Electromagnetic wave absorption on resin composite including ferrite particles with concentration gradient

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The Fe₃O₄ particles were prepared from iron chloride by the hydrothermal reaction. The resultant Fe₃O₄ particles possessed good crystallinity when using the NH₄OH precipitant and showed the high saturated magnetization value of ca. 90 emu/g. Resin compacts including above ferrite powders were prepared using a centrifugal molding technique. The resultant concentration-gradient resin composites exhibited better broadband electromagnetic wave absorption than the homogeneous resin compacts (no gradation). Such absorption ability is responsible for the suppression of undesirable reflection on the incidence plane and effective thermal loss transducing of electromagnetic wave near the reflector where the magnetic powders are condensed.

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1. Introduction

With increasing use of wireless communications such as mobile phones, wireless local area networks, and RFID reader technology, several problems such as electromagnetic interference and information leakage have become more serious. In particular, electromagnetic waves in UHF (300 MHz–3 GHz) and SHF (3–30 GHz) bands can transfer information in moderately high speed and wide area, so wireless broadband communications, e.g. ultra-wide band (UWB) and WiMAX standards have been favorably used above frequency bands. Hence, high-performance broadband electromagnetic wave absorbers should be developed to maintain the quality and convenience of wireless communication.

Electromagnetic wave absorbers are roughly classified into magnetic loss, dielectric loss, and ohmic loss types. Among them, the magnetic type absorbers can be easily designed owing to relatively high characteristic impedance matching and advantages of electrical length. According to distributed constant circuit model of an absorber in which a conductive reflector is attached at the rear, the incident impedance and reflection loss can be expressed from following equations:

\[ Z_{in} = Z_0 \sqrt{\frac{\mu_s}{\varepsilon_r}} \tan \left( \frac{2\pi d}{\lambda} \sqrt{\varepsilon_r \mu_r} \right) \]  
\[ RL = 20 \log \left( \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right) \]  

where \( \lambda \) is the wavelength of the electromagnetic wave, \( d \) is the absorber thickness, \( Z_0 \) is the characteristic impedance of air (≈377 Ω), \( Z_{in} \) is the incident impedance of the absorber, and \( RL \) is the reflection loss. So, perfect no reflection (\( RL = -\infty \)) can be gained by adjusting \( Z_{in} \) to \( Z_0 \). However, permittivity is larger than permeability in usual absorbers, which provides a low characteristic impedance (\( Z_0 \sqrt{\mu_r/\varepsilon_r} < Z_0 \)). These absorbers consequently show good performance only in a narrow band as the input impedance (\( Z_{in} \)) can barely match the characteristic impedance of air (\( Z_0 \)) taking into consideration the \( \tanh \) transcendental function 

\[ \left( \sqrt{\frac{\mu_s}{\varepsilon_r}} \tanh \left( \frac{2\pi d}{\lambda} \sqrt{\varepsilon_r \mu_r} \right) \right) = 1 \].

To enhance the absorption frequency range, multi-layer and pyramidal absorbers have been investigated. But the absorption range is limited for the former type, because its absorption is fundamentally achieved by electromagnetic wave interference derived from multiple reflections from each layer (basically same mechanism as above \( \lambda/4 \) type absorbers). For the latter type absorber is too thick for common use due to maintaining good characteristic impedance. In our previous study, it has been found that the resin composites including iron metal powders with concentration gradient possessed the good broadband absorption ability.

2. Experimental

0.4 M FeCl₂·4H₂O solution was mixed with 2 M urea solution with stirring and then the mixed solution was heated for 1 h at ca. 100°C to proceed a hydrolysis of urea completely. During the
reaction the solution color was changed from yellow to suspended brown-black, indicating that the formation of hydroxide particles. Besides the urea precipitating reagent, NH₄OH was also examined. The powders were collected by several centrifuging and water-washing treatments. The powders collected were mixed with 80 mL of 6 M NaOH in a polytetrafluoroethylene flask, and the flask was placed in a 100 mL autoclave reactor. Subsequently the sealed reactor was kept at 260°C for 72 h to ripen the crystal particles. The products were collected in a similar way as mentioned above and then dried at 323 K for 1 h in air. The obtained powders were characterized by an X-ray diffractometer (RIGAKU RINT 2200) with a Cu-Kα radiation. Surface morphology of the products was observed by a scanning electron microscope (HITACHI S-3000). Magnetic properties were measured by a vibrating sample magnetometer (TAMAKAWA TM-VSM2014-MHR type).

The concentration-gradient resin composites were prepared as followed. Mixture of the ferrite powders (60–70 wt %) and commercial thermosetting urethane resin having the permittivity values of ε′, ε′′ ≈ 2 and ε′, ε′′ ≈ 0 was injected in a polytetrafluoroethylene toroidal mold (outer diameter: 7.00 mm, inner diameter: 3.04 mm). Then the molds were centrifuged at 670–2170 G for 0–40 min and subsequently cured at 393 K for 1 h. As a reference, the homogeneous resin composites including same magnetic powders were also prepared without centrifuging (0 min). The homogeneous resin compact worked as the lossy magnetic layer was also prepared by mixing the 95 wt % iron powders (BASF, CL powder with D50 < 10 µm) and the resin in the similar procedure.

