treated particles in the frequency range from 100 MHz to 10 GHz.

Here, ω and σ^* are angular frequency and complex conductivity, respectively. In this equation, the relation between the ε'' and σ^* is approximately represented as follows:

$$\varepsilon'' \propto \frac{\sigma^*}{\omega}. \quad (2)$$

When σ^* is independent of the frequency, ε'' has $1/f$ type frequency dispersion. Thus it is considered that the ε'' of the 49 and 58 vol.% composites shows metallic characteristics. For the 22 and 28 vol.% composites, since the ε' and ε'' decreases with increasing frequency in the measured frequency range, coexistence of metallic and insulating properties can be considered. From the comparison of the permittivity spectra of heat-treated and non-treated particle composites, it is considered that the heat-treated particle composites with the particle content from 26 to 60 vol.% also have the coexistence state of metallic and non-metallic properties. Thus the frequency dispersions of the complex permittivity may be originated by the variable range hopping conduction between percolated particles in the large sized percolated clusters.

Fig. 5 shows the complex permittivity spectra of the Permalloy composites containing heat-treated particles in the frequency range from 100 MHz to 10 GHz. This figure is quoted from the reference.[4] For the 50 and 60 vol.% composites, ε' is almost constant and ε'' is almost zero in this frequency range. In the 70 vol.% composite, the permittivity spectra show small frequency dispersion. This indicates that the heat-treated particle composite material shows a non-metallic characteristic even in the percolated particle content.

Fig. 6 shows the ac electrical conductivity σ_{ac} of the heat-treated Permalloy composites in the frequency range from 100 Hz to 40 MHz. For the 36 vol.% composite, σ_{ac} increases linearly with increasing frequency in the measurement frequency range. On the other hand, the σ_{ac} of the 69 vol.% composite has a constant value up to several hundred Hz, and then slightly increases with increasing frequency. Connor et al. have reported that in the Carbon black–Polyclear (conductor–insulator) composite, the frequency variation of σ_{ac} is divided into two types by the condition that the conducting particle content is lower or higher than the electrical percolation limit ϕ_c.[11] In the former case, the σ_{ac} is frequency dependent with a constant slope in a log–log scale. When the conductor content is close to or greater than ϕ_c, σ_{ac} shows a constant value below a critical frequency f_c at which σ_{ac} begins to depend on frequency; σ_{ac} increases with increasing frequency above the f_c. Such kind of behaviour difference is observed in the frequency variation of σ_{ac} in the heat-treated Permalloy particle composites. The σ_{ac} variation of the 36 and 43 vol.% composites corresponds to the case of the lower content below ϕ_c and the latter tendency is seen in that of the 61 and 69 vol.% composites.

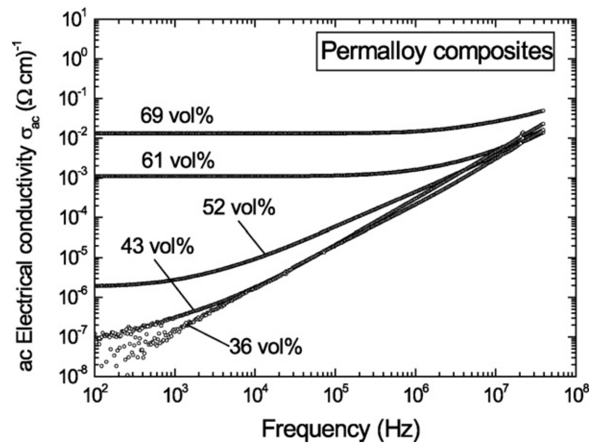

Fig. 6. The ac electrical conductivity σ_{ac} for Permalloy composites containing the heat-treated particles.

The particle content variation of σ_{ac} and the normalized permittivity $\varepsilon/\varepsilon_0$ at 1 kHz for Permalloy composites containing heat-treated particles are shown in Fig. 6(a). Normalized permittivity was obtained using the absolute value ε and ε_0 of complex permittivity for Permalloy composites and PPS resin, respectively. The thick solid line shows the Clausius–Mossotti relation which is expressed by

$$\frac{\varepsilon - 1}{\varepsilon + 1} = p, \quad (3)$$

where ε is the permittivity and p is the volume filling factor of Permalloy particles.[12] The σ_{ac} increases with increasing particle content and shows a large jump between 50 and 60 vol.%. The $\varepsilon/\varepsilon_0$ increases with increasing particle content. The variation of the $\varepsilon/\varepsilon_0$ obeys the Clausius–Mossotti relation in lower particle content up to about 10 vol.%. The permittivity enhancement is observed above it. Finally, the $\varepsilon/\varepsilon_0$ diverges with vertical asymptote around 60 vol.%. On the other hand, in non-treated particle composites, the drastic variation of σ_{ac} and $\varepsilon/\varepsilon_0$ is also observed around 40 vol.% as shown in Fig. 7(b). This result indicates that the electrical percolation of the heat-treated particles takes place at higher particle content in the composite. From the experimental and theoretical investigations, it is reported that the drastic variation of conductivity and permittivity takes place around the ϕ_c.[13,14] Since we used the same Permalloy particles in the preparation of heat-treated and non-treated particle composites, the critical particle content of the mechanical percolation

