FABRICATION AND ELECTROMAGNETIC CHARACTERISTICS OF COMPOSITES CONTAINING ELECTROLESS METAL-COATED CARBON NANOFIBERS

Ki-Yeon Park*, Sang-Bok Lee, Jin-Bong Kim**, Jin-Woo Yi**, Sang-Kwan Lee**, Jae-Hung Han***

***Department of Aerospace Engineering, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea**
****Composite Materials Laboratory, Korea Institute of Machinery and Materials (KIMM), Republic of Korea**

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Abstract

To improve the electromagnetic characteristics of conductive nano fillers, carbon nanofibers (CNFs) with nickel-phosphorous (Ni-P) and nickel-iron (Ni-Fe) have been fabricated by the electroless plating process. Observations by the electron microscopy (SEM/TEM) and element analyzer (EDS/ELLS) showed the uniform Ni-P and Ni-Fe coated CNFs. The compositions of the plating layers were about Ni-6wt%P and Ni-70wt%Fe, respectively. The average thicknesses of the plating layers were about 50 ~ 100 nm. Composites with various weight percentages (30, 50, 70 wt%) of fillers were fabricated. Composites containing Ni-Fe coated CNFs had higher dielectric and magnetic loss than Composites containing Ni-P coated CNFs.

1 Introduction

Microwaves are electromagnetic waves with a frequency range in the electromagnetic spectrum of 300 MHz to 300 GHz. However, most applications of microwave technology make use of frequencies in the range of 1 to 40 GHz [1]. The absorption and the interference shielding of electromagnetic wave have been very important issues for commercial and military purposes. The stealth technique is one of the most typical applications of electromagnetic wave absorption technology [2].

There have been many researches on radar absorbing materials (RAM) such as composites containing conductive fillers or magnetic materials. However, some problems are remained in those researches. The conductive absorbers with dielectric lossy materials have the heavy matching thickness and narrow absorbing bandwidth. Magnetic absorbers with magnetic lossy materials have the heavy weight and poor characteristics due to their Snoek's limit in the GHz range [3]. The enhanced electromagnetic wave absorbers have the conditions as lightness, thinness and wide-absorbing bandwidth. Recently, researches on nano-composites containing dielectric and magnetic lossy materials have been studied to solve these problems. Che et al. [4] fabricated the carbon nanotube/Fe composites and enhanced microwave absorption characteristics. Wang et al. [5] developed the Ni-P coated multi-walled carbon nanotubes (MWNTs) by the electroless deposition process and observed the microstructures and X-ray diffraction (XRD) of them. Pan et al. [6] fabricated the electroless Ni-P deposited strontium ferrite powders and measured the complex permittivity and permeability.

Electroless plating means the deposition of metals on a catalytic surface from solution without an external source of current. Materials fabricated by this process have the advantages such as the uniform coating thickness, good corrosion resistance and mass production. The disadvantages are the slow deposition speed and high production cost than the cases of the electric plating. However, the electric plating process is impossible and the elctroless plating process is suitable to deposit metal layers on the surfaces of nano particles such as CNFs.

This research deals with composites which consist of the metal-coated carbon nanofibers (CNFs), the dielectric and magnetic lossy materials. CNFs were used as conductive nano particles. Nickel-phosphorous (Ni-P) and nickel-iron (Ni-Fe) were used to increase the magnetic properties. Magnetic metals were deposited on the surface of CNFs by the electroless plating process. Observations of microstructures (SEM, TEM) and element analysis (EDS, EELS) for developed-powders were done. Composites containing the developed powders were fabricated and the electromagnetic properties of them were measured.

2 Experiments

The Carbon nanofibers (Showa Denko, Japan) are used as conductive fillers. Its typical diameter and length are 100~200 nanometers and 10~20 micrometers. Fig. 1(a) shows a SEM image of as-received CNFs. Initial tangled CNFs are necessary to sufficiently disperse and clean before electroless plating process. Fig. 1(b) shows a SEM image of pre-treated CNFs. Compared with the tangled CNFs of Fig. 1(a), the pre-treated CNFs were straightened and uniformly dispersed. The electroless plating process had to be conducted in this states to plate the uniform metal layers.

Electroless metal plating is divided into four stages such as pre-treatment (purification and surface modification), sensitization and activation, acceleration and metal deposition. CNFs through each process have to be cleaned and filtered well with deionized water [7, 8].