The electromagnetic absorption (reflection loss) properties were evaluated from the S₁₁ values measured by a vector network analyzer (Agilent, E8363A) using the co-axial sample folder in the range of 1–18 GHz. Details of the present measuring system are described in our previous report. A short device for calibration was used as a conductive reflector. For the concentration-gradient samples, the short device was attached to the side with a dense concentration of the magnetic powders. For the lossy magnetic layer, the scattering parameters (S₁₁, S₁₂, S₂₁, S₂₂) were measured to evaluate relative complex permittivity (ε″ = ε′ − jε″) and permeability (μ″ = μ′ − jμ″) values according to the Nicolson-Ross model for magnetic materials.

3. Results and discussion

**Figure 1** shows the XRD pattern of the samples prepared using the urea precipitant. All diffraction peaks were assigned to cubic Fe₃O₄ (JCPDS No. 19-629). Relative intensity for each peak was almost identical with the JCPDS data, indicating that the crystal was grown in isotropic. The SEM image for this sample is shown in **Fig. 2(a)**. Spherical formed particles with ca. 1–10 µm diameter were observed. This result is well coincident with the above XRD one. As seen in **Fig. 2(b)**, the particle morphology before the hydrothermal treatment is rod-like shape. The particle morphology was drastically changed during the hydrothermal treatment, indicating the crystal growth proceeds via dissolution and recrystallization in the NaOH solution.

**Figure 3** shows the magnetic hysteresis loops for the Fe₃O₄ powders prepared by using the urea precipitant. The saturation magnetization value is 50 emu/g and the coercivity one is ca. 250 Oe. The coercivity value is almost same to the reported data, but the saturation one is lower compared with the value measured on the bulk sample (92 emu/g). When the hydrothermal reaction was finished, the autoclave vessel was cooled rapidly by water. The lower saturation magnetization value may be attributed to this cooling process which induces magnetic strain. Annealing treatment was carried out to remove such stress. The Fe₃O₄ powders were sealed in vacuumed glass tube and annealed at 300°C for 24 h with elevating and lowering a temperature very slowly. The saturation magnetization value of the annealed Fe₃O₄ powders increased up to 80 emu/g with remaining the coercivity value of around 250 Oe.

The concentration-gradient resin composites were prepared from the 70 wt % annealed Fe₃O₄ powders with the centrifugal force of 2170 G. **Figure 4** shows the electromagnetic wave absorption properties for the resin composites by changing the centrifugal time of 0–40 min. Every samples have almost same thickness of ca. 7 mm. The graded resin compacts centrifuged below 20 min have better electromagnetic absorption ability than the non-graded one. The absorption ability around 5 and 13 GHz
was improved, which can be responsible for the electromagnetic advantage for the concentration-gradient resin composite mentioned in the introduction part. Compared with the usual multilayered electromagnetic wave absorbers, the concentration-gradient absorbers suppress undesirable reflection in an absorber due to the continuous impedance change derived from their gradient structure. The minimum reflection loss peaks around 3 GHz were varied with centrifugal time, suggesting that electromagnetic wave absorption by magnetic loss plays an important role in addition to the interference by phase inversion. In contrast, the absorption ability was deteriorated on the absorber of the centrifugal time over 20 min because of separation between the resin and the Fe₃O₄ powders, viz. the incident impedance mismatching by such discontinuous interface. Local average densities of the concentration-gradient resin compact (40 min) were evaluated by weighing before and after polishing. Local density gradually increased from the incidence surface to the opposite side. The local average density near the incidence surface (resin-rich part) was 1.26 g/cm³ and that in middle part was 2.39 g/cm³. The density in the Fe₃O₄-rich part was 2.54 g/cm³. Since density of the resin used here is 0.89 g/cm³ and bulk density of Fe₃O₄ is 5.2 g/cm³, suggesting that the concentration gradation could be attained by the present centrifugal molding. Although it is thought that moderate concentration-gradient was formed in the resin composite prepared with the centrifugal time of 20 min, satisfiable electromagnetic absorption performance cannot be achieved probably due to a poor characteristic of the Fe₃O₄ absorption medium. So other precipitant to prepare Fe₃O₄ particles was examined.

Instead of urea, NH₄OH was used as a precipitant. Figure 5 shows the SEM image observed on the resultant Fe₃O₄ particles. Well crystallized Fe₃O₄ particles with a 1–5 µm diameter were successfully obtained. The preparation temperature in using the urea precipitant was 100°C at which solubility of ammonia drastically dropped. On the other hand, the temperature was kept at room temperature for the case of the NH₄OH precipitant, resulting in the sufficient ripening of the iron hydroxide particles. The magnetic hysteresis loop measurement revealed that coercivity value was almost similar to the case of the urea precipitant, but saturation magnetization one was improved up to 90 emu/g, which is close to value reported on the bulk sample. The autoclave vessel was slowly cooled to room temperature after finishing the hydrothermal reaction for the present case, so it is considered the magnetic strain was not generated.

