Chemical synthesis and research nanopowder of magnetic hard alloy \(\text{Nd}_{15}\text{Fe}_{78}\text{B}_7\)

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Abstract. Hard magnetic nanopowders of the Nd\(_{15}\text{Fe}_{78}\text{B}_7\) alloy were synthesized by the reduction-diffusion reaction of a stoichiometric mixture of Nd, Fe, and Fe-B oxides with CaH\(_2\) in a hydrogen atmosphere at 800 °C. Nd, Fe, Fe-B oxides were obtained by precipitation and had the form of granules with an average particle size of neodymium oxide - 50 nm, iron oxide - 95 nm, iron borate - 57 nm. The particle size of the Nd\(_{15}\text{Fe}_{78}\text{B}_7\) alloy was 45-140 nm. It is shown that the proposed method is suitable for obtaining nanopowders of hard magnetic alloys of the Nd-Fe-B system.

1. Introduction

In the 60-70s of the last century, permanent magnets based on rare-earth metals with high anisotropy were discovered, which retained their magnetization, despite the form of manufacture [1]. Nowadays, Nd-Fe-B consider one of the most important permanent magnetic materials. Due to the unique physical properties of these materials, such as high coercive force and magnetization, these materials have a wide range in applications. Nd\(_2\text{Fe}_{14}\text{B}\) magnets are applied in electric motors, generators, magnetic separators, memory device, micro motors, medical devices, filter materials, sound speakers, sensors, etc.

Metallurgical methods are considered the most common methods that used to make these magnets. Such as electric arc melting [2], mechanochemical alloying [3], high-energy ball mill [4, 5] and rapid quenching methods [6]. Metallurgical methods have many disadvantages: a wide grain size distribution, uneven particle size distribution, long processing times that require additional energy, high purity metal, etc. These disadvantages ultimately lead to a deterioration in magnetic properties and an increase in product prices [7].

Chemical synthesis of Nd\(_2\text{Fe}_{14}\text{B}\) magnet nanopowders is the most promising alternative to metallurgical methods, since it has many advantages, such as: lower energy consumption, more uniform morphology of the resulting particles, controlled particle size, shorter preparation time, and lower cost of starting materials [8]. To date, research into the synthesis of magnets by chemical methods is being introduced. Methods such as sol-gel [9], precipitation [10], deposition in micelles [11], hydrothermal methods [12], microwave synthesis by burning organic precursors [13]. Chemical methods for the synthesis of rare earth permanent magnets have not been adequately studied. Due to the high reduction potential of neodymium (Nd - 2.43 eV) and the reduction potential of iron (Fe 0.057 eV), the samples obtained by the chemical method are rapidly oxidized. This makes the chemical methods for the synthesis of Nd\(_2\text{Fe}_{14}\text{B}\) nanopowders somewhat complicated.

The aim of this work is to study the chemical synthesis of hard magnetic Nd\(_{15}\text{Fe}_{78}\text{B}_7\) nanopowders.

The experiment was divided into three stages. The first stage is the reduction-diffusion process using CaH\(_2\) and a reducing gas H\(_2\).
2. Experimental

2.1 Reagents and devices
The following reagents were used in this work: neodymium nitrate hexahydrate Nd (NO₃)₃ * 6H₂O (99.9%), ferric chloride hexahydrate FeCl₃ * 6H₂O (99.9%), sodium borohydride NaBH₄ (99.8%), ammonium hydroxide NH₄OH (24%, 0.91 g / cm³), sodium hydroxide NaOH * 0.5H₂O (52.05%), toluene (reagent grade).

Scanning electron microscope SEM JEOL 1610LV is used with an energy dispersive spectrometer for electron probe microanalysis SSD X-Max Inca Energy (JEOL, Japan; Oxford Instruments, UK) to study the surface morphology of the synthesized powders and the surface of basic chemical elements. The elemental composition of the synthesized materials was determined using a XSeriesII ICP-MS inductive plasma mass spectrometer (Thermo Scientific Inc., USA). The acidity was determined using a Mettler Toledo SevenCompact pH meter (Mettler Toledo, USA).

Reduction-diffusion process in a tubular vacuum furnace NABERTHERM RSR 120-750 / 11 (Nabertherm GmbH). To obtain hydrogen, the used generator TsvetKhrom-60 (Russia): hydrogen purity 99.9% with a maximum productivity of 60 l / h. Centrifugation of samples on a CENTRIFUGE CM-6M Sky Line installation (ELMI Latvia).