Ni-P plating solution consists of $NiCl_6 \cdot 6H_2O$, $NaPH_2O_2 \cdot 6H_2O$, $NH_3 \cdot Cl$ and deionized water. Electroless Ni-P plating is progressed at 90 °C for 8 min. Ni-P coated CNFs are dried at 60 °C for 12 hr. Then, thermal exposure process is needed to improve the magnetic properties. Heat treatment was conducted at 400 °C for 2 hr under argon atmosphere.

Ni-Fe-P plating solution is composed of $FeSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $KNaC_4H_4O_6 \cdot 4H_2O$, $NaPH_2O_2 \cdot 6H_2O$, NaOH and deionized water. Electroless Ni-Fe-P plating is progressed at 75 °C for 8 min. Ni-Fe-P coated CNFs are dried at 40 °C for 12 hr. In this case, iron has magnetic properties fundamentally. The heat treatment was not necessary.

Specific morphology and elements of Ni-P and Ni-Fe coated CNFs were analyzed through the SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy, EDS (Energy Dispersive Spectroscopy), EELS (Electron Energy Loss Spectroscopy)

Composites were fabricated using the developed powders and resin. The mixtures of powders and resin are uniformly dispersed and fabricated. The added weight percentages of Ni-P coated CNFs were 30 and 50 wt%. The added weight percentages of Ni-Fe coated CNFs were 30, 50 and 70 wt%.

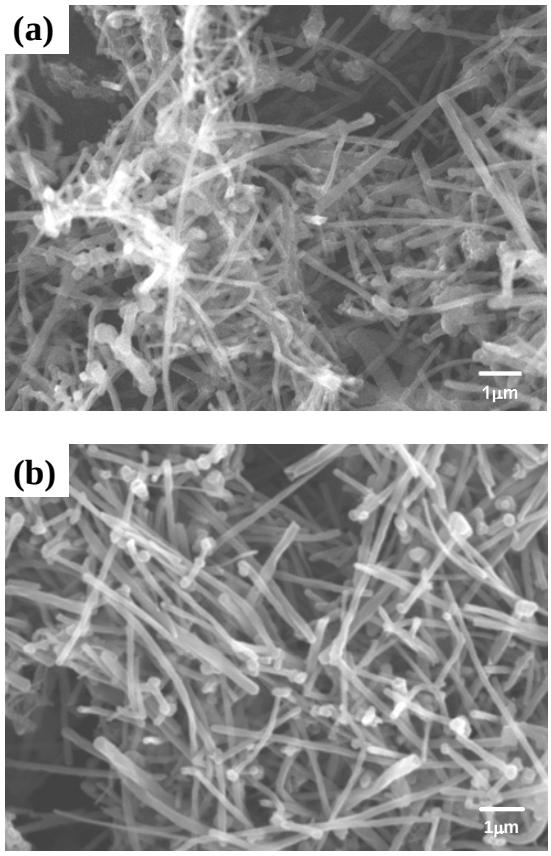


Fig. 1. SEM images of (a) as-received CNFs (b) pre-treated CNFs

3 Microstructures and elements analyses for developed powders

3.1 Ni-P coated CNFs

Fig. 2 shows the TEM BF (Transmission Electron Microscopy Bright Field) images of Ni-P coated CNFs during and after process. In the Fig. 2(a), light rods are CNFs and dark points of the edge are Ni-P coated layers. Fig. 2(b) clearly shows the Ni-P plating layers are homogenously distributed on the each surface of CNFs. The thickness of typical Ni-P deposition is about 50 ~ 100 nm. Generally,

metal plating process on the carbon substrate is very difficult due to the bad wettability between carbon and metal. Therefore the fine and uniform Pd particles on the surface of CNFs through sufficient and proper pre-treatment processes result in homogeneous metal-plating distribution and thicknesses.

EELS (Electron Energy Loss Spectroscopy) analysis was carried out to obtain the specific element contents of Ni-P layers. Fig. 3 shows the TEM BF image of Ni-P coated CNFs with uncoated region and EELS map for C, Ni and P elements. At the TEM image, light area is the uncoated region and dark area is the coated region. At the ELLS map, yellow region means carbon element, blue region means nickel element and pink region means phosphorous. The composition of the coated layers was analyzed as about 94 wt% Ni and 6wt% P.

