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Microemulsion synthesis and magnetic properties of $Fe_xNi_{(1-x)}$ alloy nanoparticles

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This paper investigates synthesis of $Fe_xNi_{(1-x)}$ bimetallic nanoparticles by microemulsion method. Through studying the mechanism of nanoparticles formation, it is indicated that synthesis of nanoparticles took placed by simultaneous reduction of metal ions and so nanoparticles structure is homogeneous alloy. $Fe_xNi_{(1-x)}$ nanoparticles with different sizes, morphologies and compositions were synthesized by changing the microemulsion parameters such as water/surfactant/oil ratio, presence of co-surfactant and $NiCl_2 \cdot 6H_2O$ to $FeCl_2 \cdot 4H_2O$ molar ratio. Synthesized nanoparticles were characterized by transmission electron microscopy, particle size analysis, X-ray diffraction, atomic absorption and thermogravimetric analyses. The results indicated that, presence of butanol as co-surfactant led to chain-like arrangement of nanoparticles. Also, finer nanoparticles were synthesized by decreasing the amount of oil and water and increasing the amount of CTAB. The results of vibrating sample magnetometer suggested that magnetic properties of $Fe_xNi_{(1-x)}$ alloy nanoparticles were affected by composition, size and morphology of the particles. Spherical and chain-like $Fe_xNi_{(1-x)}$ alloy nanoparticles were superparamagnetic and ferromagnetic, respectively. Furthermore, higher iron in the composition of nanoparticles increases the magnetic properties.

1. Introduction

Nickel-iron alloys are considered for many applications in new and advanced industries due to their special magnetic properties. In such applications, magnetic properties are highly dependent on the chemical composition and ratio of elements in the alloy. An interesting nickel-iron alloy is $Fe_xNi_{(1-x)}$, while $x = 20$–50 wt%. This alloy that called *permalloy* due to its high magnetic permeability has also high magnetic saturation and curie temperature [1,2]. Because of considerable magnetic properties, permalloy is used for many applications such as magnetic resonance imaging (MRI), sensors, recording heads, electromagnetic shielding and absorbing materials [3–5].

In the case of such magnetic alloys, changes in the size and shape of the particles can also cause various magnetic properties [1,5,6]. Decreasing the particle size to nanoscale dimensions leads to variations in magnetic properties [1,6]. Magnetic nanoparticles are particles with dimensions less than 100 nm that present size dependent magnetic properties according to two mechanisms of finite-size effect (for example, from the quantum confinement of the electrons) and surface effect (related to the symmetry breaking of the crystal structure at the boundary of each particle) [7]. Furthermore, according to *shape anisotropy* effect, different morphologies can magnetize the particles in specific directions, so lead to various magnetic properties [1].

Among different methods reported for synthesis of magnetic nanoparticles, *water in oil microemulsion* method has great tendency for the synthesis of particles with controllable sizes and morphologies [8,9]. In this method, nanoparticles are synthesized in small reactors called *reverse micelles;* numerous water droplets distributed in an organic phase by the means of a surface active agent (surfactant). Here, size and morphology of synthesized particles are proportional to the size and shape of water droplets. Therefore, particles with different sizes and morphologies can be synthesized by controlling the parameters of microemulsion method [8]. The most important parameters of microemulsion method can describe as follows:

a) parameters of micellar structure; such as type of organic phase and surfactant, aqueous/organic/surfactant ratio and benefits of co-surfactants to control the shape of water droplets,
b) parameters of chemical composition or type and concentration of the reactants,
c) process parameters such as temperature, pH, mixing method, rate of mixing, stirring method and stirring time [8–11].

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In the only report about synthesis of FeNi particles by microemulsion method, Ban et al. [10] studied synthesis of nano-sized $Fe_{0.2}Ni_{0.8}$ particles through reduction of metal salts by sodium borohydride ($NaBH_4$). Synthesized nanoparticles had primitive cubic (PC) lattice and their structure changed to body-centered cubic (BCC) after heat treatment at 700 °C. Reflecting the influence of nano-dimensions, magnetization of such nanoparticles was much lower than that of the bulk material [10].

