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# Effect of alumina percentage on size and superparamagnetic properties of Ni-$Al_2O_3$ nanocomposite synthesized by solution combustion

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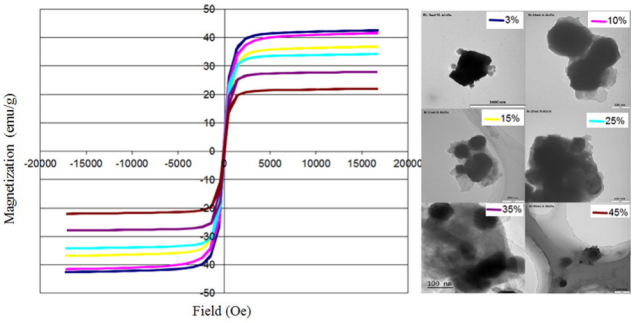
## HIGHLIGHTS

- Nanocomposite for 45 wt.% $Al_2O_3$ showed $H_c = 30.7$ Oe and $M_S = 22.007$ emu/g.
- Nickel particles decreased from 644 to 38 nm by increasing alumina content from 3 to 45 wt.%.
- Close to superparamagnetic behavior found in large particles size of nickel (38 nm)
- Surface area decreased from about 35 to 15 $m^2$/g by increasing alumina content.

## GRAPHICAL ABSTRACT




Ni-3,10,15,25,35 and 45wt.% $Al_2O_3$

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## ABSTRACT

This paper investigates a method to achieve a close to superparamagnetic behavior in Ni-$Al_2O_3$ nanocomposite synthesized by solution combustion. The starting materials used are nickel and aluminum nitrates, as oxidizers, and urea, as fuel. Samples with 3, 10, 15, 25, 35 and 45 wt.% alumina are produced on a hot plate at 330 °C in air. The results show that the change in the content of $Al_2O_3$ can change the size of nickel crystallites and particles. The nickel particle size decreased by increasing the alumina content (from about 644 nm to 38 nm) and resulted in linear hysteresis loops and a relatively high magnetic saturation. The smallest mean nickel particle size measured using TEM images was larger than the critical size that indicates a typical superparamagnetic behavior. The observed linear hysteresis loops and the close to superparamagnetic behavior observed in the nanocomposite are mainly attributed to the combination of two different magnetic behaviors of ferromagnetic nickel and diamagnetic alumina.



## 1. Introduction

Different methods such as sol–gel, hydrothermal, solvothermal and high energy ball milling can be used to produce nanomaterials. While each of these methods has its own advantages, the presence of such common disadvantages as highly time-consuming, the need for calcination step, susceptibility to foreign contaminations, and the need for special equipment and rigorous monitoring encourages researchers to constantly look for alternative methods [1–5].

Solution combustion synthesis (SCS) is an attractive synthesis process used in the production of different types of ceramics, composites, perovskites, catalysts and oxides. SCS depends on a few initial conditions and does not have high requirements for equipment and process control. In SCS, the required energy is supplied by internal reactions between the fuel(s) and oxidant(s). Also, the high temperature of the reaction

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guarantees crystalline products [6,7]. Such characteristics lend a special appeal to this method compared to others.

The SCS method is based on two main groups of reactants: fuels and oxidizers. Urea, glycine, hydrazine and acid citric are some of the fuels that can be used in SCS, while having different reaction behaviors and reduction potentials. A suitable fuel must easily dissolve in water, avoid producing hazardous gases, and should have a low ignition temperature [8]. Due to it being cheap, easily available and safe, urea is one of the most popular fuels used in this method [9]. Although other fuels, e.g., hydrazine and hydrazine-based fuels can have a greater reduction potential and result in aggressive reactions, urea is still favorable because of it being harmless and having a more controllable combustion reaction [8]. Urea can react with the products from the decomposition of the oxidizers and abruptly increase the reaction temperature [10].

The other important group in SCS is the oxidizers. The main role of oxidizers is to produce suitable components to react with the fuel(s). Oxidation-reduction reactions between the fuel(s) and oxidizers act as a source of energy that increase the temperature [8]. Metal nitrates are the base of oxidant agents. These nitrates easily dissolve in distilled water and help produce a homogeneous solution. Such homogeneity increases the chance to have a more uniform final product [11].

Nowadays, the application of nanostructured magnetic materials and nanocomposites is of high priority, because nanomaterials can have different hysteretic behavior as compared to their bulk form [12,13]. Nickel is a ferromagnetic metal and its magnetic structure can change to superparamagnetic when its particle size is <18 nm [14]. Ni nanoparticles with superparamagnetic structures have different applications in electronics, ferrofluids and solar cells. The main problems which limit the applications of such small nanoparticles are their low magnetic saturation, oxidation and grain growth at higher temperatures (250 °C). If the nickel particles are surrounded by a ceramic (oxide) phase, the nickel grain growth and oxidation are prevented and the product keeps its superparamagnetic behavior even at high temperatures. Also, the oxide portion can increase the magnetic corrosion resistance [15–17]. Alumina is one of the most suitable ceramics because of its great resistance in corrosive media, structural stability at high temperatures and wear resistance [18]. Different forms of alumina from amorphous to $\alpha$-$Al_2O_3$ and $\gamma$-$Al_2O_3$ can be synthesized by using urea as a fuel just by changing the fuel to oxidizer ratio [19].