The concentration-gradient resin composites including the improved Fe₃O₄ powders (60 wt%) were prepared with optimizing a centrifugal condition. All samples have almost same thickness of 14 mm. Figure 6 shows the electromagnetic wave absorption properties on the above resin composites. All composites with the concentration-gradient possessed superior performance compared with the non-gradient one. The reflection loss below almost −10 dB, meaning 90% absorption, was achieved in a frequency range of 2–8 GHz. Local average densities were evaluated by dividing the above concentration-gradient resin compacts into quarters. The first part (resin rich one) near the incident surface was 1.11 g/cm³ on the sample obtained at 670 G for 40 min. The density values were increased along with the inner side: those on the second, third, and forth (magnetic powder rich) parts were 1.30, 1.86, and 2.93 g/cm³, respectively. In a similar way, the respective local average densities were 0.92, 1.23, 2.12, and 2.82 g/cm³ on the sample prepared by the centrifugal condition of 1510 G for 15 min. The sample made by the centrifugal condition of 2170 G for 15 min provided the local average densities of 0.91, 1.16, 1.55, and 2.88 g/cm³, respectively. The smooth gradation was obtained for the above samples. Slight difference of gradation pattern affects the electromagnetic wave absorption properties, suggesting that more excellent absorption ability can be realized by optimizing the centrifugal condition such as time and force.
together with controlling the particle size distribution.

The above absorption range, however, does not cover completely the UWB (3.1–10.6 GHz) and WiMAX (2–9 GHz) standards. As mentioned above, the \( \lambda/4 \) type absorbers show good absorption ability only in a narrow frequency range mainly due to an oscillation characteristic of the \( \tanh \) function. In our previous work, the mathematical deliberation for Eq. (1) led to the finding that such oscillation characteristic can be considerably suppressed when the imaginary part (loss value) of permeability and/or permittivity is increased.\(^{16} \) So this technique was applied to the present absorption system. The lossy magnetic layer (thickness of 2.2 mm) including 95 wt % carbonyl iron powders homogeneously was inserted between the absorber and the reflector. Relative real and imaginary parts of permeability of the lossy magnetic layer is shown in Fig. 7, and the electromagnetic wave absorption ability on the resin composite (670 G centrifugal force for 40 min) combined with the lossy magnetic layer is displayed in Fig. 8. The addition of the lossy magnetic layer could enhance the electromagnetic absorption ability by reducing the oscillation feature of the \( \tanh \) function. In other words, improvement impedance matching by the oscillation feature reduction of the \( \tanh \) function means good electromagnetic absorption by the magnetic loss (\( \mu_r'' \)) in a wide frequency range. The reflection loss observed on the gradient resin compact with the lossy magnetic layer was almost below \(-10 \) dB in the frequency range of 1–8 GHz. As shown in Fig. 7, imaginary part of permeability (\( \mu_r'' \)) comparable to magnetic loss) for the magnetic layer has a broad peak in the measurement frequency range. So the insertion of the lossy magnetic layer contributes to improve the electromagnetic wave absorption ability in a wide frequency range, especially around 4 GHz. To further improve the absorption ability, the polyurethane foam plate having lower permittivity (\( \varepsilon_r \approx 1.5, \varepsilon_r'' \approx 0 \) ) was also attached on the gradient absorber surface. The electromagnetic absorption ability of the resultant stacked type absorber was well increased as seen in Fig. 8. The urethane foam thickness is 2.6 mm and the total absorber thickness becomes to be 18.8 mm. As the permittivity of the urethane foam gets close to that of air (\( \varepsilon_r \approx 1, \varepsilon_r'' \approx 0 \)), the matching frequencies hardly changed, but the absorption ability around 10 GHz was fairly improved. This enhancement of reflection loss was responsible for the greater suppression of the undesirable first reflection on the surface of the absorber. This result bears out the absorption model on the present graded absorber proposed above.

4. Concluding remarks

The well crystallized Fe\(_3\)O\(_4\) particles can be prepared by using a NH\(_2\)OH precipitant and a successive hydrothermal reaction from a starting iron source of FeCl\(_2\) which is much generated as a by-product during making steel. The saturation magnetization value of the above Fe\(_3\)O\(_4\) powders is almost same to that of sintered bulk sample. The resin composites including the resultant powders with concentration-gradient can absorb electromagnetic wave in a wide range from 2–8 GHz. Better performance (\( RL < \) c.a. –10 dB, 1–8 GHz) is obtained when combining the above gradient absorber and the lossy magnetic layer due to reducing oscillation of the incident impedance by increase of \( \mu_r'' \). The electromagnetic wave absorption ability can be further improve by attaching the low permittivity urethane foam on the absorber surface due to the suppression of primary reflection on the absorber surface plane. The resultant stacked type absorber can cover the wide band wireless communication standards such as
UHF and WiMAX.

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