Fig. 4 shows the SEM images of as-fabricated Ni-P coated CNFs and heat treated powders. From Fig. 4(a), the coated Ni-P layers were homogeneously distributed on the surfaces of CNFs. These results are definitely caused by the proper pre-treatment processes and plating conditions.

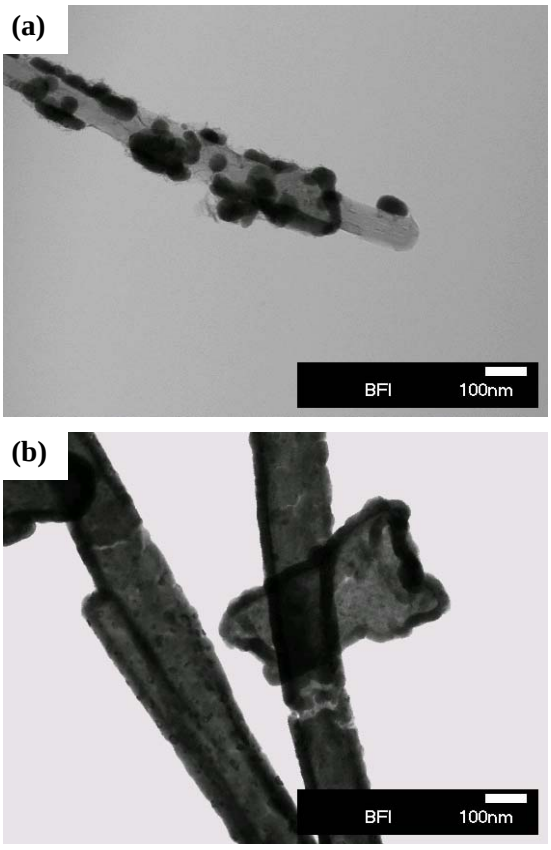


Fig. 2. TEM BF images of Ni-P/CNFs
(a) during process (b) after process

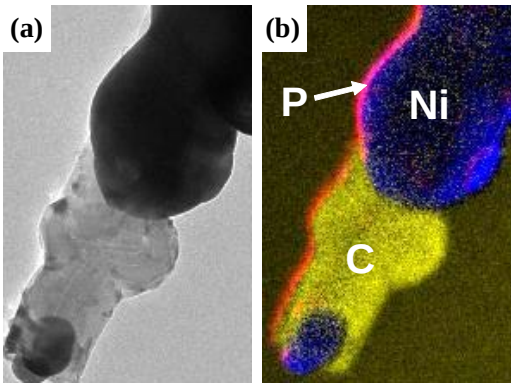


Fig. 3. (a) TEM BF image and (b) ELLS map of Ni-P/CNFs with uncoated layers

The heat treatment process converts the amorphous Ni-P layers into crystalline Ni and Ni3P intermetallic compound layers. Ni-P of amorphous state do not have the magnetic properties. To increase the magnetic properties, the heat treatment has to be conducted at temperature above 350 °C, for time over 1 hr under argon atmosphere. Fig. 4(b) shows a SEM image of heat treated Ni-P coated CNFs. Heat treated Ni-P coated CNFs sustained the

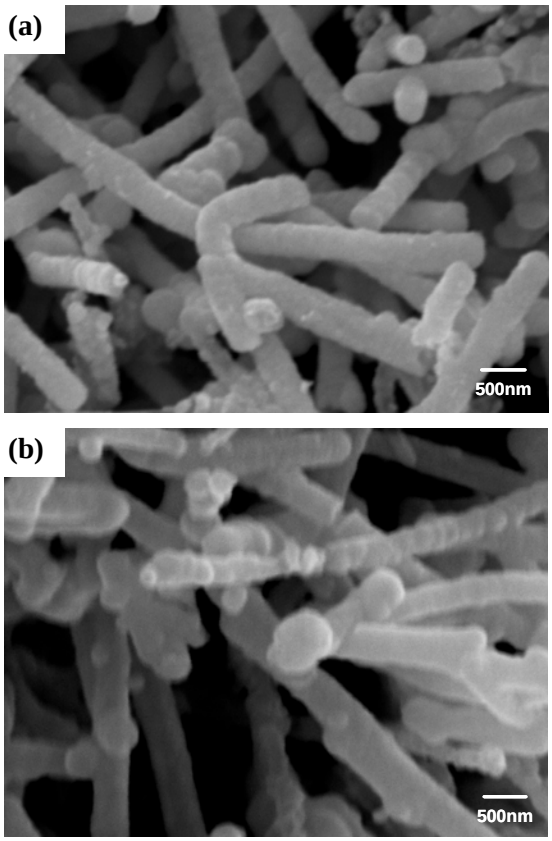


Fig. 4. SEM images of (a) as-fabricated Ni-P/CNFs
(b) heat-treated Ni-P/CNFs

fundamental shapes and agglomerated at the partial region. Therefore, the additional experiments are needed to obtain the optimal heat treatment conditions.

