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Effects of Ni content on nanocrystalline Fe–Co–Ni ternary alloys synthesized by a chemical reduction method

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ABSTRACT

Magnetic properties of Fe–Co–Ni ternary alloys could be altered by changing of the particle size, elemental compositions, and crystalline structures. In this work, $Fe_{50}Co_{50-x}Ni_x$ nanoparticles ($x=10$, 20, 40, and 50) were prepared by the novel chemical reduction process. Hydrazine monohydrate was used as a reducing agent under the concentrated basic condition with the presence of poly(vinylpyrrolidone). We found that the nanoparticles were composed of Fe, Co and Ni with compositions according to the molar ratio of the metal sources. Interestingly, the particles were well-crystalline at the as-prepared state without post-annealing at high temperature. Increasing Ni content resulted in phase transformation from body centered cubic (bcc) to face centered cubic (fcc). For the fcc phase, the average particle size decreased when increased the Ni content; the $Fe_{50}Ni_{50}$ nanoparticles had the smallest average size with the narrowest size distribution. In additions, the particles exhibited ferromagnetic properties at room temperature with the coercivities higher than 300 Oe, and the saturation magnetiation decreased with increasing Ni content. These results suggest that the structural and magnetic properties of Fe–Co–Ni alloys could be adjusted by varying the Ni content.

1. Introduction

Magnetic nanoparticles are undoubtedly important materials in both fundamental and applied research today [1,2]. Monodisperse ferromagnetic nanoparticles are of potential candidates for using in ultrahigh magnetic recording [3] while superparamagnetic nanoparticles are mostly employed in biomedical applications such as MRI contrast enhancement and cancer hyperthermia treatment [4,5]. To enhance the efficiency of such applications, magnetic properties of the nanoparticles have been tuned by various strategies including doping, size and shape control, and core–shell design [6].

Among outstanding magnetic nanoparticles, FeCo alloy is of great interest due to its excellent magnetic properties such as high saturation magnetization (M_s) and low coercivity (H_c) [7]. However, diverse values of these magnetic properties have been obtained depending on the elemental compositions as well as size and shape of the particles [8,9]. Therefore, various methods have been used to control size and shape of the FeCo nanoparticles [10–14]. Among them, chemical reduction process is the prominent route in obtaining the air-stable FeCo nanoparticles with different shapes including sphere [15], cube [9,16], and flower-like structure [17–19]. In the past, besides the high cost of Co in manufacturing process, it was also interesting in the alteration of morphology and magnetic properties of the FeCo nanoparticles when another transition metal such as Ni was introduced to their crystalline structures [20–22]. The Ni substitution produces the Fe–Co–Ni ternary alloys that could be employed in many applications including magnetic recording [20], magnetoresistive sensor [23], and microwave absorption [24]. Kovar alloy that consists of 29% Ni, 17% Co and balanced Fe is also an important material using in electronic industry, for examples, fabrication of power tubes and X-ray tubes [25]. Recently, Dalavi and colleagues reported the magnetic properties of $Fe_xNi_{80-x}Co_{20}$ nanoparticles prepared by the sodium borohydride reduction route [26]. They found that the M_s are in the range of 54.3–41.2 emu/g which are notably lower than those of bulk values (175–180 emu/g). The particles with higher Ni content exhibit the higher M_s which is attributed to the size effects, spin canting at the surface and the surface oxidation.

In this work, we report effects of Ni content on the structural and magnetic properties of $Fe_{50}Co_{50-x}Ni_x$ nanoparticles ($x=10$, 20, 40, and 50). The particles were synthesized by a novel chemical reduction process modified from the preparation of the FeCo nanocubes [16]. Interestingly, without post-annealing at high

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temperature, the as-prepared nanoparticles were well-crystalline. Moreover, when Ni ions emerged in the reduction process, the nearly spherical particles were formed instead of the cubic particles. The average size and magnetic properties of the as-prepared nanoparticles also depended on the amount of substituent Ni. Increasing Ni content decreased the M_s; however, the M_s as high as 94.7 emu/g was still obtained in the case of $Fe_{50}Ni_{50}$ nanoparticles.

2. Experimental procedure

All starting materials were purchased from Sigma-Aldrich Co., and used as received. The nanocrystalline Fe–Co–Ni ternary alloys were synthesized by the chemical reduction process modified from the previous report on the synthesis of FeCo nanocubes [16]. In the typical procedure, 2.5 mmol of $Fe(SO)_4 \cdot 7H_2O$, 2.0 mmol of $CoCl_2 \cdot 6H_2O$, 0.5 mmol of $NiCl_2 \cdot 6H_2O$, and 2.0 g of PVP were dissolved in 50 mL of deionized water. The obtained solution was then purged with Ar for 20 min before sonicated for 90 min. The sonicated solution was subsequently heated to 80 °C by an oil bath. After the desired temperature was reached, a beforehand solution of 3.0 g of NaOH dissolved in 20 mL of hydrazine monohydrate was slowly injected into the solution by a syringe (~10 mL/min). After injection of the reducing agent, the reaction was dwelled for 30 min before cooled down to room temperature naturally. The particles were separated and purified by magnetic decantation with deionized water for 5 times and acetone for 3 times. The final precipitate was dried at 60 °C in an oven for 2 h. The described procedure was repeated for several times using different amounts of $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ as illustrated in Table 1. The four samples are named according to the atomic percentage of Ni contents, i.e. FCN10 for 10% Ni, FCN20 for 20% Ni, FCN40 for 40% Ni, and FCN50 for 50% Ni.

