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Bulk nanogranular composite of magnetic metal and insulating oxide matrix

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ABSTRACT

A novel bulk nanogranular composite of millimeter thickness which was composed of magnetic nanogranular flakes and insulating matrix was fabricated. In the flakes, magnetic metallic nanoparticles were highly dispersed in the oxide matrix, and the nanogranular structure of metal/oxide produced low eddy-current loss at high frequency. Furthermore, each of the nanoparticles interacted with the neighboring particles through magnetic exchange coupling in the flakes, and the composite exhibited good soft magnetism of low coercivity and high permeability. The maximum saturation magnetization of the composite was 0.94 T, which was much higher than that of conventional NiZn ferrites.

1. Introduction

In power supply devices and systems that use silicon carbide or gallium nitride power semiconductors, magnetic components such as inductors and transformers can be miniaturized by increasing the working frequency [1,2]. The soft magnetic materials used in these components need to have high permeability and low magnetic loss at high frequencies in the megahertz band. Low coercivity is needed to obtain low hysteresis loss, and high electrical resistivity is needed to obtain low eddy-current loss. High saturation magnetization is also necessary to prevent magnetic saturation, particularly when high electrical current flows in the power supply circuits. Recently, there has been increasing demand for dealing with high electrical currents at high frequencies in power supply devices and systems, making it important that the soft magnetic materials satisfy both high saturation magnetization and low magnetic loss at high frequencies. In general, there are two types of magnetic materials: magnetic metallic materials and magnetic oxide materials (ferrites). Magnetic metallic materials exhibit high saturation magnetization but low electrical resistivity, which causes high eddy-current loss particularly at high frequencies. In contrast, ferrites exhibit high electrical resistivity but low saturation magnetization. To satisfy both high saturation magnetization and high electrical resistivity, nanogranular thin films composed of magnetic metallic nanoparticles with high saturation magnetization and an insulating matrix with high electrical resistivity have been proposed in the field of high-frequency devices [3]. When the total length of the size of each magnetic metallic nanoparticle plus the interparticle distance is smaller than the magnetic exchange length, each nanoparticle interacts with its neighbors through magnetic exchange coupling. Therefore, the magnetization of the nanoparticles is likely to proceed concurrently, and the films of these particles are expected to exhibit excellent soft magnetism with low coercivity and high permeability [4,5]. However, these films are extremely thin (at most a few micrometers), making them unsuitable for the magnetic components in high-power power supply devices and systems. Thicker bulk materials are desirable for these devices and systems. There have been no known reports of metal/oxide nanogranular structured bulk soft magnetic materials of millimeter-order thickness with high permeability, high saturation magnetization, low coercivity, high electrical resistivity, and low magnetic loss at high frequencies in the megahertz band, and there is therefore a need to develop materials with these attributes.

In this communication, we report a novel bulk nanogranular composite composed of magnetic nanogranular flakes and an insulating matrix. The flat shape of the flakes enables high magnetic permeability by decreasing the demagnetizing field, high ferromagnetic resonance (FMR) frequency as derived from the Kittel equation, and low eddy-current loss by decreasing the thickness of the conductive flake [6–8]. In each magnetic nanogranular flake, the magnetic metallic nanoparticles were highly dispersed in the oxide matrix, and the nanogranular structure of metal/oxide produced low eddy-current loss at high frequency. Each nanoparticle interacted with the neighboring particles through magnetic exchange coupling in the flakes, and the composite exhibited good soft magnetism of low coercivity and high permeability.

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Table 1
Crystalline grain size, root-mean-square-strain, saturation magnetization, and coercivity of the material before milling (starting material), after milling, and after annealing in hydrogen.

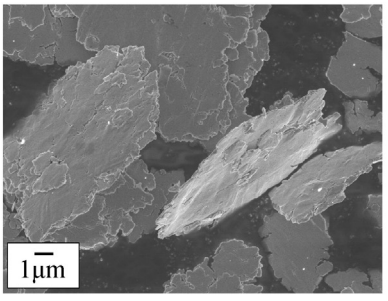
	$Fe_{0.7}Co_{0.3}$–4 wt.%Si			$Fe_{0.5}Ni_{0.5}$–4 wt.%Si		
	Starting material	After milling	After annealing in H_2	Starting material	After milling	After annealing in H_2
Crystalline grain size [nm]	65	9	12	33	9	11
Root-mean-square strain [%]	0.07	0.46	0.23	–	–	–
Saturation magnetization [emu/g]	196	188	210	105	111	120
Coercivity [Oe]	504	118	26	111	36	10

2. Experimental procedure

To fabricate a bulk nanocomposite, we selected the very simple technique of mechanical milling and mixing with equipment such as a high-power planetary ball mill. In this technique, the metal and oxide raw materials are easily milled and mixed when the kinetic energy is properly controlled. It is crucial to start from metal/oxide materials that have sufficient phase segregation at the nanolevel in order to produce synthesized nanocomposites with a more sophisticated nanostructure. We had previously developed techniques for synthesizing metal/oxide core/shell nanoparticles using the thermal plasma method [9]. Here, we started from metal/oxide core/shell nanoparticles obtained by the direct thermal plasma method.

