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Size-controlled synthesis of Fe–Ni alloy nanoparticles by hydrogen reduction of metal chlorides

Yong Jae Suh [a], Hee Dong Jang [a,*], Hankwon Chang [a], Won Baek Kim [a], Heon Chang Kim [b]

[a] Minerals and Materials Processing Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, South Korea
[b] Department of Chemical Engineering, Hoseo University, Asan 336-795, South Korea

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Abstract

We synthesized crystalline Fe–Ni nanoparticles with various particle sizes by reducing $NiCl_2$ and $FeCl_2$ vapors with hydrogen simultaneously. To control the primary particle size, processing variables of evaporator temperature, reaction zone temperature, and total gas flow rate were varied. The nanoparticles were nearly spherical and formed directional linkage between them due to magnetic interaction. The XRD patterns and elemental compositions measured by EDS showed that the Fe–Ni nanoparticles were mainly composed of cubic $FeNi_3$. With various evaporation temperatures from 800 to 900 °C, the reactant concentrations were estimated to range from 7.94×10^{-6} to 2.68×10^{-5} mol/l, which resulted in the specific surface area and Sauter diameter of the particles from 11.1 to 8.8 m^2/g and from 65 to 82 nm, respectively. The geometric standard deviations of the primary particle sizes obtained from TEM micrographs ranged from 1.24 to 1.27, indicating very narrow particle size distribution. The increase in the reaction temperature from 850 to 950 °C led to the reduction of the Sauter diameter from 69 to 63 nm. As the total gas flow rate decreased from 5 to 3 l/min, the Sauter diameter increased from 56 to 69 nm.

Keywords: Synthesis; Fe–Ni; Nanoparticles; Iron chloride; Nickel chloride; Hydrogen reduction

1. Introduction

Magnetic nanoparticles have important applications in catalysts, magnetic fluids, and high-density recording media. In such applications, composition of the particles is considered the key characteristic affecting their magnetic properties. Many kinds of compositions including Fe, Ni, and Co have been investigated [1–4]. To further improve the properties of metallic particles, it has been of practical interest to synthesize metallic alloy particles composed of Fe–Ni [5–7], Fe–Co [1], or Ni–Co [8].

Ohno [5] has prepared particles made up of Fe–Ni alloys, which have been widely used as magnetic materials, by evaporating starting materials in an inert gas atmosphere at temperatures over 1600 °C. The particles prepared from Fe–36 at.% Ni foil have ranged from 20 to 100 nm in diameter and mostly consisted of a single phase of ferrite or austenite. Li et al. [6] have synthesized nanoparticles of six kinds of Fe–Ni alloys by hydrogen plasma reaction. The spherical Fe–Ni nanoparticles with a mean particle size less than 35 nm have been prepared. Dong et al. [7] have synthesized Fe–Ni nanoparticles ranging from 19 to 34 nm in their mean size using the hydrogen plasma reaction method in a mixture of H_2 and Ar. They have found that two phases with austenite and martensite structures coexist over a wide compositional range in the nanoparticles.

In addition to the compositions, particle size is also a key factor in the applications mentioned above. For example, magnetic recording density is remarkably enhanced as the magnetic particle size decreases. However, control of the size of Fe–Ni alloy nanoparticles has not been studied systematically yet to date although many studies on the magnetic properties with wide varieties of compositions have been made as mentioned above.

In this study, we synthesized crystalline $FeNi_3$ nanoparticles by reducing $NiCl_2$ and $FeCl_2$ vapors with hydrogen simultaneously according to the overall reaction as follows:

$$FeCl_2(g) + 3NiCl_2(g) + 4H_2(g) \rightarrow FeNi_3(s) + 8HCl(g) \quad (1)$$

Concentrations of the reactants and reaction temperature were systematically manipulated to control the growth of the

* Corresponding author. Tel.: +82 42 868 3612; fax: +82 42 861 9727.
E-mail address: hdjang@kigam.re.kr (H.D. Jang).

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particles. In addition, residence time of the reactants in the reaction zone was varied. Then, we investigated the effect of the process variables on the particle size and crystallinity by a transmission electron microscopy (TEM), a BET method, and an X-ray diffraction (XRD). To examine the compositional homogeneity of each particle, we performed an elemental analysis for individual nanoparticles and a collection of them using two energy-dispersive X-ray spectroscopy (EDS) systems.