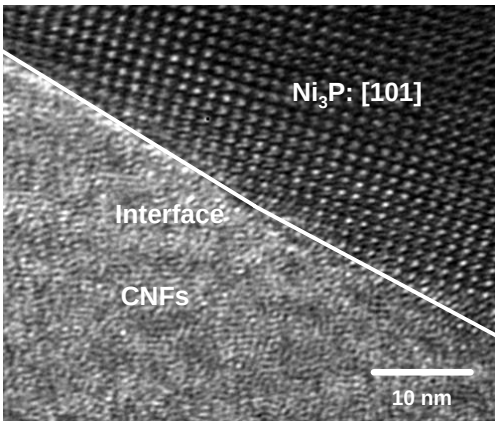


Fig. 5 HR TEM image containing the interface region of Ni-P coated CNFs.

Fig. 5 shows the HR (High Resolution) TEM image containing the interface region of Ni-P coated CNFs. From this image, Ni-P layers deposited fully on the surfaces of the CNFs and the amorphous Ni-P layers converted into crystalline Ni_3P intermetallic compound layers.

3.2 Ni-Fe coated CNFs

Fig. 6 shows the SEM image of Ni-Fe coated CNFs. The experiment results showed similar characteristics in comparison with Ni-P coated CNFs. Mostly, Ni-Fe coated layers formed homogeneous distribution on the surfaces of CNFs These characteristics clearly result from the proper pre-treatment processes and plating conditions. In this case, the heat treatment process was not conducted because iron elements had the magnetic characteristics.

Fig. 7(a) shows the TEM BF images of Ni-Fe coated CNFs. Light rods are CNFs and dark points of the edge are Ni-Fe coated layers. Table 1 shows the EDS results for Ni-P and Ni-Fe coated CNFs. From the results of Ni-Fe coated CNFs, a little amount of nickel, a large quantity of iron and a very small amount of phosphorus were detected. Fig. 7(b), (c) and (d) show the EDS map of Ni-Fe coated CNFs. From these figures, the deposition distribution and density of metal elements can be graphically observed. On the whole the Ni-Fe deposited layers are homogenously distributed on

Table 1. EDS results for metal coated CNFs

Ni-P/ CNFs	Wt %	At %	Ni-Fe/ CNFs	Wt %	At %
Ni	93.95	89.12	Ni	26.20	24.50
P	6.05	10.88	Fe	70.05	68.85
-	-	-	P	3.75	6.65
Total	100	100	Total	100	100