This research focuses on the rapid synthesis of Ni-$Al_2O_3$ nanocomposites in order to obtain different magnetic properties from nickel and alumina. In the present work, efforts are made to prove that the combination of these phases can transcend the ordinary magnetic behavior of ferromagnetic nickel and diamagnetic alumina into a “close to superparamagnetic” behavior in the final nanocomposite product, even with a large nickel particle size. The term close to superparamagnetic is used in this research because superparamagnetic is a property defined as the magnetic properties of ferromagnetic materials while their particle size is decreased to less than the critical limit called “superparamagnetic critical size”. The superparamagnetic behavior has been observed in ferromagnetic structures while their particle size is decreased to about 10 to 30 nm (this limit is below 18 nm for Ni) [14,20]. In this research the magnetic structure of the composite is a mixture of ferromagnetic and diamagnetic and also the particle size of Ni in the composite is larger than the superparamagnetic limit for Ni therefore, the term “close to superparamagnetic behavior” is used. The lowest $H_C$ achieved in this investigation is 30.7 Oe for a mean nickel particle size of about 38 nm in the synthesized nanocomposite. This is a considerably low coercive field for such particle size while $M_s$ is 22 emu/g.

## 2. Experimental

### 2.1. Materials and methods

A solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (≥99% - Merck) and $Al(NO_3)_3 \cdot 9H_2O$ (≥99% - JHD), as oxidizers and urea (≥98.5% - Panreac) as fuel, is used in this research. The percentages of alumina are set at six levels of 3, 10, 15, 25, 35, and 45 wt.%. Eq. (1) represents a general form of the reaction between the starting compounds.

$$xNi(NO_3)_2 + 1.6Al(NO_3)_3 + (2x+4)\varphi CO(NH_2)_2 + 9(\varphi-1)O_2 \rightarrow xNi + 0.8Al_2O_3 + (2x+4)\varphi CO_2 + (4x+8)\varphi H_2O + ((2x+4)\varphi + 2.4 + x)N_2 \quad (1)$$

Where x is the mole numbers of nickel nitrate and $\varphi$ is the fuel to oxidizer ratio calculated by method of Jain et al. [7,21].

When the ratio of fuel to oxidizer is >1 (F/O > 1), nickel can be produced in metallic form. However, metallic nickel oxidizes in the postcombustion region when in contact with air-oxygen [22]. Accordingly, the equation is set to synthesize metallic nickel instead of NiO, although it is necessary to use an auxiliary material like graphite to prevent the oxidation of nickel and maintain the metallic form. Therefore, enough graphite is added to the solution to prevent the oxidation of metallic nickel at high temperatures. The best fuel to oxidizer ratio (F/O) for the synthesis of the final nanocomposite is reported to be 1.5 [23]. The amount of nitrates and urea for the reactions are given in Table 1.

According to Table 1, in order to have a homogenies solution, urea, aluminum nitrate and nickel nitrate are dissolved in 6 ml distilled water. The solution containing the raw materials is completed at room temperature with the stirring speed of 80 rpm in <2 min. The solution is poured in a 100 ml alumina cap as a container. A hot plate which is preheated to 330 °C is used as a means to provide the ignition temperature for the reaction. It takes about 3 min for the raw mixture to transform to a gel. As the temperature increases, the gel becomes more viscous and the reaction starts after about 3 min. If the initial amount of nickel nitrate is 2.25 g (45 wt.% alumina), about 0.45 g metallic nickel can be produced. This amount of nickel can be oxidized by 0.004 mol of oxygen. Based on this amount of oxygen, the amount of graphite is calculated to be about 0.09 g. The added graphite can react with oxygen instead of metallic nickel at high temperatures. Graphite is insoluble in water. In order to have a homogenous mixture, the solution is stirred till the solution on the hot plate becomes a viscous gel; after that, separation of graphite was no longer observed and the stirring was stopped.

### 2.2. Materials characterization

Philips X'pert diffractometer with $CuK_\alpha$ is used for X-ray diffraction (XRD) analysis. A Zeiss Supra 55VP model scanning electron microscope (SEM), equipped with EDS is used for the initial microstructural and composition analysis. A Philips Tecnai F20 FEG-STEM model transmission electron microscope (TEM), is used for the microstructural analysis. Specific surface area is measured by Brunauer–Emmett–Teller (BET) analysis using a BET-210-A sorptometer. In order to prepare the samples for BET analysis, they are kept at 100 °C for 1 h to remove any moisture. The test is carried out with $N_2$ adsorption at −195 °C. The hysteretic behavior is measured by a VSM 7400 Lake Shore with a maximum magnetic field of 2 T. A SETARAM instrument (SETYS Evolution-1750) differential scanning calorimetry (DSC) is used for calorimetric analysis. An AVATAR 370 FT-IR (Thermo Nicolet) is used for Fourier transform infrared spectroscopy (FTIR) test. The ignition and combustion temperatures are recorded by a data acquisition set, Advantech

**Table 1**
Amount of raw materials to have Ni-$Al_2O_3$ nanocomposite at F/O = 1.5.

| Alumina (wt.%) | Aluminum nitrate (g) | Nickel nitrate (g) | Urea (g) |
|---|---|---|---|
| 3 | 0.22 | 4.78 | 4.57 |
| 10 | 0.7 | 4.3 | 4.65 |
| 15 | 1.04 | 3.96 | 4.69 |
| 25 | 1.65 | 3.35 | 4.78 |
| 35 | 2.20 | 2.80 | 4.86 |
| 45 | 2.75 | 2.25 | 4.95 |