

Production of iron oxide nanopowders by radiation-chemical method

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Abstract. Were continued the studies of nanopowders (NP) of iron oxide produced by radiation-chemical method at irradiation of iron sulfate solutions in water and iron nitrate in isopropyl alcohol on electron accelerator URT-0,5. With an increase in the concentration of iron sulfate in the solution, the specific surface area of the NP decreases, and the yield increases. For iron nitrate, with an increase in its concentration in solution, both the yield of NP and the specific surface area grow under irradiation under the same conditions (absorbed dose of 2.3 MGy at an accelerator frequency of 10 Hz). Since the particles produced from the iron nitrate solutions are amorphous, they were annealed, followed by X-ray phase analysis. It has been found that these are hematite, Fe₂O₃ particles (unlike maghemite γ -Fe_{21.33}O₃₂ particles from iron sulfate). The specific surface area of the particles increases with the annealing temperature (from 2.4 nm at 400°C to >> 200 nm at 1200°C). The produced NPs can be used to create promising upconversion materials for medicine based on them.

Keywords: electron accelerator, iron oxide, nanopowders.

1. Introduction

Iron oxide nanoparticles (NPles) are used in many areas of human activity [1] and are of particular interest for research in biology and medicine [2, 3]. The main requirements that determine the effectiveness of NPles for use in these areas are biocompatibility and non-toxicity. Magnetic iron oxide nanoparticles are used for cell separation [4]; production of contrast agents for magnetic resonance imaging [5]; magnetically controlled medicinal products for targeted delivery of medicinal products [6]; purification and isolation of proteins [7]; immobilization of enzymes [8], magnetic sorbents for isolation of cell populations, subcellular cultures, proteins and DNA [9]; hyperthermia [10]; immunodiagnosics [11]. Fe₂O₃ iron oxide nanoparticles coated with dextran are used to treat malignant tumors [12]. It is possible to use nanopowders (NP) based on iron oxides to create fuel cells on solid solutions [13], synthesis of high-strength laser ceramics [14], etc.

There are many ways to produce NP: chemical (precipitation [4, 12], pyrolysis, plasma chemical synthesis, etc.), physical (spraying, evaporation – condensation, electrical explosion, etc.), mechanical (by mechanical grinding). The most common are chemical methods.

The purpose of this work was to produce by the radiation-chemical method [15], the essence of which is to initiate a chemical reaction in precursor solutions with a nanosecond electron beam, which leads to the formation of an insoluble compound falling out in the form of NP, and to study the properties of NP iron oxides.

2. Materials and methods

Solutions of iron sulfate (FeSO₄) in water and iron nitrate (Fe(NO₃)₃·9H₂O) in isopropyl alcohol were used to prepare iron oxide nanopowders. The solutions were prepared by adding 0.6 g of sulfate or nitrate, respectively, to 100 ml of solvent. Irradiation was carried out in Petri dishes on an electron accelerator URT-0,5 [16] (electron energy 0.5 MeV, beam current about 300 A, pulse duration 50 ns) at different pulse repetition rates. The thickness of the solution layer did not exceed 1 mm.

The resulting powders were produced by the following methods. The X-ray diffraction analysis (XRD) used a D8 DISCOVER copper diffractometer (Cu K α 1, K α 2 γ = 1.542Å) with a graphite monochromator on a diffracted beam. Processing was performed using the TOPAS 3 program. Isotherms of nitrogen adsorption and desorption at 77 K were obtained on a Micromerics TriStar

3000 V6.03 A. Thermal analysis was performed by differential scanning calorimetry (DSC-TG) on a synchronous thermoanalytic complex NETZSCH STA-409 with dynamic heating in an argon atmosphere at the rate of 10 °C/min.

