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Fabrication and characterization of spherical Co/Ni alloy particles

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Abstract

Spherical ferromagnetic Co/Ni alloy particles have been synthesized via a polyol process assisted by solvothermal treatment. XRD, EDX and SEM analyses have shown that the equal molar $Ni(CH_3COO)_2{\cdot}4H_2O$ and $Co(CH_3COO)_2{\cdot}4H_2O$ were reduced by ethylene glycol at 200 °C, resulting in the formation of $Co_{50}Ni_{50}$ alloy particles with a narrow particle size ranging from 200 nm to 500 nm. Magnetic properties of the sample at room temperature were measured using a vibrating sample magnetometer. The saturation magnetization and coercivity of the Co/Ni particles exhibit 123.21 emu/g and 108.23 Oe, respectively, which indicates that the alloy is ferromagnetic at room temperature.

Keywords: Co/Ni alloy; Solvothermal method; Saturation magnetization; Coercivity

1. Introduction

Magnetic materials are broadly classified into two main groups with either hard or soft magnetic characteristics. Soft magnetic materials can be magnetized by relatively low-strength magnetic fields, and when the applied field is removed, they return to a state of relatively low residual magnetization and typically exhibit a low coercivity [1–3]. Soft magnetic materials are a central component of electromagnetic devices such as step motors, magnetic sensors, transformers and magnetic recording heads [4–6]. In particular, for the electromagnetic device applications at high frequencies [7,8], researchers have long been searching for soft magnetic materials with high saturation magnetization (M_s), high permeability (μ), and low energy losses [9–11].Transition metal particles, especially those of Fe, Co and Ni are considered to be very important for these technological applications.

Among the alloy systems, the Co/Ni alloy has been least explored, and most of the studies have focused on the Fe/Ni or Fe/Co systems [12,13]. To our knowledge, crystalline Co/Ni alloy particles were obtained by sonochemical decomposition method [14] and electrochemical method [15], and then followed by heat treatment at high temperatures. Uzawa et al. reported the preparation of ultrafine crystalline Co/Ni alloy particles by leaching technology [16]. However, the complexity involved in the above synthetic procedures is quite evident, requiring many steps and the use of non-regular chemicals. It is also clear that scaling up of these synthetic procedures will be rather cumbersome. Furthermore, Co/Ni alloys obtained by the above synthetic procedures exhibited low saturation magnetization. For these reasons, we have to look for alternative synthesis methods for Co/Ni alloys using simple salts routinely available in the laboratory as metal sources with an option for scaling up the yield relatively easily. The polyol process is known to be a suitable method for preparing various metallic particles, in particular ferromagnetic ones [17–19]. Homogeneous nucleation leads to particles in the micrometer-size range. By modifying the nucleation step, using seed particles acting as nuclei (heterogeneous nucleation), it is possible to obtain submicrometer-sized particles and to control accurately their average diameter by varying the number of foreign nuclei. In the polyol process, liquid polyol acts as the solvent of the metallic precursor, the reducing agent and in some cases as a complexing agent for

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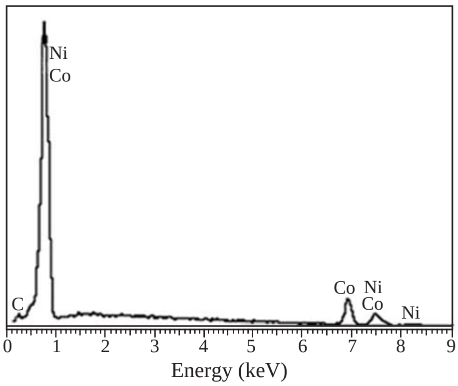

Fig. 1. EDX profile of as-obtained alloy particles.

the metallic cations. The solvothermal method has drawn our attentions due to the low energy costs and the resulting ultrafine, highly reactive, crystalline and impurity free particles, with controlled stoichiometry, size and shape. To our best knowledge, there is no report on fabrication of Co/Ni alloy particles in the submicrometer-size range by means of homogeneous nucleation in the polyol process.

In this paper, we extended the polyol process for one-step synthesis of Co/Ni alloy particles assisted by solvothermal treatment. Magnetic properties of Co/Ni alloy particles were investigated.

