



Facile synthesis of atomically mixed Fe₅₀Co₅₀ nanoalloys via a simple combustion-based route



Deyin Zhang^a, Mingli Qin^{a,*}, Ye Liu^b, Min Huang^a, Baorui Jia^a, Yuxiao Wang^a, Xuanhui Qu^a

^a Institute for Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China

^b School of Material Science and Engineering, Xiangtan University, Xiangtan 411105, China

ARTICLE INFO

Article history:

Received 13 January 2017

Received in revised form

28 February 2017

Accepted 21 April 2017

Available online 22 April 2017

Keywords:

Magnetic nanomaterials

Solution combustion synthesis

Fe-Co nanoalloys

Magnetic properties

ABSTRACT

Solid solution Fe₅₀Co₅₀ nanoalloys (NAs) with body centered cubic (bcc) structure have been successfully synthesized via a facile combustion-based route with two simple steps. Firstly, the mixed oxides (CoFe₂O₄ and CoO) were prepared by solution combustion synthesis. Subsequently, the Fe₅₀Co₅₀ NAs were synthesized through hydrogen reduction of mixed oxides. The influence of the fuel-to-oxidizer ratio (φ) on the phase constituents, specific surface area and morphology of the combustion products were discussed. The phases, morphology and magnetic properties of reduction products at various temperatures were investigated. The product reduced at 500 °C exhibits the bcc Fe₅₀Co₅₀ NAs structure with crystallite size ~50 nm and the two elements are evenly distributed in a single nanoparticle. The saturation magnetization of Fe₅₀Co₅₀ NAs reduced at 500 °C reaches 214.77 emu/g. Considering the simple and facile preparation process, the synthesized Fe₅₀Co₅₀ NAs with high saturation magnetization will present a wide range of potential applications in data storage, magnetic resonance imaging and biomedicine.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Magnetic nanomaterials with high magnetic moments have potential applications in various fields, such as data storage, magnetic resonance imaging, high performance transformers and biomedicine, etc. [1–4]. Nano-scale alloys (nanoalloys : NAs) of Fe₅₀Co₅₀ are promising materials for these applications due to the high saturation magnetization (233 emu/g for bulk bcc alloy) and high Curie point (1173K) [5,6]. Various techniques for the preparation of Fe-Co NAs have been proposed, including mechanical alloying [7–12], mechanochemical processing [13,14], electrospinning [15], solution-phase chemical synthesis [5,16–19]. However, these methods have more or less encountered several limitations, such as time-consuming, sophisticated instrumentation and costly raw materials. Solution phase synthesis strategies for Fe-Co NAs have advantages that the size and shape of the nanoparticles can be controlled well by tuning the reaction conditions, but the disadvantage is that the surfactants or stabilizers

are often introduced, which can hinder the interaction between the hard and soft magnetic grains, an important factor for fabricating exchange coupled permanent magnet with high energy product [20]. It is a challenge to develop a simple, low-cost, surfactant-free solution phase method to prepare Fe-Co NAs.

Solution combustion synthesis (SCS) has been successfully applied to the preparation of diverse nanomaterials, e.g., binary and complex metal oxide nanomaterials [21,22], nano-crystalline metallic materials [23] and nanocomposites [24,25]. SCS is a time-saving and energy-saving method, especially for the synthesis of complex oxides which can be easily adapted for scale-up applications [26]. The other prominent advantages of SCS can be seen from the aspects of using simple instruments, low-cost raw materials, without adding surfactant, easiness of chemical composition design. Moreover, aqueous combustion reaction facilitates the mixture of raw materials at molecular level. However, as far as we know, there are no literature to report the preparation of Fe-Co NAs via SCS.

Herein we report a facile combustion-based route to prepare Fe₅₀Co₅₀ NAs with two simple steps. Firstly, the mixed oxides (CoFe₂O₄ and CoO) were prepared by SCS using ferric nitrate and cobalt nitrate as oxidizer and metal sources, glycine as fuel. Subsequently, Fe₅₀Co₅₀ NAs were synthesized through hydrogen

* Corresponding author.

E-mail address: qinml@mater.ustb.edu.cn (M. Qin).

reduction of mixed oxides. The influence of the fuel-to-oxidizer ratio (referred to as φ hereafter) on the phase constituents and morphology of combustion products were discussed. The phases, morphology and magnetic properties of reduction products at various temperatures were investigated in detail.

2. Experimental

The $\text{Fe}_{50}\text{Co}_{50}$ NAs were prepared by SCS followed by reduction treatment. A quantitative amount of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) used as oxidants in combustion reaction were the sources of Fe and Co. Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) was used as fuel for combustion. All the starting materials were of analytical reagent grade.

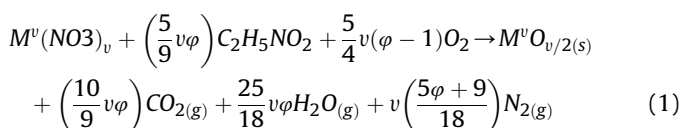
To prepare reactive solution, the above raw materials with different fuel-to-oxidizer ratios ($\varphi = 0.3, 0.75, 1, 3$) were dissolved in 200 ml distilled water under stirring to obtain mixture solution. This solution was filled into a 1000 ml glass, and then was heated at ambient atmosphere on an electrical furnace which could be operated up to peak temperature of 300 °C. This mixture solution was evaporated at around 95 °C to gradually form a clear brown-colored gel. The gel swelled and became foamy, and was then ignited suddenly at ambient atmosphere. The yellow flame rapidly spread and combustion reaction lasted for about several minutes. After the reactants were exhausted, puffy, porous oxide powders were obtained. Subsequently, the powder mixtures were reduced by a flow of hydrogen for 2 h.