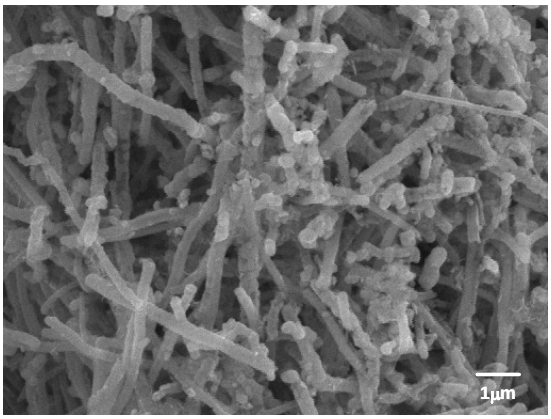


Fig. 6. SEM image of Ni-Fe/CNFs

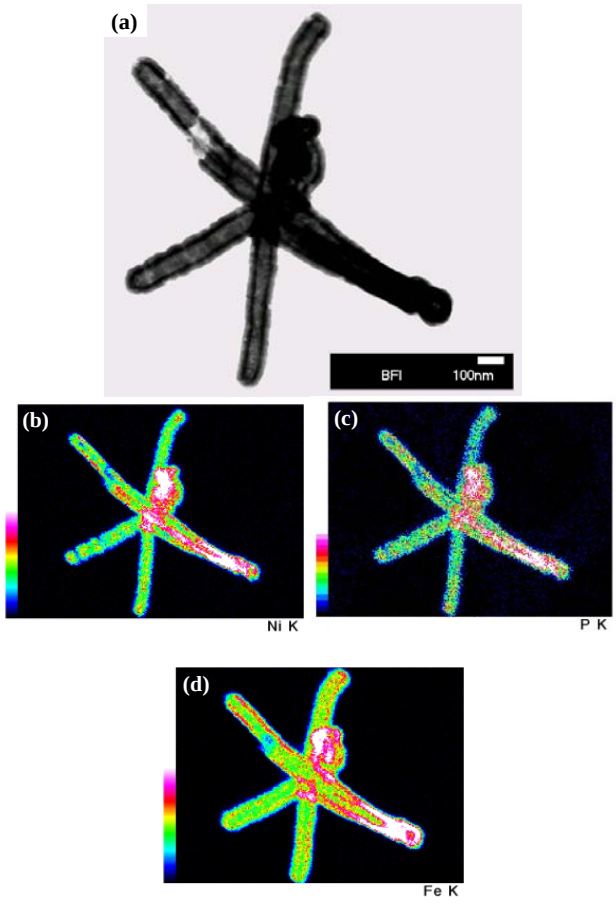


Fig. 7. (a) TEM BF image and (b), (c), (d) EDS map of Ni-Fe/CNFs

the each surface of CNFs. The thickness of typical Ni-Fe deposition is about 50 ~ 100 nm. Therefore the electroless Ni-Fe deposition experiment also were successfully worked.

4 Measurement of complex permittivity and permeability for fabricated composites

4.1 Composites containing metal coated CNFs

Composites containing Ni-P coated CNFs were prepared the 2 kinds of specimens. The weight percentages of developed powders were 30 wt% and 50 wt%. Conveniently, these specimens are indicated as Ni30 and Ni50 in this paper. Composites containing Ni-Fe coated CNFs were prepared the 3 kinds of specimens. The weight percentages of developed powders were 30 wt%, 50 wt% and 70 wt%. Likewise, these specimens are indicated as Fe30, Fe50, and Fe50 in this paper.

Table 2 shows the density of fabricated specimens. Because the atomic weight of nickel is heavier than that of iron, Ni-P/CNFs composites have higher density than Ni-Fe/CNFs composites relatively. Fig. 8 shows the cross section of fabricated Ni30 composites. Ni-P coated CNFs were homogeneously distributed with resin. From the extended image, the inner CNF (black) was enclosed with the outer Ni-P layer (gray).

Table 2. Density distribution of fabricated specimens

Denotations	Ni30	Ni50	Fe30	Fe50	Fe70
Density(g/cm^3)	1.47	1.69	1.41	1.63	1.73

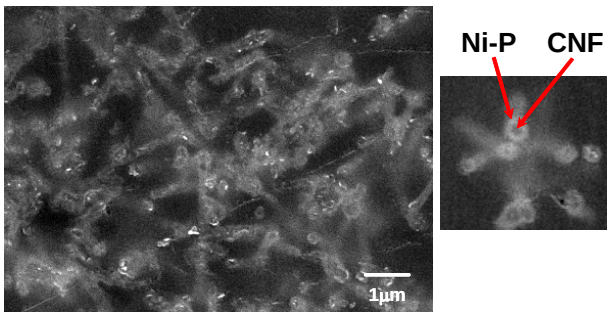


Fig. 8. Cross section of Ni30 composites

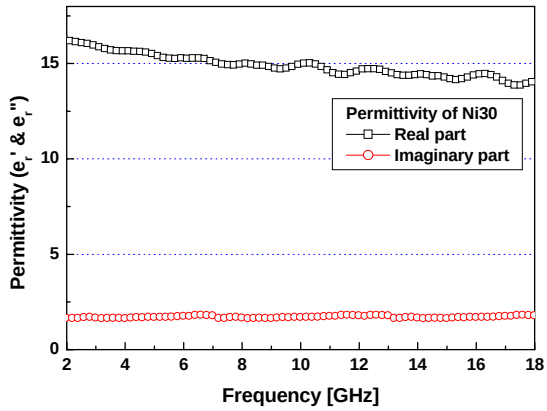
4.2 Measurement systems

S-parameter measurement system using the transmission line technique has been used. Using network analyzer Agilent N5230A, S-parameters of fabricated specimens were measured in the frequency range from 2 to 18 GHz. The specimens for measurement had the shape of cylindrical toroid. Complex permittivity and permeability of those specimens were calculated by using magnitude and phase of measured S-parameters.