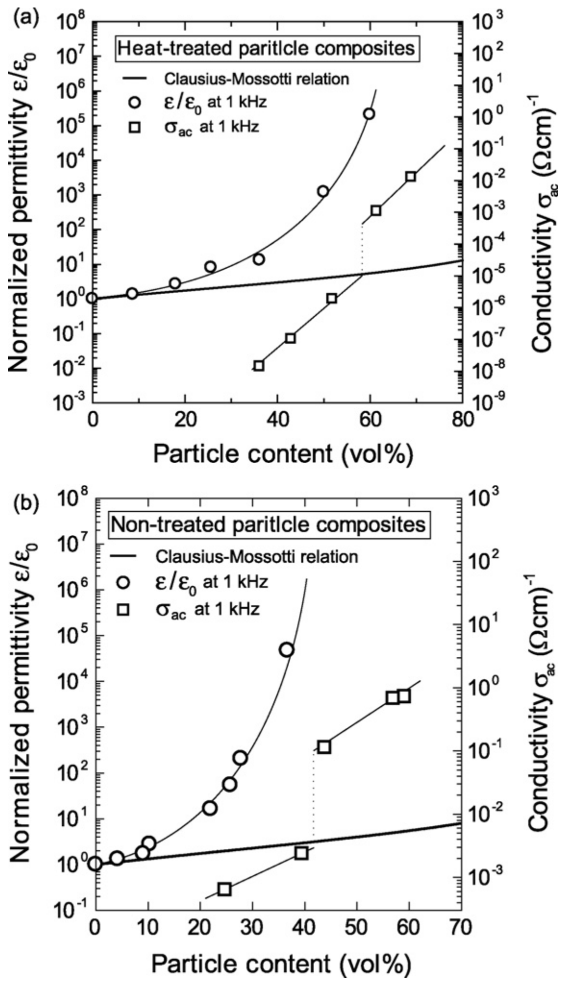

Fig. 7. The σ_{ac} (open squares) at 1 kHz and the variation of normalized permeability $\varepsilon/\varepsilon_0$ at 1 kHz (open circles) for Permalloy composites containing heat-treated (a) and non-treated (b) particles. The thick solid line is the Clausius–Mossotti relation. The thin solid lines are guide for the eyes.

must be the same in the two particle conditions. Therefore, it is considered that the critical particle content ϕ_c in the electrical percolation was increased by the decrease of the electrical conductivity due to the heat-treatment of particles. However, in the 60 vol.% composite containing heat-treated particles, the complex permittivity spectra indicate the non-metallic property as shown in Fig. 6 although the particle content is close to or greater than the ϕ_c. This result can be considered as follows. In high frequency region, the alternative current flow is decreased due to the skin depth effect of electromagnetic field and a large contact resistance among the embedded particles takes place. Therefore, dielectric property by the electrical polarization in the embedded particles is maintained.

The permittivity enhancement in the composite structure is observed above 10 vol.% in both heat-treated and non-treated composites. Since the ε' value of the host resin (PPS) is about 3 as shown in Fig. 4 and this value is constant up to 6 GHz, the enhancement of the $\varepsilon/\varepsilon_0$ can be attributed to the dielectric polarization of the embedded particles or particle clusters having the metallic and semiconductive layers. Further, in the 26 and 36 vol.% particle content composites, it is expected that the ε' and ε'' have a constant value and no loss in higher frequency region. Because the ε' and ε'' of the 50 and 60 vol.% composites indicates a constant value and zero, respectively, in the frequency range from 100 MHz to 10 GHz as shown in Fig. 4. Considering that these composites have various sized clusters, the permittivity by the dielectric polarization in particle clusters decreases with increasing frequency. Therefore, the dielectric polarization in the embedded particle mainly contributes to the permittivity of composites in the high frequency region.

4. Conclusions

In this work, dielectric and electrical properties of Permalloy granular composite materials containing heat-treated particles have been studied. The temperature variation of electrical conductivity in compacted particles revealed that the oxidized layer of heat-treated particles has the semiconductive property and prevents the high frequency current flow in composites. Among percolated particles in composites, the variable range hopping takes an important role in the electrical conduction. The σ_{ac} at 1 kHz of heat-treated particle composites increased with increasing particle content and indicated a large jump at the particle content between 50 and 60 vol.%. It is considered that the electrical percolation limit ϕ_c actually locates at the lower particle content of the mechanical percolation, and the ϕ_c shifts to higher particle content due to the decrease of conductivity by the heat-treatment of particles. For heat-treated particle composites, the permittivity enhancement was observed by the dielectric polarization of the embedded metallic particles with the semiconductive layer or these particle clusters. The dielectric polarization in the particle clusters decreases with increasing frequency but dielectric property is maintained in the microwave range. For further investigations, the left-handed meta-material having the composite structure of Permalloy composites and the WAC are now in progress.

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