2. Experimental

A typical experimental apparatus and procedure for the preparation of nanoparticles were used as in the previous studies [4,9]. The experimental apparatus consists of a multi-stage aerosol reactor, a particle collector and an off-gas treatment part (Fig. 1). A multi-stage aerosol reactor is made of quartz and divided into three sections: 40 cm long evaporation section, 40 cm long preheating section, and 75 cm long reaction section. The temperature of each section was controlled separately in an electrical tubular furnace. In the evaporation section (I.D. 5 cm), two quartz boats loaded with solid phases of $FeCl_2$ (Junsei Chemical Co., 99.5%) and $NiCl_2$ (Showa Chemical Co., 96%) were placed separately. The feed rate in mol/min of the metal chlorides was controlled by evaporation temperature and their concentration in mol/l by the carrier gas (Ar, 99.995%) flow rate. The preheating section consists of two concentric tubes with inner diameters of 3 cm and 5 cm for inner and outer tubes, respectively. Ar gas containing metal chloride vapors flowed through the inner tube while hydrogen (H_2) and additional Ar gases through the outer. Reactants that have been separately heated to the reaction temperature were mixed at the exit of the nozzle installed between preheating and reaction sections. The nozzle has inner and outer diameters of 1.0 cm and 1.4 cm, respectively, constituting concentric tubes together with the outer tube of I.D. 1.8 cm. Fe–Ni nanoparticles that have been synthesized in the reaction zone (I.D. 3 cm) are collected by a Teflon membrane filter with an average pore diameter of 20 μm. These nanoparticles were allowed to react with small amount of oxygen existing in Ar gas for about 12 h since Fe–Ni nanoparticles are easily oxidized in ambient air. This might result in a thin oxide film on the particle surface, protecting the particles from oxidizing further [3,7]. Then the nanoparticles were analyzed by a TEM (Philips Co. Model CM12) for particle morphology and size distribution. The specific surface area of the particles was measured by nitrogen adsorption at −196 °C using a BET (Micrometrics Model ASAP 2400) and in turn Sauter diameter, surface area mean diameter, was calculated. And the crystalline structure was examined by an X-ray diffractometer (Rigaku Co. Model RTP 300 RC). The compositional homogeneity of each particle was estimated by an elemental analysis for individual nanoparticles and an area analysis using EDS systems equipped with a TEM (Technai G2 F30) and a scanning electron microscope (SEM, JEOL, JSM 6380LA), respectively.

To synthesize nanoparticles with desired properties, processing variables of evaporator temperature (T_E), reaction zone temperature (T_R), and total gas flow rate (Q) were controlled. In this type of reactor, particles are first formed by homogeneous/heterogeneous nucleation and grow by coagulation, surface reaction, and sintering between neighboring particles. Since the nucleation is largely temperature dependent, the preheating temperature may be an important factor in controlling the nucleation and consequently the particle size distribution. Thus, the preheating section was set at the same temperature as the reaction zone so that the nucleation and growth can take place under the same condition. The reaction temperature was set above 850 °C, at which the conversion of $NiCl_2$ vapor has been estimated to be 90% in the previous study [10]. The molar ratio of reactant vapors $FeCl_2$ to $NiCl_2$ was kept constant at about 0.5 for all the experiments in this study. This ratio was empirically determined to supply $FeCl_2$ vapor the same amount as $NiCl_2$ because the vaporization rates of two chlorides are different from each other. Otsuka et al. [1] reported on the synthesis of nanoparticles composed of Ni, Co and Fe by the hydrogen reduction of respective chlorides. They have successfully synthesized Fe nanoparticles by this process in spite of relatively small equilibrium constants, probably because the reaction proceeded rapidly enough to form nanoparticles. The equilibrium constant (K_p) of Fe chloride is much smaller than that of Ni chloride at reaction temperatures, e.g., $\log(K_p)=0.11$ and 3.5 for $FeCl_2$ and $NiCl_2$ at 950 °C,

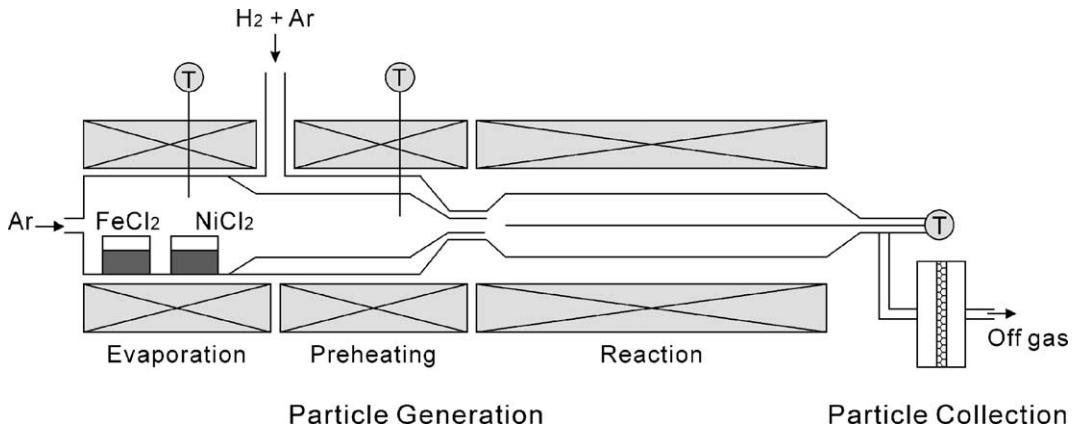

Fig. 1. Schematic drawing of experimental apparatus for the production of Fe–Ni nanoparticles.