The thermal gravimetric analysis (TG) and differential scanning calorimetry (DSC) of the formed gel sample were performed in air at a heating rate of 10 °C/min by using a Rigaku DT-40 thermal analyzer. Phase constituents of the combusted products and reduction products were studied by Siemens D 5000 X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 0.1542$ nm) radiation. The average crystallite sizes of reduction products were calculated by using the Scherrer's formula. The morphologies of the combusted products and reduction products were observed by field emission scanning electron microscopy (FESEM, JEOL, JSM-7001F). The specific surface area (SSA) of the combusted products was measured by the BET method. The microstructure of the combusted products and reduction products were characterized by transmission electron microscopy (TEM, JEOL, JEM-2010). High-angle annular dark-field scanning TEM (HAADF-STEM) and scanning TEM energy dispersive X-ray spectra (STEM-EDS) mappings of reduction products were obtained by a microscope (Tecnai G2 F30 S-TWIN). The magnetic properties of reduction products were measured on a Lakeshore 7410 vibrating sample magnetometer (VSM) with a maximum applied field of 15 kOe at room temperature.

3. Results and discussion

3.1. Solution combustion synthesis

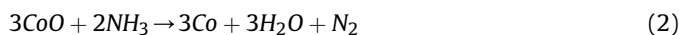
SCS is in essence a redox exothermic reaction between oxidizer and fuel. The function of glycine during the synthesis is 2-fold: first, it acts as a complexing agent for the cations in the nitrate solution; second, it is the fuel during the following combustion [27]. During the combustion process, metal nitrates were transformed into ultrafine oxides by Eq. (1) [28]



where v is the metal valence and a tunable parameter, φ is the fuel-to-oxidizer ratio. $\varphi = 1$ implies that all oxygen required for complete combustion of fuel derives from the oxidizer, while $\varphi > 1$ (< 1) implies fuel-rich (or lean) conditions. It is well-known that φ is the key parameter for the combustion reaction, which can affect the phases, specific surface area and morphology of the combustion products.

As mentioned in the synthesis procedure, with continuous heating condition, the homogeneous mixed solution involving ferric nitrate, cobalt nitrate and glycine gradually developed into gel, and the subsequent thermal behavior of the gel was studied. The TG and DSC curves of the formed gel with $\varphi = 0.75$ are shown in Fig. 1. It is noticed that up to 173 °C, the gel sample undergoes a mass loss of ~15% on the TG curve. In the same temperature region, an endothermic peak at 150 °C is presented on the DSC curve, which can be ascribed to the vaporization of remaining water and the desorption of chemically absorbed water in gel sample. As heating continues, a sharp mass loss of nearly 55% is observed on the TG curve, accompanied by a drastic exothermic peak at approximately 173 °C on the DSC curve. This is originated from the exothermic combustion reaction between nitrates and glycine, which can be described by Eq. (1). As temperature continues to ascend, the mass of the sample keeps almost constant.

Fig. 2 demonstrates the XRD patterns of the combustion products synthesized from the solutions with various fuel-to-oxidizer ratio (φ). As can be noticed, the Bragg diffraction peaks of CoFe_2O_4 (JPCDS #22-1086) [29,30] have been detected in the combustion product with $\varphi = 0.3$. It is observed that the combustion products are composed of CoFe_2O_4 and CoO (JPCDS #43-1004) with $\varphi = 0.75, 1$ and 3. However, the peaks of Co (JPCDS #15-0806) are present with $\varphi = 3$. The literature data [31] on pyrolysis of glycine suggests that at initial decomposition stage (below 300 °C) the solid glycyglycine (dipeptide) and glycine anhydride as well as NH_3 , H_2O , and CO_2 gases form. At $T > 300$ °C, the solid products (dipeptide and glycine anhydride) decompose gradually, forming CO_2 , HCNO , HCN , and NH_3 . In this case, the formation of pure cobalt phase may be achieved by reduction of CoO with excessive amounts of NH_3 , which is represented by the following endothermic reaction [32]:



The measured specific surface area of combustion products in the nitrate-glycine system as a function of φ is present in Table 1. It

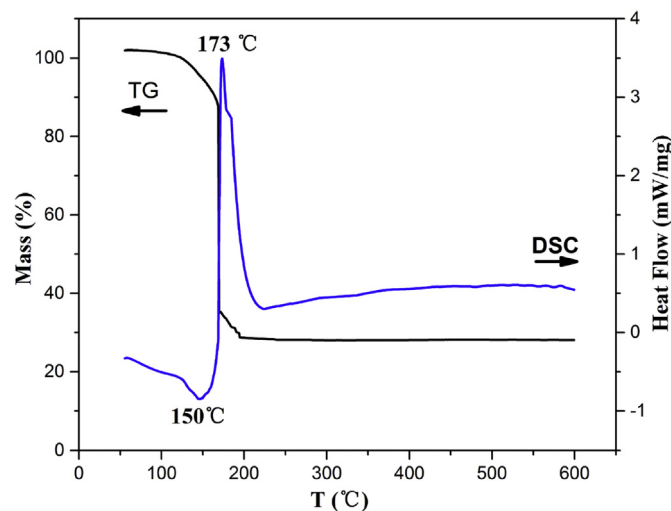


Fig. 1. The TG and DSC curves of the formed gel.

Download English Version:

<https://daneshyari.com/en/article/5459101>

Download Persian Version:

<https://daneshyari.com/article/5459101>

[Daneshyari.com](https://daneshyari.com)