



Synthesis of self-forming core/shell nanoparticles of magnetic metal/nonmagnetic oxide

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Abstract

Various kinds of self-forming core/shell nanoparticles with a core consisting of magnetic metal and a protective shell consisting of nonmagnetic metal oxide (magnetic metal: Co or FeCo; nonmagnetic metal: Al or Si) were synthesized. The synthesis conditions and compositions of the materials were controlled in order to obtain homogeneous core/shell nanoparticles with high dispersivity. The process of applying carbon coating to the nanoparticles using thermal plasma and subsequently removing the carbon shell by heating in hydrogen was effective for obtaining relatively homogeneous core/shell nanoparticles with crystalline grain sizes of approximately 20 nm. Partial oxidation after the carbon-coating process suppressed aggregation of the core/shell nanoparticles and promoted phase segregation of the oxide shells from metallic cores. Similar effects were also achieved by either increasing the amount of nonmagnetic metal or adding a small amount of another nonmagnetic metal to the metal. The bulk nanocomposite of the self-forming core/shell nanoparticles with high dispersivity that were obtained by phase segregation of oxide shells from metallic cores exhibited low magnetic losses with a high ferromagnetic resonance frequency in the gigahertz band.

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1. Introduction

Magnetic metallic nanoparticles have recently received much attention as soft and hard magnetic materials in fields such as high-frequency magnetic devices, microwave absorbers, drug delivery systems, recording media, and magnets. In high-frequency magnetic devices, such as inductors, transformers, transmission line devices and antennae, a soft magnetic material is required to exhibit high permeability and low magnetic losses at high frequencies [1,2]. A nanogranular material composed of metallic nanoparticles with high saturation magnetization and an insulating matrix with high electrical resistivity is a good candidate for obtaining high permeability and low

magnetic losses at high frequencies [3]. It is important to reduce the size of the magnetic metallic particles and to electrically insulate them from each other in order to reduce eddy current losses at high frequencies. However, magnetic metallic nanoparticles are prone to oxidation, leading to a decrease in saturation magnetization. Therefore, it is necessary to improve the oxidation resistance of magnetic metallic nanoparticles.

In general, an oxide coating on the surface of metallic nanoparticles is effective for improving the oxidation resistance of the metallic nanoparticles. Many studies have reported on core/shell nanoparticles of metal/oxide synthesized by coating methods employing gas-phase or liquid-phase reactions [4–6]. However, almost all of these works have investigated nanoparticles, and there have been few reports on bulk nanocomposites comprising large amounts of nanoparticles or the technology leading to production of

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the bulk nanocomposites. In the process of producing bulk material, large amounts of nanoparticles are exposed to quite severe conditions such as mixing of the particles and matrix, and further improvements in the oxidation resistance of each core/shell nanoparticle are thus required in order to obtain bulk nanocomposites.

In this work, a bulk nanocomposite of self-forming core/shell nanoparticles was synthesized. The self-forming core/shell nanoparticles were synthesized by partial oxidation of the metallic nanoparticles. The core/shell nanoparticles exhibit high adhesion at the interface between the core and shell because the metal cations from the core diffuse from the inside toward the surface to form a dense oxide shell through reactions with oxygen ions. The core/shell nanoparticles thus exhibit high oxidation resistance in the severe environment of the bulk material production process. In order to realize superior magnetic properties of high permeability and low magnetic loss at high frequencies, it is necessary to employ a more sophisticated core/shell nanostructure and to improve the homogeneity of grain sizes. In this work, a new synthesis process for self-forming core/shell nanoparticles that starts from carbon-coated precursor nanoparticles was proposed and the compositions of the material were controlled in order to obtain homogeneous small nanoparticles with high dispersivity. The effects of reducing magnetic loss at high frequency in the nanocomposite using highly homogeneous small core/shell nanoparticles with high dispersivity were investigated.