2. Experimental

All the chemicals were analytic grade reagents without further purification. Experimental details were as follows: a given amount of the starting materials $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.67 g) and $Co(CH_3COO)_2{\cdot}4H_2O$ (0.67 g) was put into 30 ml ethylene glycol. The suspension was stirred and heated to 60 °C for 30 min until a purple black solution was obtained. The solution was then transferred into Teflon-lined stainless steel autoclaves, sealed, and maintained at 200 °C for 5 h without shaking or stirring. It was noted that the solution volume must be below 70% of the total volume for the autoclave. After natural cooling to room temperature, the resulting black solid product was centrifuged and washed with distilled water and acetone several times to remove the ions and other organic materials possibly remaining in the final product, and finally dried in a vacuum at 40 °C for 72 h.

The obtained product was characterized by X-ray power diffraction (XRD) using a M18XCE X-ray power diffractometer (Japan) equipped with graphite-monochromated Cu-Kα radiation (λ = 1.54178Å), employing a scanning rate 0.02° s^{-1} in the 2θ ranging from 20 to 60°. The scanning electron microscopy (SEM) images and electron dispersive X-ray analysis (EDX) were obtained using a HITACHI S-4300 microscope (Japan) and EMAX Horiba (Japan), respectively. The magnetic properties at room temperature were investigated using a vibrating sample magnetometer (VSM, Model 7307, U.S.A.).

3. Results and Discussion

Alloy compositions were determined by elemental and energy-dispersive X-ray (EDX) analysis under N_2 atmosphere. Fig. 1 shows the EDX profile of the as-prepared samples by solvothermal treatment. Since the atomic numbers of Ni and Co are similar, the ratio of the X-ray intensities from these elements approximates the alloy composition. The elemental analysis of the Co/Ni alloys obtained by solvothermal treatment for 5 h showed that the alloy particles have over 98% metal by mass, with small amounts of carbon (<2%). The presence of small amounts of C could be anticipated from the conducting resin during measurements. The ratio of Co to Ni in the alloys is 1.0 in agreement with stoichiometric proportion, which indicated that the reduction reaction was rather complete.

Fig. 2 shows SEM images of the as-obtained alloy particles prepared by solvothermal treatment for 5 h. It is found that the alloy particles were made up of particles with the isotropic crystal and the size in the sub-micron ranges. The panoramic morphology of the product was obtained by the scanning electron microscopy (SEM), in which the solid sample was mounted on a copper mesh with dispersion treatment, indicating that all samples (Fig. 2A) are near-spherical nanostructures with diameter of 200–500 nm. Careful observation (Fig. 2B) can find that submicrospherical nanostructures consist of weak agglomerates of small particles. This conjunction may be attributed to inherent characteristics of metals. Compared to metal particles prepared by polyol process [19], the alloy particle size is about five times smaller.

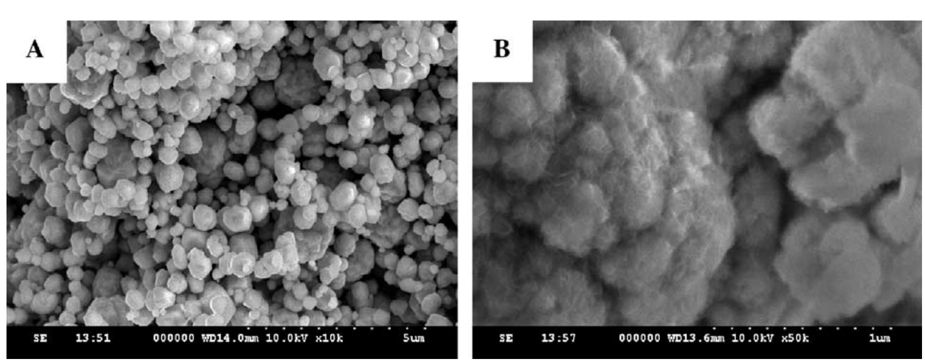

Fig. 2. SEM images of Co/Ni alloy particles. (A) Low magnification; (B) high magnification.