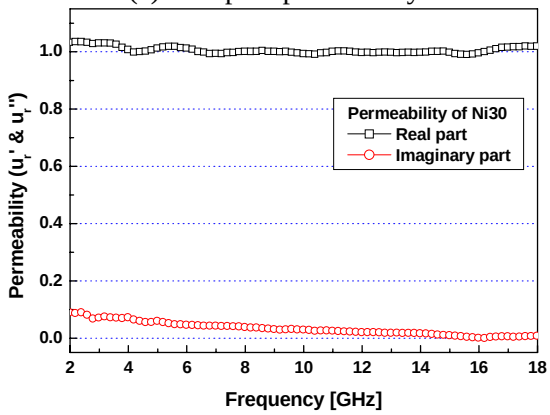
4.3 Measurement results

Fig. 9 shows complex permittivity and permeability of Ni30. The real part and imaginary part of complex permittivity at 10 GHz are about 15 and 1.8 respectively. The real part and imaginary part of complex permeability at 10 GHz are about 1 and 0.03 respectively. The electric and magnetic loss tangents are about 0.12 and 0.03 at 10 GHz. Ni30 is the composites that have the low electric loss and no magnetic properties.

Fig. 10 shows the measured S-parameters of Ni50. S11 and S21 are the reflected and transmitted power [dB]. The S11 and S21 results mean nearly the perfect reflection without the transmitted electromagnetic wave. The conductivity of Ni50 is too high to measure the complex permittivity and permeability of Ni50. Probably, these results would originate from a large quantity of conductive interm-



(a) Complex permittivity



(b) Complex permeability

Fig. 9. Electromagnetic characteristics of Ni30

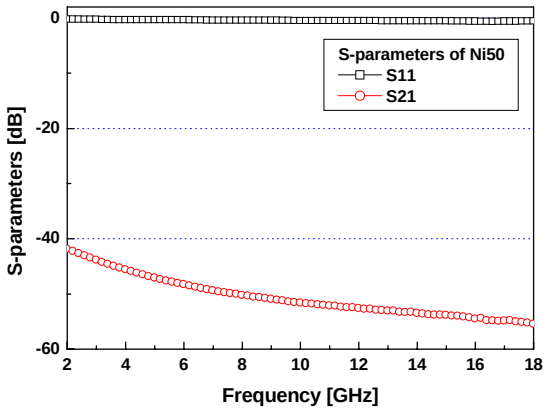


Fig. 10. S-parameters of Ni50

etallic compounds formed by the heat treatment or dispersion problems by re-agglomeration phenomena among the developed powders when composites were mixed and fabricated. To solve these problems fully, experimental approaches about optimal heat treatment and dispersion would be progressed.

Fig. 11 and 12 show complex permittivity and permeability of Fe30, 50 and 70. As the weight percentage of developed powders increased, the permittivity and imaginary part of permeability got larger. But, the real part of permeability had nearly the constant values. Table 3 shows the complex permittivity (ε_r',ε_r''), electric loss tangent ($\tan\delta_\varepsilon$), complex permeability (μ_r',μ_r'') and magnetic loss tangent ($\tan\delta_\mu$) at 10GHz of fabricated specimens. The relations between loss tangent and complex permittivity (permeability) can be expressed as given in Eq. 1 [9]. In the cases of Fe specimens, the permittivity data showed the high level results relatively and the electric loss tangents over 0.5 could be expected to induce high conductive characteristics. Also, the imaginary parts of permeability were values than 0.1 in the GHz ranges.

$$\tan\delta_e = \frac{\varepsilon_r''}{\varepsilon_r'}, \quad \tan\delta_\mu = \frac{\mu_r''}{\mu_r'} \qquad (1)$$

Table 3. Electromagnetic properties of fabricated specimens at 10 GHz

	ε_r'	ε_r''	$\tan\delta_\varepsilon$	μ_r'	μ_r''	$\tan\delta_\mu$
Ni30	15.0	1.8	0.12	1.0	0.03	0.03
Ni50	-	-	-	-	-	-
Fe30	29.6	13.9	0.47	1.0	0.1	0.1
Fe50	89.8	50.8	0.57	1.0	0.2	0.2
Fe70	118.9	81.5	0.69	1.0	0.4	0.4