2.2 Obtaining nanopowders of the Nd15Fe78B7 alloy

Synthesis of neodymium oxide
The number of the initial was calculated from the stoichiometric initial. Solutions of 0.438 g of Nd (NO₃)₃ * 6H₂O and 0.24 g of NaOH * 0.5H₂O in bidistilled water were prepared separately. After that, sodium hydroxide solution was fed to the neodymium salt solution, with continuous stirring using a magnetic stirrer, using a peristaltic pump at a rate of 170 ml / h. The resulting salt solution, without stopping stirring, was heated to 80 °C and kept at this temperature 80 °C for an hour. Upon completion of the precipitation process, the reaction mixture was centrifuged at 3000 rpm. The resulting precipitate was washed three times with bidistilled water, dried, and kept in air at 300 °C for two hours.

Iron oxide synthesis
For the synthesis of iron oxide nanoparticles, 1.35 g of chloride hexahydrate FeCl₃ * 6H₂O was dissolved in 100 ml of bidistilled water. Stir the solution with a magnetic stirrer for a few minutes to completely dissolve the iron salt. Further, similar to the method for producing neodymium oxide particles, 30 ml of ammonium hydroxide containing 2 mmol of NH₄OH was added to the resulting solution with continuous stirring using a peristaltic pump. After stirring for 60 min, the brown precipitate was separated by centrifugation. The precipitate was washed with bidistilled water three times and dried in a vacuum chamber for four hours. To obtain iron oxide, the precipitate was calcined at 600 °C for two hours.

Iron borate synthesis
FeBO₃ nanoparticles by chemical deposition. First, 0.54 g of ferric chloride hexahydrate FeCl₃ * 6H₂O (99.9%) was dissolved in 200 ml of bidistilled water. The solution was stirred for 15 minutes and then heated to 50 °C. In another glass in bidistilled water a solution of 0.226 g sodium borohydride NaBH₄ (99.8%). Then to a solution of ferric chloride hexahydrate with continuous stirring was added 200 ml of sodium borohydride solution. The salt solution was cooled to room temperature, after which the resulting dark precipitate was separated using a magnet, the solution was removed, and the precipitate was washed somewhat with ethanol. The resulting precipitate was dried in a vacuum chamber and then calcined at 800 °C for two hours.

Obtaining nanopowders of the Nd₁₅Fe₇₅B₇ alloy
To obtain nanopowders of a hard magnetic alloy with the nominal composition Nd₁₅Fe₇₅B₇, the synthesized powders of neodymium oxide, iron oxide, and iron borate were mixed in toluene with calcium hydride in a stoichiometric proportion. To ensure the homogeneity of the mixture, the powders in tolu were mixed in an ultrasonic bath.

The obtained mixture of powders in toluene was placed into a crucible and then into a vacuum tube furnace. To remove toluene, the furnace was heated to 90 °C for 60 minutes, after which, with a constant
flow of hydrogen, it was heated to 800 °C at a rate of 10 °C / min and held at this temperature for 120 minutes. The furnace was cooled naturally to room temperature without interrupting the H₂ flow.

The obtained powder of a mixture of Nd, Fe and B oxides of black color was mixed with CaH₂ powder (≥95%) using 1: 1.4 wt. % and pressed into compact tablets under a pressure of 160 MPa, which were placed in crucibles made of aluminum oxide, and then in a vacuum tube furnace. The furnace was evacuated to a residual pressure <5 × 10⁻³ Pa, filled with high-purity argon, and heated to 900 °C for 60 min, after which it was naturally cooled to room temperature. Thereafter, the powders were washed with 200 ml of deionized water and acetic acid to remove CaO.

A schematic representation of the above discussed syntheses and the process of obtaining nanopowders of the Nd₁₅Fe₇₈B₇ alloy is shown in figure 1.

![Diagram](image_url)

**Figure 1.** Schematic representation of the process of obtaining nanopowders of the Nd₁₅Fe₇₈B₇ alloy.

### 3. Results and discussion

In figure 2 shows histograms of the distribution of particles of neodymium oxide, iron oxide and iron borate synthesized by the deposition method. As seen in figure 2 (a, b), neodymium oxide powder particles have a granular shape and a fairly uniform size distribution, with an average size of about 60 nm. Iron oxide powders (figure 2 (c, d)) also have a granular shape, but they are rather unevenly distributed in size. The average particle size of iron oxide is approximately 95 nm. Iron borate powder has the same granular shape with an average transverse size of about 57 nm (figure 2 (e, f)).
Figure 2. a, c, e - SEM images of neodymium, iron and iron borate oxides, respectively; b, d, f - histogram of the particle size distribution of neodymium, iron and iron borate oxides, respectively.

