Preparation and magnetic properties of amorphous Co-Fe-B nanoparticles

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Abstract. Amorphous Co-Fe-B nanoparticles coated with PVP (polyvinyl pyrrolidone) were prepared by reduction of metal ions in aqueous solution by use of NaBH₄ at room temperature. The size of nanoparticles was in the range of 10-20 nm and from the XRD patterns, these nanoparticles were amorphous. FE-SEM-WDX analyses showed the B content to be in the range of 38-45 at%. The saturation magnetization and coercivity for the samples was in the range of 45-50 emu·g⁻¹ and 31-110 Oe, respectively. The composites of nanoparticles with the minimum coercivity and PVP as the binder (particle weight percent = 75 wt.%) showed permeability of \( \mu_r \) \(_{\text{max}} = 1.9 \) at 0.7 GHz and a good microwave absorption property (reflection loss: RL < -20 dB).

1. Introduction

Powder material has been studied extensively in the last years because of their novel properties and technological applications in optical, magnetic and electronic fields. Specifically, Fe, Co based amorphous powders have a high potential as soft magnetic materials for high frequency applications [1-5]. Amorphous powders are usually synthesized by various methods such as atomizing and rapid quenching. However, the size of these particles is a few micrometers, and the frequency range of their applications is limited due to eddy current loss. The particle size must be less than about 1 \( \mu \)m to avoid eddy current loss when used in the gigahertz range, where a wide variety of new applications of high permeability particles such as planer inductors, antennas, and EM noise suppressors, are expected. Therefore, the size of powders must be decreased in nanometer size with monodisperse form to avoid eddy current loss. On the other hand, chemical reduction methods give a possibility to obtain the alloys in the form of nanoparticles with a wide range of compositions [6-10]. The chemical reduction method involves the addition of a reductor (usually NaBH₄ or KBH₄) into metallic salt aqueous solution, resulting in the precipitation of nanometer scale metallic particles.

In this study, we paid attention to Co-Fe-B that has zero magnetostriction and tried to prepare Co-Fe-B amorphous nanoparticles with soft magnetism by chemical reduction method. However, it is difficult to obtain the nanoparticles with soft magnetism and good dispersibility because the rapidly response set off extraction with aggregated form, generally. To avoid
aggregation, PVP was used as a dispersing agent. We report on properties of PVP coated amorphous Co-Fe-B nanoparticles and their magnetic properties in a gigahertz range.

2. Experimental

Co-Fe-B nanoparticles were prepared by chemical reduction of Co(II), Fe(II) ions in aqueous solution by NaBH₄. PVP (polyvinyl pyrrolidone) was used as a dispersing agent. First, PVP (11.1 g) and CoCl₂·6H₂O (2.4 g), FeSO₄·7H₂O (0.28 g) was dissolved in deionized water (125-250 mL). The concentration of metal ions, [Co + Fe] is 40-100 mM. Then, aqueous solutions (25-50 mL) of NaBH₄ (0.38 g) and NaOH (adjust solution’s pH to 13) were added to the above solutions under vigorous stirring with the drop rate of 30 drops/min. The solution changed to black immediately, the mixtures were stirred for another 1 hr to finish the reaction completely. And the entire operation was performed under a nitrogen atmosphere. Then, Precipitated nanoparticles were collected by centrifugation at 5,000 rpm for 5 min and rinsed in distilled water and ethanol. Then, the nanoparticles were dried by vacuum pomp. After drying at room temperature in vacuum box, the gel was ground into a powder for the measurements. For measurements of high frequency magnetic properties, the nanoparticles were mixed with PVP at ratio of about 75 wt.% (particle weight percent) and then pressed into toroidally shaped samples. (φout = 7.00 mm, φin = 3.04 mm, t = 0.5–1.5 mm).

The phases present in samples were characterized by X-ray powder diffraction (XRD) and composition of samples was determined by FE-SEM-WDX. Microstructure was checked with transmission electron microscopy (TEM). Magnetic properties were measured using a vibrating sample magnetometer (VSM). The relative complex permeability (μr) and permittivity (εr) were calculated by vector network analyzer. Microwave absorption properties were evaluated by the reflection loss (RL) which was derived from the following formulae (1), (2)

\[
RL = 20 \log \left| \frac{Z_m - Z_0}{Z_m + Z_0} \right|, \quad (1)
\]

\[
Z_m = Z_0 \left( \frac{\mu_r}{\varepsilon_r} \right)^{1/2} \tanh \left\{ \frac{2 j \mu_r \varepsilon_r^{1/2}}{c} \right\}, \quad (2)
\]

Where \(Z_m\) is the input impedance of absorber and \(Z_0\) is the impedance of air, \(c\) is the velocity of light, \(f\) is frequency, \(d\) is the absorber thickness. When RL was less than -20 dB (matching situation), the sample shows adequate microwave absorption.