The crystalline structures of the as-prepared nanoparticles were determined by a powder X-ray diffractometer (XRD, Bruker D2 phaser) which was operated with Cu Kα radiation (λ=1.54060 Å). The scattering angle (2θ) was varied from 20° to 100° with the scanning rate of 0.02°/0.2 second. A transmission electron microscope (TEM, FEI Tecnai G^2 20) with accelerating voltage of 200 kV was employed to examine the particle morphology and size distribution. An energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments) equipped with the TEM was performed for 3 times in different areas to obtain an average value of the elemental compositions. Magnetizations of the particles were measured by a vibrating sample magnetometer (VSM, VersaLab Quantum Design) at 50 K and 300 K with varying magnetic field between −30 and 30 kOe. The zero field cooled (ZFC) and field cooled (FC) measurements were performed under the magnetic field of 1000 Oe while temperature was raised from 50 to 390 K.

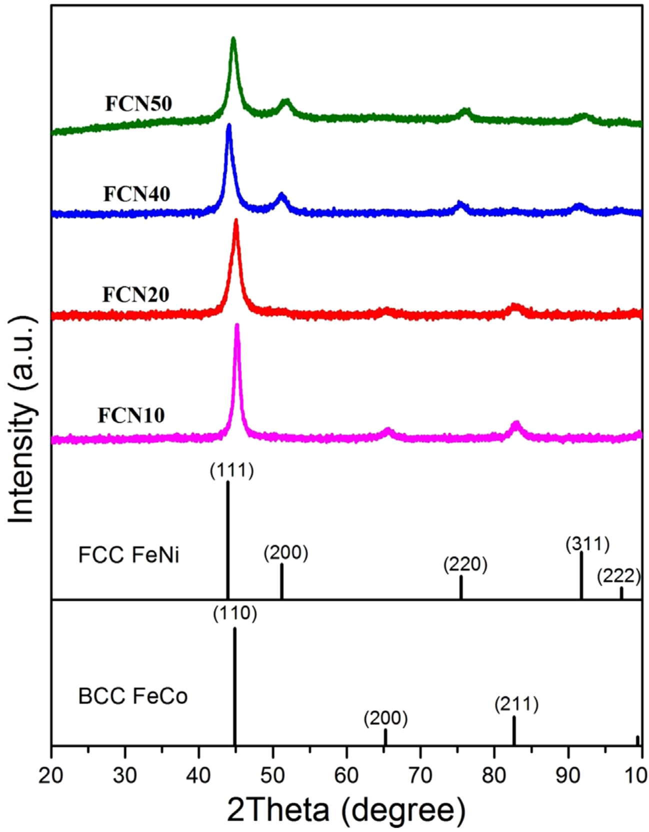

Fig. 1. XRD patterns of the samples compared with the standard bcc FeCo and fcc FeNi.

3. Results and discussion

3.1. Elemental compositions

The average elemental compositions of the as-prepared Fe–Co–Ni alloys are shown in Table 1. It is clearly seen that the obtained compositions are consistent with the molar ratio of the starting materials, and can be approximated as $Fe_{50}Co_{40}Ni_{10}$, $Fe_{50}Co_{30}Ni_{20}$, $Fe_{50}Co_{10}Ni_{40}$, and $Fe_{50}Ni_{50}$ for the FCN10, FCN20, FCN40, and FCN50 samples, respectively. These consequences reveal that the metal ions are mostly reduced to metal atoms and rapidly formed to be the alloys. However, the negligible amount of oxygen was also found in the EDS measurements. The partial oxidation is attributed to the high mass fraction of Fe in the samples; Fe has a higher oxidation potential compared with Co and Ni, therefore, Fe–Co–Ni alloys with the high Fe fraction have more opportunity in oxidation [26].

3.2. Crystalline structures

Fig. 1. illustrates the XRD patterns of the samples. All XRD spectra indicated that the as-prepared alloys were single phase

Table 1
The synthetic conditions and elemental composition of as-prepared nanoparticles.

Sample	Amount of starting materials (mmol)			Elemental composition (at%)		
	$Fe(SO)_4 \cdot 7H_2O$	$CoCl_2 \cdot 6H_2O$	$NiCl_2 \cdot H_2O$	Fe	Co	Ni
FCN10	2.5	2.0	0.5	44.55	42.95	12.50
FCN20	2.5	1.5	1.0	47.05	32.52	20.43
FCN40	2.5	0.5	2.0	47.87	10.96	41.17
FCN50	2.5	0	2.5	47.56	0	52.44