Journal of Magnetism and Magnetic Materials 332 (2013) 85–88

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Controlled synthesis of magnetic Ni–Fe alloy with various morphologies by hydrothermal approach

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ARTICLE INFO

Article history:
Received 2 February 2012
Received in revised form
13 November 2012
Available online 12 December 2012

Keywords:
Ni–Fe
Alloy
Hydrothermal approach
Magnetic property
Electrical property

ABSTRACT

Ni–Fe alloy with various morphologies has been synthesized by the hydrothermal approach. The structure of Ni–Fe alloy was characterized by scanning electron microscopy, X-ray diffraction and X-ray energy-dispersive spectroscopy. The result showed that the morphologies (e.g. flower, snowflake and tree) of Ni–Fe alloy strongly depended on the volume ratios of ethanol to water. Furthermore, the magnetic and electrical properties of Ni–Fe alloy with various morphologies were investigated. The Ni–Fe alloy has higher magnetic (M_s=89.6 emu/g) and electrical properties (76.9 S/cm) compared with the Ni–Fe alloy reported in previous work. The stepwise growth mechanism of Ni–Fe alloy with various morphologies is also discussed. It indicates that this strategy is effective for the synthesis of Ni–Fe alloy micro/nanostructures.

1. Introduction

Ni–Fe alloy has been extensively studied in recent years because of its electrical, catalytic and magnetic properties as well as its potential technological applications in catalysis, sensors, electromagnetic shielding, absorbing materials, and so forth [1,2]. It has been demonstrated that the physical properties and application of Ni–Fe alloy are usually closely related to the particle shape and independent of size [3]. Hence, in the past years, controlled synthesis of Ni–Fe alloy has attracted considerable interest for scientific research by these traditional methods such as the oblique sputtering [4], the hydrogen plasma reaction [5], the solution-phase co-reduction route [6,7], a high-energy milling method [8–10] and the melt drag casting process [11]. Among these methods, the solution-phase co-reduction route usually has advantages of mildness, simplicity, low-cost and large-scale production and has been adopted to successfully prepare some low-dimensional Ni–Fe alloy nanostructures, including nanospheres and polycrystalline nanorods [6,7]. There were few works reporting the fabrication of 3D hierarchical Ni–Fe alloy nanostructures via a solution-phase chemical reduction approach. Recently, 3D flower-like Ni–Fe alloy nanostructures composed of nanorods have been synthesized via a facile hydrothermal approach in aqueous solution [12]. However, the yield of 3D hierarchical Ni–Fe alloy was relatively low by the hydrothermal approach. In addition to this, dendritic fractals are a new type of functional nanomaterials, which are generally formed by hierarchical self-assembly under nonequilibrium conditions [13,14]. But the dendritic Ni–Fe alloy has not been reported in previous works.

In this work, the 3D dendritic Ni–Fe alloy was prepared by a new method. This present method shows an easy processing, in which morphology of Ni–Fe alloy is easily controlled by adjusting the volume ratios of ethanol to water. Furthermore, with this method, the Ni–Fe alloy with various morphologies can be produced with a high yield and purity. At the same time, electrical and magnetic properties of Ni–Fe alloy with various morphologies have been also compared, which is expected to be applied in electronic, magnetic and sensing nanodevices.

2. Experimental section

2.1. Chemicals

The chemicals used in the experiments are ferric chloride ($FeCl_3 \cdot 6H_2O$), nickel(II) chloride ($NiCl_2 \cdot 6H_2O$), sodium hydroxide (NaOH), ethanol and hydrazine hydrate, which were purchased from Shanghai Chemical Reagents Company. All chemicals were of analytical grade and used without further purification.

2.2. Preparation of Ni–Fe alloy

In a typical procedure, 0.71 g $NiCl_2 \cdot 6H_2O$ and 0.27 g $FeCl_3 \cdot 6H_2O$ were dissolved in 22.5 ml ethanol/water mixing solution (V/V: 0/1, 1/1, 3/1 and 1/0). Subsequently, 7.5 ml hydrazine hydrate solution

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http://dx.doi.org/10.1016/j.jmmm.2012.11.043

(85%) containing 2.0 g NaOH was added into the above solution. The mixture was stirred vigorously and then transferred into a Teflon cup in a stainless steel-lined autoclave. The autoclave was maintained at 100° C for 6 h and then cooled down to room temperature. A black fluffy solid product was deposited at the bottom of the Teflon cup, indicating the formation of nickel–iron alloys. The final product was collected by a magnet and rinsed with distilled water and ethanol several times to remove any salts, and then dried in a vacuum oven at 40° C for 6 h.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku D/Max-2000 diffractometer equipped with a Cu KR radiation source ($\lambda = 0.15418$ nm). The scanning range was from 20° to 80° and the scanning interval was 0.5°.

Morphologies of the samples were studied by a Hitachi Su-1500 scanning electron microscope (SEM). The element composition was characterized by a Horiba EX-250 X-ray energy-dispersive spectrometer (EDX) associated with SEM.

The hysteresis loops were conducted by using a Model-4HF vibrating sample magnetometer at room temperature with a maximum magnetic field of 10 kOe. For magnetization measurements, the powder was pressed strongly and fixed in a small cylindrical plastic box.