3. Result and Discussion

Co-Fe-B nanoparticles were prepared by chemical reduction method with PVP. The reduced particles were found to consist of amorphous particles for all concentrations of metal ions from XRD patterns. Figure 1 shows the relationship between concentration of metal ions and (a) magnetic properties, (b) composition of Co-Fe-B nanoparticles. The saturation magnetization \(\sigma_s\) (emu g⁻¹) were measured with applying a magnetic field of 10 kOe. The saturation magnetization changed slightly regardless of concentration of metal ions. The coercivity was decreasing with approaching the ratio of Co to Fe in the particles to 0.90, that corresponded to composition of zero magnetostriction, and showed minimum value 42 Oe for sample of [Co + Fe] = 0.06 M. Although the B contents increased 38 ~ 43 at.% in proportion to concentration of metal ion, the correlation with the magnetic properties was not seen in Fig. 1.

Next, the concentration of metal ions was fixed to 0.06 M where the ratio of Co to Fe was 0.90, and the relationship between the concentration of reductor, [NaBH₄] and particle characteristics was investigated (Figure 2). The saturation magnetization changed slightly same with Fig. 1 except for sample of [NaBH₄] = 0.1 M. The reason of this is seemed that the reaction has not completed because of low concentration of reductor solution. The ratios of Co to Fe in the samples of [NaBH₄] = 0.2 ~ 0.4 M were 0.90. And in same Co to Fe ratio, the coercivity lowered value with decreasing B content and showed minimum value 31 Oe for sample of [NaBH₄] = 0.3 M. The decrease of B content is due to increasing the frequency of particles
formation with increasing of [NaBH$_4$]. This value is considerably lower than other amorphous nanoparticle (about 200 Oe [7, 8, 10]). This may be because of isolated amorphous nanoparticle form coated with PVP, from the XRD pattern and TEM images of this sample (shown in Figure 3). Fig. 3 indicates that these nanoparticles were consists of amorphous with particle size of 10 - 50 nm. However, coercivity of this sample is larger than the particles prepared by atomizing and rapid quenching. From larger amount of B (40 at%) than zero magnetostriction composition (about 26 at.%) and thin ring pattern (inset Fig. 3 (c)), it seems that coercivity increased by the precipitation of Co-B nanocrystalline phase. Therefore, Co-Fe-B amorphous nanoparticles with lower coercivity can be expected by decreasing the amount of B content.

![Fig. 1. The relationship between concentration of metal ions, [Co + Fe] and (a) magnetic properties, (b) composition of Co-Fe-B nanoparticles ([NaBH$_4$] = 0.2 M).](image1.png)

![Fig. 2. The relationship between concentration of reductor, [NaBH$_4$] and (a) magnetic properties, (b) composition of Co-Fe-B nanoparticles ([Co + Fe] = 0.06 M).](image2.png)

Last, the high frequency magnetic properties of Co-Fe-B nanoparticles which showed the minimum coercivity were investigated and as an example of application of high frequency device, the microwave absorption properties were evaluated. Figure 4 shows the frequency dependences of (a) the relative permeability, (b) reflection loss, RL of the composites of Co-Fe-B nanoparticles and PVP (75 wt.% particles). When RL was less than -20 dB (matching situation), the sample shows adequate microwave absorption. The PVP composite showed relative permeability of $\mu'_r = 3.9$ at 0.1 GHz and $\mu''_r \max = 1.9$ at 0.7 GHz, permittivity of $\varepsilon_r \avg = 50 - 3.1j$. The resonance profile in Fig. 4 (a) is broad because of the influence of local demagnetizing fields and local anisotropies. This is because the possible factors that determine resonance profile in particles are demagnetizing fields imposed on individual particles and local defects giving rise to dispersed local anisotropy. The PVP composite RL values less than -20 dB in the 0.2–0.35 GHz frequency range. In particular, a minimum RL value of -32 dB is obtained at 0.3 GHz with thickness, d of 17.0 mm. This suggested that these PVP-coated Co-Fe-B nanoparticles prepared can be used as microwave absorber.

To conclude, Co-Fe-B amorphous nanoparticles were obtained by chemical reduction using PVP as dispersing agent. The nanoparticles exhibited lower coercivity than other amorphous nanoparticles. They are small enough to suppress eddy current loss at high frequencies and the PVP composite had good microwave absorption properties.
Fig. 3. (a) XRD pattern and (b,c) TEM images of Co-Fe-B nanoparticles ($H_c = 31$ Oe).

Fig. 4. The frequency dependencies of (a) the relative permeability, (b) reflection loss, RL of PVP composite (75 wt.% particle) of Co-Fe-B nanoparticles ($H_c = 31$ Oe).

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