2. Experimental

Carbon-coated nanoparticles containing magnetic metal and nonmagnetic metal (magnetic metal: Co or FeCo; nonmagnetic metal: Al or Si) were synthesized by a thermal plasma method, similar to the methods used in other research [7]. Mixed powders of magnetic and nonmagnetic metals of several micrometers in size were introduced into plasma, and the powders were evaporated and rapidly cooled in an argon flow that contained diluted hydrogen. Methane gas was injected into the plasma to coat the nanoparticles in carbon. Partial oxidation before removing the carbon shell was conducted as necessary in order to promote phase segregation of the oxide shell from the metallic core. Typical partial oxidation conditions were 200 °C in flowing air. The carbon-coated nanoparticles were heated in flowing hydrogen to remove the carbon shell. The typical heat treatment conditions were 600 °C for 20 min in flowing hydrogen. After removing the carbon shell, synthesis of the core/shell nanoparticles composed of magnetic metal-rich core and protective nonmagnetic metal-rich oxide shell was completed. The compositions of the synthesized core/shell nanoparticles of Co–4 wt.% Al, FeCo–5 wt.% Al, FeCo–10 wt.% Al, FeCo–6 wt.% Al–3 wt.% Si, and FeCo–4 wt.% Si are summarized in Table 1. The core/shell nanoparticles were mixed with resin, ground in

a mortar and pressed uniaxially to synthesize the nanocomposite.

The crystalline phases of the nanoparticles were identified by X-ray diffractometry (XRD; M18XHF²²-SRA, MacScience Co. Ltd., Japan), using Cu K_{α} radiation at 40 kV and 100–300 mA. Lattice constants were examined by mixing the sample powders with silicon standard powder (640c, National Institute of Standards and Technology, USA; the lattice constant at 22.5 °C is 5.4311946 ± 0.0000092 Å). The crystalline grain size was investigated by applying Scherrer's equation to the strongest peak using the diffraction angle of the peak and the half-width of the peak area. The compositions of the nanoparticles were examined by inductively coupled plasma spectrometry (SPS4000, SII NanoTechnology Inc., Japan). The nanostructures and compositions were examined by transmission electron microscopy (TEM) using a JEM-2100F microscope (JEOL Ltd., Japan) with an accelerating voltage of 200 kV; this microscope was also equipped for energy-dispersive X-ray spectroscopy (EDX; JED-2300T, JEOL Ltd., Japan). The thermal decomposition behavior of the carbon-coated nanoparticles in the flowing hydrogen was investigated by thermogravimetry (TG; TGD-9600, ULVAC-RIKO, Inc., Japan) and quadrupole mass spectrometry (QMS; M-100GA-DTS, CANON ANELVA Corp., Japan). The permeability of the plate-like sample $4 \times 4 \times 1$ mm in size was measured at room temperature in the range 1–9 GHz by a high-frequency permeameter (PMM-9G1, Ryowa Electronics Co. Ltd., Japan).

3. Results and discussion

3.1. Synthesis of core/shell nanoparticles: effects of the carbon-coating process

The synthesized carbon-coated nanoparticles of FeCo–5 wt.% Al had an FeCo core of body-centered cubic (bcc) phase with crystalline grain size of approximately 10 nm. The surface of the nanoparticles was coated in a 2–3 nm thick carbon shell, as shown in Fig. 1a. The carbon-coated nanoparticles were heated in flowing hydrogen to remove the carbon shell by the following reaction: $C + 2H_2 \rightarrow CH_4$.

Fig. 2 shows the thermal decomposition behavior of carbon-coated nanoparticles of FeCo–5 wt.% Al in flowing hydrogen as investigated by TG and QMS. A large decrease in weight occurred at around 500 °C, with gas species of mass numbers 14, 15 and 16, attributed to methane, being produced at the same time. After removal of the carbon shell, core/shell nanoparticles were synthesized. Fig. 1b shows TEM images of the synthesized core/shell nanoparticles of FeCo–5 wt.% Al with crystalline grain sizes of approximately 20 nm after removing the carbon shell. (Fig. 3a shows low-magnification TEM images of these same particles.) A shell of AlFeCo oxide of thickness 2–4 nm formed on the surface of the FeCoAl core instead of a carbon shell. This oxide phase was formed by

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