Magnetic Properties and Microwave Absorption Properties of Polymer-Protected Cobalt Nanoparticles

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This paper describes magnetic properties and microwave absorption properties of polymer-protected cobalt nanoparticles. Cobalt nanoparticles were prepared using the thermal decomposition of dicobalt octacarbonyl in ethylene glycol. They were stabilized and dispersed by coexisting with poly(N-vinyl-2-pyrrolidone) (PVP), resulting in an average diameter of 45 nm. The X-ray diffraction (XRD) analysis revealed that the Co-PVP sample synthesized at 170°C for 3 h, with the mole ratio of cobalt : PVP = 1 : 10 (mol : unit mole), consisted of two phases ofhcp and fcc cobalt. Their saturation magnetization measured using a vibrating sample magnetometer (VSM) was 1.53 × 10−4 Wb·m·kg−1. The compacted sample, produced from the PVP-protected cobalt nanoparticles, showed a reflection loss (R.L.) less than −20 dB at the frequency (matching frequency: f0m) of 0.54 and 0.64 GHz with the thickness (matching thickness: dm) of 6.16 and 5.04 mm, respectively. Therefore, it is concluded that polymer-protected cobalt nanoparticles have a possibility for the use as microwave absorption materials.

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1. Introduction

In the recent information-oriented society, the number of wireless communication tools using high frequency electromagnetic waves, such as mobile phone (800 MHz, 1.5 GHz), PHS (1.9 GHz), Bluetooth (2.45 GHz) etc., are increasing rapidly. However, the electromagnetic interference (EMI) has become a serious problem,1 resulting in erroneous operations of wireless communication tools and influences on human body. The use of microwave absorbers is one promising technique to help to prevent EMI problems. Some materials, such as ferrites with spinel,2,3 M4,5 and W-type6 structure or metallic magnetic materials, have been applied to microwave absorbers. Especially, resin composites of metallic magnetic materials7–9 have been paid much attention as microwave absorbers in the frequency range of 1–5 GHz. Because these materials have large values of saturation magnetization and show high relative complex permeability in this frequency range, which leads thinner thickness of absorbers.

A magnetic sheet made of Fe–Si–Al flakes was found to have excellent permeability and electromagnetic interference characteristics in a quasimicrowave band.8 The Fe–Si–Al flakes produced by attrition of water atomized powders, which have a thickness close to the skin depth and a large aspect ratio, were embedded in a polymer with their planes lying parallel to the sheet plane. Maeda et al.9 reported that a magnetic powder with a fine α-Fe structure produced by the disproportionation reaction of Sm2Fe17 exhibited good microwave absorption properties in the GHz frequency range.

Recently, many researchers reported the synthesis of metallic fine particles, such as Au,10 Co,11,12 Pd,13,14 Pt,14 Pt–Fe15, etc., with nano-meter size using chemical methods. In these chemical methods, reduction of metal salts or thermal decomposition of metallic carbonyl is used for the production of metallic nanoparticles. In addition, these nanoparticles are stabilized and their particle size is controlled by coexisting polymer or chain-polymer (polymer-protected nanoparticles). Comparing these two methods, the thermal decomposition of metallic carbonyls has an advantage because the reduction process can be skipped.

However, the metallic nanoparticles synthesized by chemical methods have not been applied to use microwave absorption materials. Therefore, in this study, polymer-protected metallic nanoparticles were prepared by the thermal decomposition of the cobalt carbonyl coexisting chain-polymer, and their magnetic properties and electromagnetic wave absorption properties were investigated.

2. Experimental Procedure

Magnetic nanoparticles were prepared by the thermal decomposition of dicobalt octacarbonyl: Co2(CO)8. Poly(N-vinyl-2-pyrrolidone) (PVP), which molecular weight was 55000, was used to disperse magnetic nanoparticles and to control their particle size.

Co2(CO)8 and PVP (5.557 g = 0.05 mol) were dissolved in ethylene glycol (200 ml), and then heated to 130–198°C (198°C: boiling point of ethylene glycol) for 3 h under argon gas flow. Co2(CO)8 and PVP were mixed as Co/PVP (mole/unit mol) = 0.05, 0.10 and 0.50. A color change of the solution from light red brown to black occurred during this process. Then the reaction mixture was allowed to cool to room temperature. The black synthetic colloid was gathered under argon atmosphere and then the carrier solvent was evaporated.

The present phases in the samples were characterized by X-ray diffraction (XRD) and the microstructures were observed using a transmission electron microscope (TEM). The samples for TEM observations were prepared by drying syn-
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The black synthetic powders were pressed at about 70 MPa and formed into the toroidally shaped samples ($\phi_{out}$: 7.00, $\phi_{in}$: 3.04, $t$: about 1.0 mm). The scattering parameters ($S_{11}$, $S_{21}$) were measured by the coaxial method using a Hewlett-Packard HP8722ES vector network analyzer in the frequency range, 0.05 to 20.05 GHz. These parameters were then used to determine the relative complex permeability ($\mu_r = \mu'_r - j\mu''_r$) and permittivity ($\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$), and also used to calculate the frequency ($f$) dependence of reflection loss (R.L.) at a thickness ($d$) with the following formulae, which characterize the electromagnetic wave absorption properties.