Dependence of magnetic properties to composition, size and morphology of particles also studied for FeNi particles synthesized by other methods. For example, magnetic properties of $Fe_{100-x}Ni_x$ alloys produced by mechanical alloying affected by chemical composition [12,13]. Maxwell-Garnett and Bruggeman theories were also investigated the effects of particle size on the magnetic behavior of FeNi micro-particles [14]. Different magnetic properties were also reported for FeNi particles with different morphologies of chain-like [5,15], nanowires and nanotubes [16], leaf-like [17], flower-like [18] and triangular [19].

Present study aims to study magnetic properties of FeNi particles regarding to the composition, size and morphology of the particles. For this purpose, various microemulsion compounds are used to synthesis particles with different morphologies. The effects of water/surfactant/oil ratios are investigated on the particle size, and nanoparticles with different compositions are synthesized by changing the reaction stoichiometry. The research results are important because illustrate the capability of microemulsion method for synthesis of nanoparticles with various compositions, sizes and morphologies. Other sides, interesting magnetic properties of $Fe_xNi_{(1-x)}$ nanoparticles can be provided by controlling the synthesis parameters.

2. Experimental

2.1. Materials

Nickel chloride ($NiCl_2 \cdot 6H_2O$, JHD) and iron chloride ($FeCl_2 \cdot 4H_2O$, Merck) as the source of nickel and iron, hydrazine ($N_2H_4 \cdot H_2O$, Scharlau) as the reducing agent, sodium hydroxide (NaOH, Merck) for controlling the pH, deionized water, 1-hexanol ($C_6H_{14}O$, Sigma) and octane (C_8H_{18}, Scharlau) as the organic phases of microemulsion, CTAB ($C_{19}H_{42}BrN$, Suvchem) and *n*-butanol (C_4H_9OH, Flucka) as surfactant and co-surfactant, respectively.

2.2. Synthesis method

Two microemulsions with a similar oil/surfactant/water ratio were prepared. The water in the first microemulsion was aqueous solution of $N_2H_4 \cdot H_2O$ (5 M), while NaOH was added to increase its pH to 12. In the second one, the water was aqueous solution of metal chlorides (0.05 M). Here, three different molar ratios of $NiCl_2 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ were used for synthesis of $Fe_{0.1}Ni_{0.9}$, $Fe_{0.2}Ni_{0.8}$ and $Fe_{0.3}Ni_{0.7}$ bimetallic particles. Bimetallic particles were synthesized one hour after mixing the two microemulsions at 70 °C, and according to the following reactions:

$$7NiCl_2 \cdot 6H_2O + 3\ FeCl_2 \cdot 4H_2O + 5\ N_2H_4 \cdot H2O + 20NaOH \rightarrow 10Fe_{0.3}Ni_{0.7} + 5\ N_2 + 79H_2O + 20\ NaCl \quad (1)$$

$$8NiCl_2 \cdot 6H_2O + 2\ FeCl_2 \cdot 4H_2O + 5\ N_2H_4 \cdot H2O + 20\ NaOH \rightarrow 10\ Fe_{0.2}Ni_{0.8} + 5\ N_2 + 81H_2O + 20\ NaCl \quad (2)$$

$$9NiCl_2 \cdot 6H_2O + 1\ FeCl_2 \cdot 4H_2O + 5\ N_2H_4 \cdot H2O + 20\ NaOH \rightarrow 10\ Fe_{0.1}Ni_{0.9} + 5\ N_2 + 83H_2O + 20\ NaCl \quad (3)$$