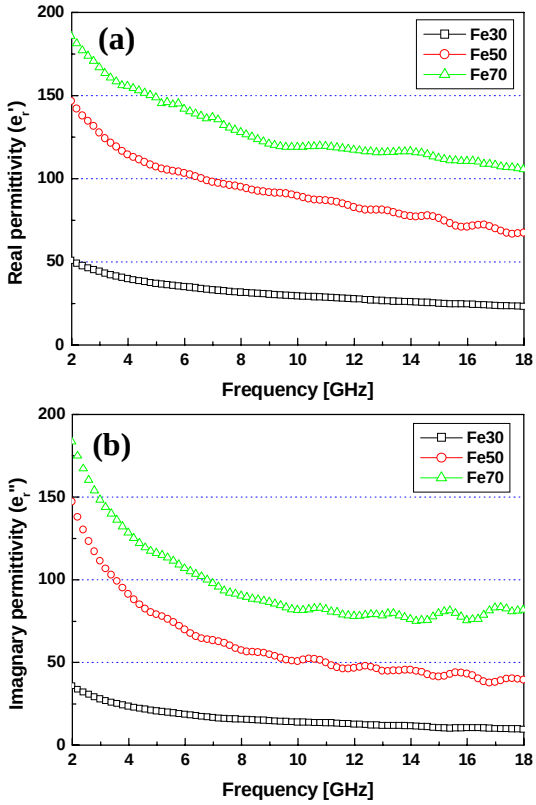


Fig. 11. Complex permittivity of Fe30, 50 and 70

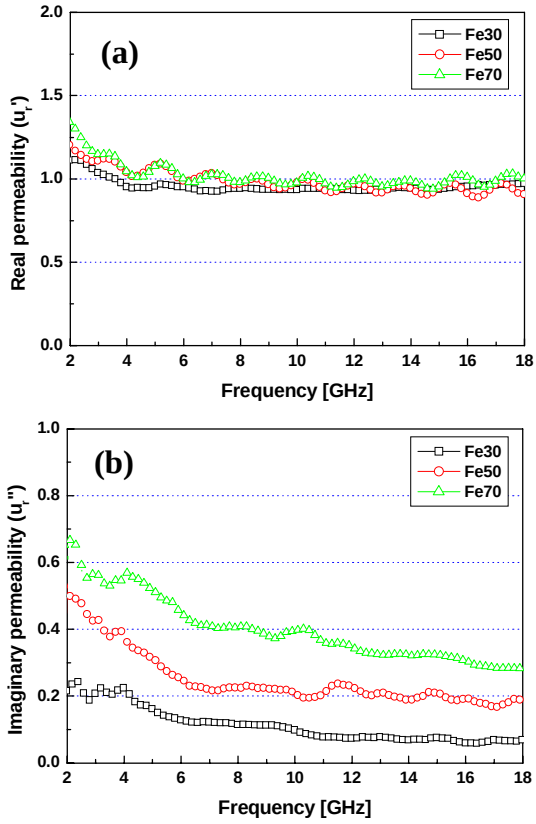


Fig. 12. Complex permeability of Fe30, 50 and 70

Therefore, the composites containing Ni-Fe coated CNFs are the dielectric and magnetic lossy materials with high dielectric loss and low magnetic loss.

5 Conclusions

This research focused on the fabrication of the dielectric and magnetic lossy materials, the observation of their microstructures and elements and the measurement of their electromagnetic properties. CNFs were used as conductive nano particles. Ni-P and Ni-Fe were used to increase the magnetic properties. Ni-P and Ni-Fe coated CNFs have been successfully fabricated by the electroless deposition process. Through the SEM, TEM, EDS etc., Ni-P and Ni-Fe deposited layers were homogenously distributed on the each surface of CNFs. The thickness of typical deposition was about 50 ~ 100 nm. It is very important to carry out a series of pre-treatments fully and control the plating conditions properly for the successful uniform deposition. Composites containing the developed powders were fabricated and the complex permittivity and permeability of them were measured in the frequency range from 2 to 18 GHz. Composites containing Ni-P coated CNFs had the low electric loss and no magnetic properties. Composites containing Ni-Fe coated CNFs were materials with the high dielectric loss and low magnetic loss.

This proposed research can be usefully extended to synthesize the new and advanced materials. Further experimental research and the optimal design for the fabrication of good electromagnetic wave absorbers are going to be progressed.

Acknowledgement

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