$$R.L. = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left( j \frac{2\pi fd}{c} \sqrt{\mu_r\varepsilon_r} \right)$$

where $Z_{in}$: input impedance of absorber, $Z_0$: impedance of free space, $c$: light velocity.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of PVP-protected Co (Co-PVP) particles synthesized at 130–198°C for 3 h with Co/PVP = 0.10. The X-ray diffraction peaks marked by a triangular sign (▽), which are from an unknown phase (not cobalt and cobalt oxide phase), were observed in the sample synthesized at 130°C. However their peaks disappeared in the samples synthesized at temperatures above 150°C, and the X-ray diffraction peaks of cobalt with hcp structure marked by a white circular sign (○) and fcc structure marked by a black circular sign (●), were observed. It suggested that the thermal decomposition of Co$_2$(CO)$_8$ occurred at temperatures above 150°C. It is well known that the fcc-Co is stable at temperatures above 450°C and the hcp-Co preferred to be below the temperature. However, because of using chemical method and small particle size, the fcc-Co can be considered to be present at room temperature. The existence of hcp and fcc cobalt at room temperature was also reported by Hull. The ratio of hcp-Co and fcc-Co in the samples was calculated as hcp-Co : fcc-Co ≒ 4 : 9 from the integrated intensity of their X-ray diffraction peaks.

Figure 2 shows the TEM image of Co-PVP nanoparticles synthesized at 198°C for 3 h in ethylene glycol with Co/PVP = 0.10. The average diameter of cobalt particles is around 45 nm, which reveals that cobalt nanoparticles are synthesized by this method.

In next, magnetic properties of these samples were investigated. Figure 3 shows the variation of saturation magnetization ($I_s$) with the respect to reaction temperatures ($T$) in PVP-protected Co nanoparticles synthesized at 130–198°C for 3 h in ethylene glycol with Co/PVP = 0.10. The $I_s$ values of all samples were over $1.3 \times 10^{-4}$ Wb·m·kg$^{-1}$. The $I_s$ increased with increasing the reaction temperature ($T$), and
saturated at temperatures above 170\(^\circ\)C. Consequently, the maximum value of 1.53 \(\times 10^{-4}\) Wb-m-kg\(^{-1}\) was obtained at 170\(^\circ\)C. The relationship between saturation magnetization \((I_s)\) and Co/PVP ratio was also investigated. These samples were synthesized at 170\(^\circ\)C for 3 h in ethylene glycol with Co/PVP = 0.05–0.50. The \(I_s\) values of the samples with Co/PVP = 0.05, 0.10 and 0.50, were 1.53 (1.5328), 1.53 (1.5331) and 1.67 \(\times 10^{-4}\) Wb-m-kg\(^{-1}\), respectively, which suggested that the \(I_s\) increases with increasing the Co/PVP ratio. In addition, it was found that these Co-PVP nanoparticles exhibited coercivities larger than 16.0 kA-m\(^{-1}\) from the measurement of hysteresis loops.

Using these Co-PVP nanoparticles, the compacted samples were prepared and their microwave absorption properties were measured. Figure 4 shows the frequency dependence of real \((\mu_r')\) and imaginary \((\mu_r'')\) parts of relative complex permeability of the Co-PVP compacts synthesized at 170\(^\circ\)C for 3 h in ethylene glycol with Co/PVP = 0.05–0.50.

It is well known that the natural resonance frequency \((f_i)\) of PVP-protected Co nanoparticles prepared by this method can be used for electromagnetic wave absorption materials.

\[ f_i = \frac{\gamma}{2\pi} H_A \]  

where \(\gamma\) is gyromagnetic constant. Using this relationship, the natural resonance frequency \((f_i)\) of hcp-Co and fcc-Co are calculated as 18.1 and 1.3 GHz, respectively. Therefore, it is considered that the decrease in \(\mu_r'\) and the increase in \(\mu_r''\) at around 1 GHz is considered to be due to the natural resonance of fcc-Co. In the Co/PVP = 0.1 sample, the another \(\mu_r''\) peak at the frequencies around 5 GHz was observed. It is considered that this \(\mu_r''\) peak is due to the shape anisotropy, which is caused by forming lump shapes and/or chains of cobalt particles from the results of relative high coercivities in samples. The maximum values of \(\mu_r'\) in the samples with Co/PVP = 0.05, 0.10 and 0.50, were 4.29 (at 0.62 GHz), 5.77 (at 0.78 GHz) and 1.69 (at 0.30 GHz), respectively. The corresponding \(\mu_r''\) peak values were 1.99 (at 1.54 GHz), 2.32/2.33 (at 1.62/5.36 GHz) and 0.71 (at 1.04 GHz), respectively. From this results, it is found that the Co-PVP sample with Co/PVP = 0.10 showed the highest \(\mu_r'\) and \(\mu_r''\) values.

The electromagnetic wave absorption properties were estimated from the reflection loss \((R.L.)\). Figure 5 shows the frequency dependence of the reflection loss \((R.L.)\) of PVP-protected Co compacts synthesized at 170\(^\circ\)C for 3 h with Co/PVP = 0.10. The average values of \(\varepsilon_r'\) and \(\varepsilon_r''\) in the measured frequency range were 82.7 and 23.9, respectively. The \(R.L.\) less than \(-10\) dB, which means the microwave absorption \((M.A.)\) more than 99%, was obtained at 1.04 GHz (matching frequency, \(f_m\)), when the sample thickness was 3.16 mm (matching thickness, \(d_m\)). The \(R.L.\) less than \(-20\) dB, which equals to the \(M.A.\) more than 99%, was obtained at \(f_m = 0.64\) and 0.54 GHz with \(d_m = 5.04\) and 6.16 mm, respectively.

Therefore, it is concluded that polymer-protected Co nanoparticles prepared by this method can be used for electromagnetic wave absorption materials.

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