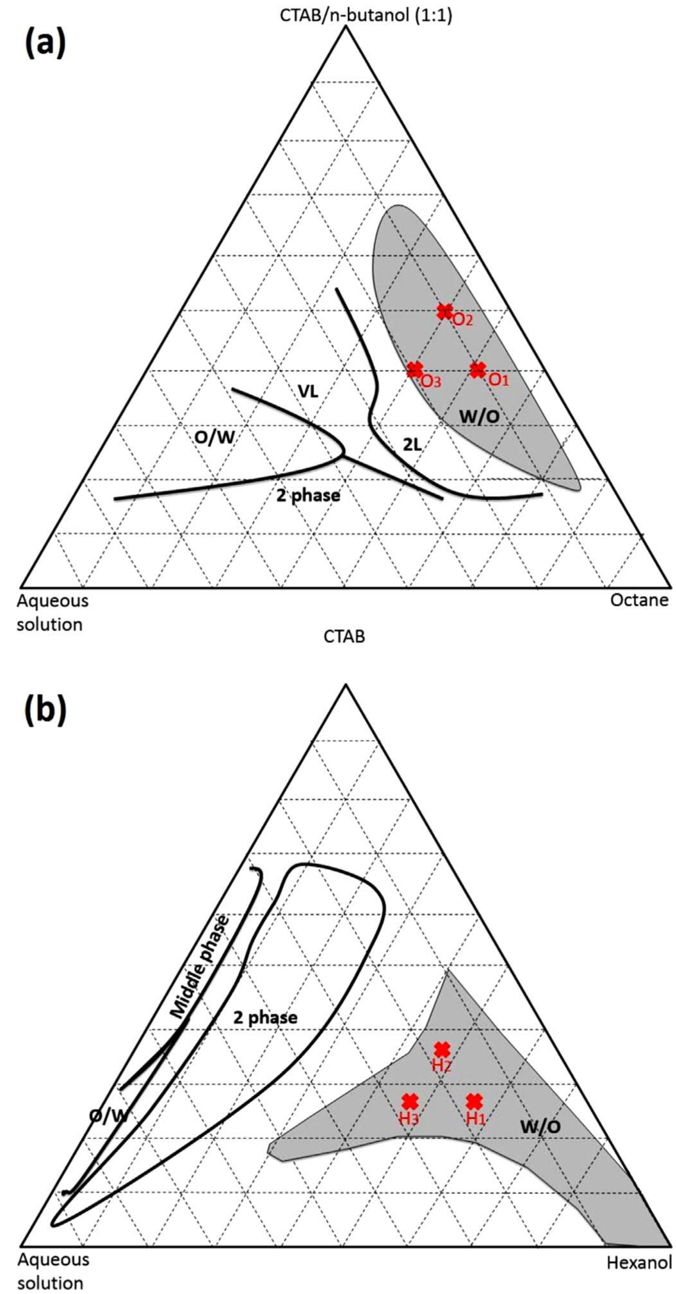

Fig. 1. (a) Ternary diagram of octane/CTAB+butanol/water [20], (b) Ternary diagram of hexanol/CTAB/water [21].

2.3. Design of experiments

In this study, two microemulsion systems of octane/CTAB+butanol/water and hexanol/CTAB/water (with various oil/surfactant/water ratios) are selected to synthesis nanoparticles with different sizes and morphologies. The compositions of both microemulsion systems are chosen in such a way that stable reverse micelles can be formed according to the ternary diagrams of Fig. 1. Selected microemulsion compositions and array of designed experiments present in Table 1. First, synthesis of $Fe_{0.2}Ni_{0.8}$ particles is studied; experiments No. 1 to 3 in the octane/CTAB+butanol/water microemulsion system, and experiments No. 4 to 6 in the microemulsion system of hexanol/CTAB/water. Subsequently, the microemulsion composition that leads to synthesis of the finest nanoparticles is used for synthesis of $Fe_{0.3}Ni_{0.7}$ and $Fe_{0.1}Ni_{0.9}$ bimetallic nanoparticles.