For electrical conductivity measurement, the standard four probe techniques using a Keithley 797A instrument was employed to measure the electrical conductivity of a pellet made with each sample:

$$\rho = (3.14/\ln 2) \times [U(V)/I(A)] \times \text{thickness of film (mm)}$$

3. Results and discussion

The morphologies of Ni–Fe alloy are characterized by the SEM as shown in Fig. 1. When the volume ratio of ethanol to water is 0:1, flower-like products are obtained as shown in Fig. 1A. A similar result was observed in previous work [12], in which the smaller flower-like Ni–Fe alloy composed of nanorods was synthesized in pure water. When the volume ratio of ethanol to water increases from 0:1 to 1:1, the snowflake-like Ni–Fe alloy is obtained (in Fig. 1B), and the same result is observed at 3:1 volume ratio of ethanol to water (in Fig. 1C). However, with a further increase in ethanol content (1:0), the tree-like Ni–Fe alloy is formed as shown in Fig. 1D. These results clearly show that the solvent composition has an obvious effect on the morphology of the Ni–Fe alloy, and choosing a proper solvent is an effective strategy for the controllable nanostructures.

The formation of Ni–Fe alloy is confirmed by the XRD as shown in Fig. 2A. The XRD pattern of the sample shows three distinctive diffraction peaks at 2θ of 44.06°, 51.37° and 75.73°, corresponding to (111), (200) and (220) planes of Ni–Fe alloy, respectively [12,15]. The result indicates that these 3D dendritic products (in SEM images) are the face-centered cubic (FCC) γ-phase Ni–Fe alloy. In addition to this, no impurity peak is found in the XRD pattern, indicating the Ni–Fe alloy to be of high purity. The formation of Ni–Fe alloy is further confirmed by EDX spectrum as shown in Fig. 2B. It obviously shows the Fe and Ni peaks [12], and no impurity peak is found in the EDX spectrum. From the peak intensity, the atomic percentage of Ni is measured to be 74.2% of the sum of Fe and Ni atoms, close to the theoretical value of 75.0% calculated by the content of the precursor. It proves that Ni(II) and Fe(III) salts are almost reduced to zero-valent metals. These results indicate the formation of $Ni_{74.2}$–$Fe_{25.8}$ alloy with high purity and high yield at such a low temperature of 100° C. The effect of different proportions of ethanol and water on the formation of Ni–Fe alloy is slight. So, XRD and EDX spectra of all samples are similar; hence those of other samples are not discussed.

The yield of Ni–Fe alloy prepared with different proportions of ethanol and water is summarized in Table 1. The yield of Ni–Fe alloy prepared in pure water is lower than 50%. The low yield is attributed to $Fe(OH)_3$ and $Ni(OH)_2$ is formed and instability in

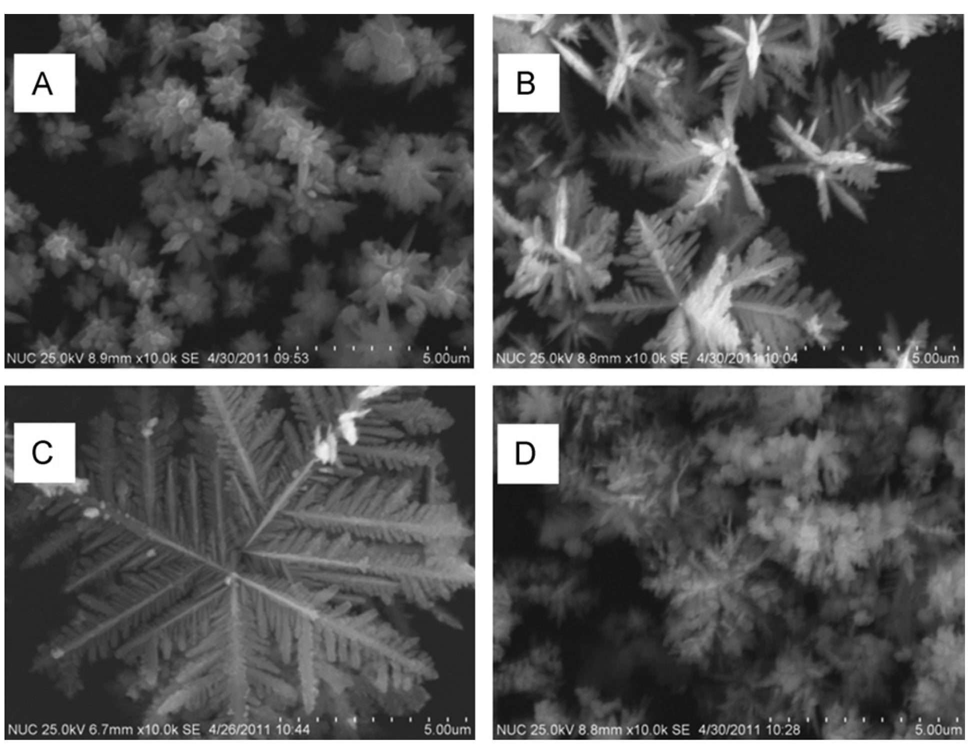

Fig. 1. SEM images of products prepared in ethanol/water mixing solution with various volume ratios of (A) 0:1, (B) 1:1, (C) 3:1 and (D) 1:0.