In Table 1 shows the results of ICP-MC analysis, which the synthesized neodymium oxide powders contain 53.82% Nd, iron oxide 60.13% Fe, iron boride 73.46% Fe and 4.08% B.

| Compound   | Fe, ppm  | Fe, %   | Nd, ppm   | Nd, %   | B, ppm  | B, %   |
|------------|----------|---------|-----------|---------|---------|--------|
| Nd$_2$O$_3$| 1276.90  | 0.13    | 538161.10 | 53.82   | 560.99  | 0.06   |
| Fe$_2$O$_3$| 601344.00| 60.13   | 513.00    | 0.05    | 1812.57 | 0.18   |
| FeBO$_3$   | 734623.00| 73.46   | 461.00    | 0.04    | 40770.20| 4.08   |
An alloy of nominal composition Nd$_{15}$Fe$_{78}$B$_7$ is formed as a result of a reduction-diffusion reaction of a stoichiometric mixture of Nd, Fe, and Fe-B oxides with CaH$_2$. It can be assumed that the expected reactions of this process proceed in accordance with the following equations:

\[
2Nd_2O_3 + 6CaH_2 = 2H_2Nd_2 + 6CaO + H_2 \uparrow \tag{1}
\]
\[
2Fe_2O_3 + 6CaH_2 = 4Fe + 6CaO + 6H_2 \uparrow \tag{2}
\]
\[
4FeBO_3 + 12CaH_2 = 4Fe + 4B + 12CaO + 12H_2 \uparrow \tag{3}
\]
\[
7.5H_2Nd_2 + 78Fe + 7B = Nd_{15}Fe_{78}B_7 + 18.75H_2 \uparrow \tag{4}
\]

Powders of the Nd$_{15}$Fe$_{78}$B$_7$ alloy (figure 3 (a, b)) synthesized by the above method had a granular form with a wide grain-size composition, with an average particle size of approximately 90-100 nm.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure3a.png}
\includegraphics[width=0.4\textwidth]{figure3b.png}
\caption{a - SEM image of an alloy of nominal composition Nd$_{15}$Fe$_{78}$B$_7$; b - histogram of particle size distribution, c - results of EDS analysis: spectrum and elemental composition of a mixture of Nd$_{15}$Fe$_{78}$B$_7$ alloy powders.}
\end{figure}

**Conclusion**

Chemical deposition method was used to form nanopowders oxides, which the average particle size of granules of neodymium oxide of 50 nm, iron oxide - 95 nm, iron borate - 50-60 nm. The particle size of the Nd$_{15}$Fe$_{78}$B$_7$ alloy was 45-140 nm. It can be concluded that the proposed method is suitable for obtaining nanopowders of hard magnetic alloys of the Nd-Fe-B system.

**References**

[1] Coey J M D 2020. *Engineering* 6(2) 119-131
[2] Saito T 2010. *J. Alloys and Compounds* 505(1) 23-28
[3] Liu X, Hu L, & Wang E 2013 *J. Alloys and Compounds* 551 682–687
[4] Zhong Y, Chaudhary V, Tan X, Parmar H & Ramanujan R V 2017 *Nanoscale* **9**(47) 18651–18660
[5] Oleszak D, Kaszuwara W, Wojciechowski S. 1996 *J. Materials Science* **31** 5725-5729
[6] Liu J F, Davies H A 1996 *J. Magn. Magn. Mater.* **29** 157–158
[7] Guo Y et al. 2019 *J. Alloys and Compounds* **777** 850-859
[8] Rahimi H, Ghasemi A, Mozaffarinia R, Tavoosi M. 2017 *J Magnetism and Magnetic Materials* **444** 111–118
[9] Deheri P, Swaminathan V, Bhide Sh, Liu Z, Ramanujan R 2010 *Chem. Mater.* **22** 6509–6517
[10] Km C W, Km Y H, Cha H G & Kang Y S 2007 *Physica Scripta T129* 321–325
[11] Maya M, Castro T, Ryan F, 2014 Nat. Conf. Undergraduate Research (NCUR) University of Kentucky, Lexington, KY, 994-1000.
[12] Zawadzki M, Kepinski L2004 *J. Alloys and Compounds* **380** 255–259
[13] Yonekura H, Wakayama H 2017 *Intermetallics* **85** 125-129