Core/shell nanoparticles of $Fe_{0.7}Co_{0.3}$–4 wt.%Si or $Fe_{0.5}Ni_{0.5}$–4 wt.%Si were synthesized by the direct thermal plasma method. The core/shell nanoparticles were milled and mixed by using a high-power planetary ball mill (Planet M2-3F, Nagao System Inc., Japan). The ball and container were made of partially-stabilized zirconia. The weight ratio of ball to nanoparticles was 40, the speed ratio of rotation to revolution was 2.5, and the revolution speed was 700 rpm. The milling using acetone was performed during the time between 20 and 50 min in an argon atmosphere (Dry milling was performed at the revolution speed of 850 rpm before the milling in acetone only in the case of the $Fe_{0.7}Co_{0.3}$–4 wt.%Si, because $Fe_{0.7}Co_{0.3}$–4 wt.%Si was more difficult to be milled and mixed at the nanolevel than $Fe_{0.5}Ni_{0.5}$–4 wt.%Si). After the milling, the magnetic nanogranular flakes were synthesized. It was easy to obtain flaky shape by the milling with acetone. The flakes were annealed in flowing hydrogen to relieve internal stress and to reduce partial oxidation of the flakes. Annealing conditions were optimized to minimize the coercivity. The typical optimized annealing conditions were from 400 to 450 °C for one hour. The surfaces of the flakes after annealing were covered with a SiO_2 layer by the conventional sol–gel method in order to improve electrical resistivity; The flakes were stirred in the solution of tetraethyl orthosilicate (TEOS), water, and acetone (TEOS:water:acetone = 1:6:11 (mol)) at 80 °C, and then heated at up to 350 °C in an argon atmosphere to obtain the SiO_2-covered flakes. The SiO_2-covered flakes were then mixed with 10–20 wt.% insulating B_2O_3 matrix; the flakes were stirred in the water including B_2O_3 (the B_2O_3 was solved completely to form boric acid water) and then dried at 120 °C in argon atmosphere. The mixed powder of the SiO_2-covered flakes and boric acid was molded to form a ring, and hot-pressed uniaxially at 3000-6000 kgf/cm^2 at 285 °C for one hour in vacuum by using a conventional hot-press equipment (3143605, DIAVAC LIMITED, Japan). In the hot-pressing process, the boric acid in the mixed powder was partially melted and decomposed to form B_2O_3. The hot-pressed bulk was annealed at from 390 to 400 °C for one hour in flowing hydrogen to relieve the internal stress and to reduce partial oxidation of the bulk.

The crystalline phases of the nanoparticles were identified by X-ray diffractometry (XRD; SmartLab (9 kW) XG, Rigaku Corp., Japan) using Cu-Kα radiation at 45 kV and 200 mA. The crystalline grain size and root-mean-strain were investigated by using Halder–Wagner approximation in the case of the $Fe_{0.7}Co_{0.3}$–4 wt.%Si system [10]. For the $Fe_{0.5}Ni_{0.5}$–4 wt.%Si system, however, the crystalline grain size was investigated by applying the Scherrer equation to the strongest peak because the intensities of the diffraction peaks other than the strongest ones after milling were weak. The macroscopic structures were examined by scanning electron microscopy (SEM; SU8020, Hitachi High-Technologies Corp., Japan). The nanostructures and compositions were examined by transmission electron microscopy (TEM; JEM-2100F, JEOL Ltd., Japan; accelerating voltage: 200 kV) with an energy-dispersive X-ray spectroscopy (EDX) elemental analysis system (JED-2300T, JEOL Ltd., Japan). Semi-quantitative EDX analysis was performed by averaging five sets of metallic nanoparticles and the neighboring matrix. The electrical current mapping was examined by conductive atomic force microscopy (conductive AFM; E-sweep, Hitachi High-Tech Science Corp., Japan) and corresponding tapping AFM (Dimension Icon and NanoScope V, Bruker AXS K.K., Japan). Static magnetic properties were investigated using a vibrating sample magnetometer (VSM-5, Toei Industry Co., Ltd., Japan) at room temperature.



EDX semi-quantitative analyses

	Point 1	Point 2
O	8.1 at%	40.0 at%
Si	1.2 at%	9.5 at%
FeCo	90.7 at%	50.5 at%

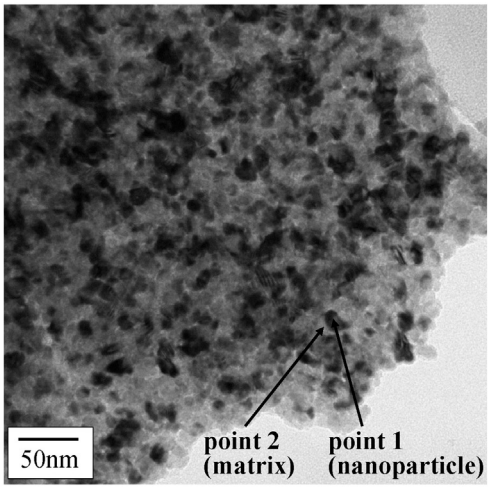


Fig. 1. SEM and TEM images of the synthesized $Fe_{0.7}Co_{0.3}$–4 wt.%Si magnetic nanogranular flakes after annealing, and semi-quantitative EDX results.