3. Results and discussions

According to the XRD, by irradiation of the iron sulfate solution yielded single-phase NPles maghemite C, γ – Fe_{21.33}O₃₂ with a cubic lattice ($a \approx 8.40$ (± 0.57)), coherent scattering region (CSR) ≈ 2.3 nm), the specific surface area (SSA) of which reached 12.57 m²/g. Amorphous particles with specific surface area up to 186 m²/g were produced from iron nitrate solutions [17].

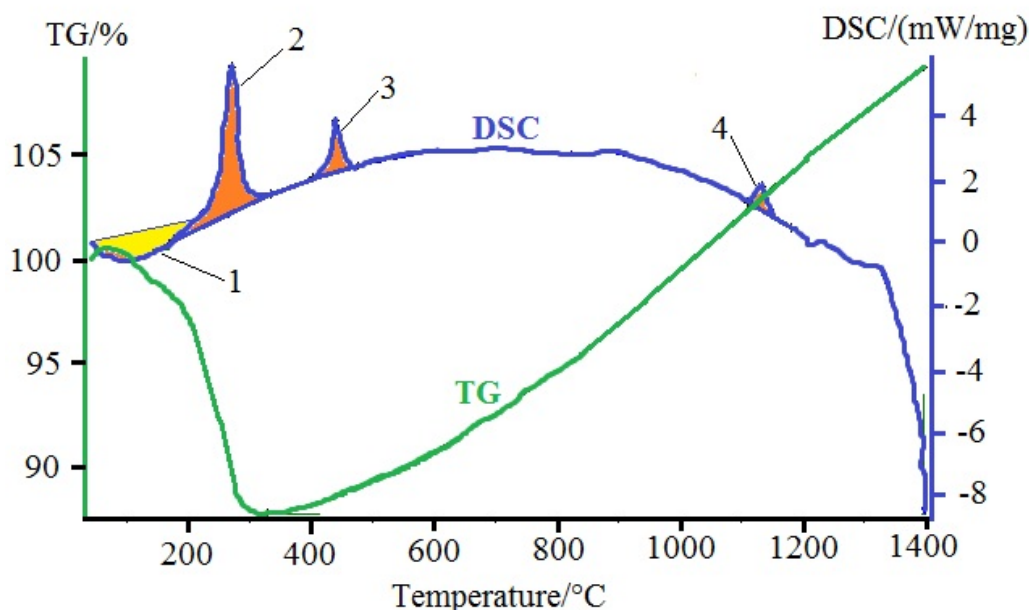


Fig.1. Thermogram of amorphous sample heating.

On the DSC curve of the amorphous NP sample (Fig.1) are observed four thermal peaks: an endothermic peak (1) associated with evaporation of adsorbed water and three exothermic peaks of unknown nature. In order to determine the start temperature of crystallization of the amorphous phase, isothermal annealing of the amorphous sample was carried out at the temperature of $T = 400^\circ\text{C}$ in air, and then was performed the XRD of the annealed sample. XRD (Fig.2) showed that after crystallization of the amorphous phase were formed hematite particles Fe₂O₃ with a rhombohedral lattice (periods $a = 5.036$ (4) Å, $c = 13.757$ (8) Å). The thermal stability of crystalline NPles hematite was tested by isothermal annealing at 500 and 1200°C (according to Fig.1 thermal analysis).

Annealing showed high thermal stability of NPles hematite up to 1200°C. After annealing, the CSR of the particles increased from 2.4 nm ($T = 400^\circ\text{C}$) to 39 nm ($T = 500^\circ\text{C}$). CSR increased significantly after annealing at $T = 1200^\circ\text{C}$ – $\gg 200$ nm, which indicates the formation of submicron powder at this temperature.

Was investigated the effect of the concentration of precursors in solutions on the specific surface area (SSA) and the yield of the resulting particles under radiation under the same conditions (absorbed dose 2.3 MGy at a pulse repetition rate of 10 pps, Table 1). The SSA of maghemite C drops with increasing concentration and the surface area of hematite grows (Fig.3). At the same time, the yield of powders increases in both cases (Fig.4).

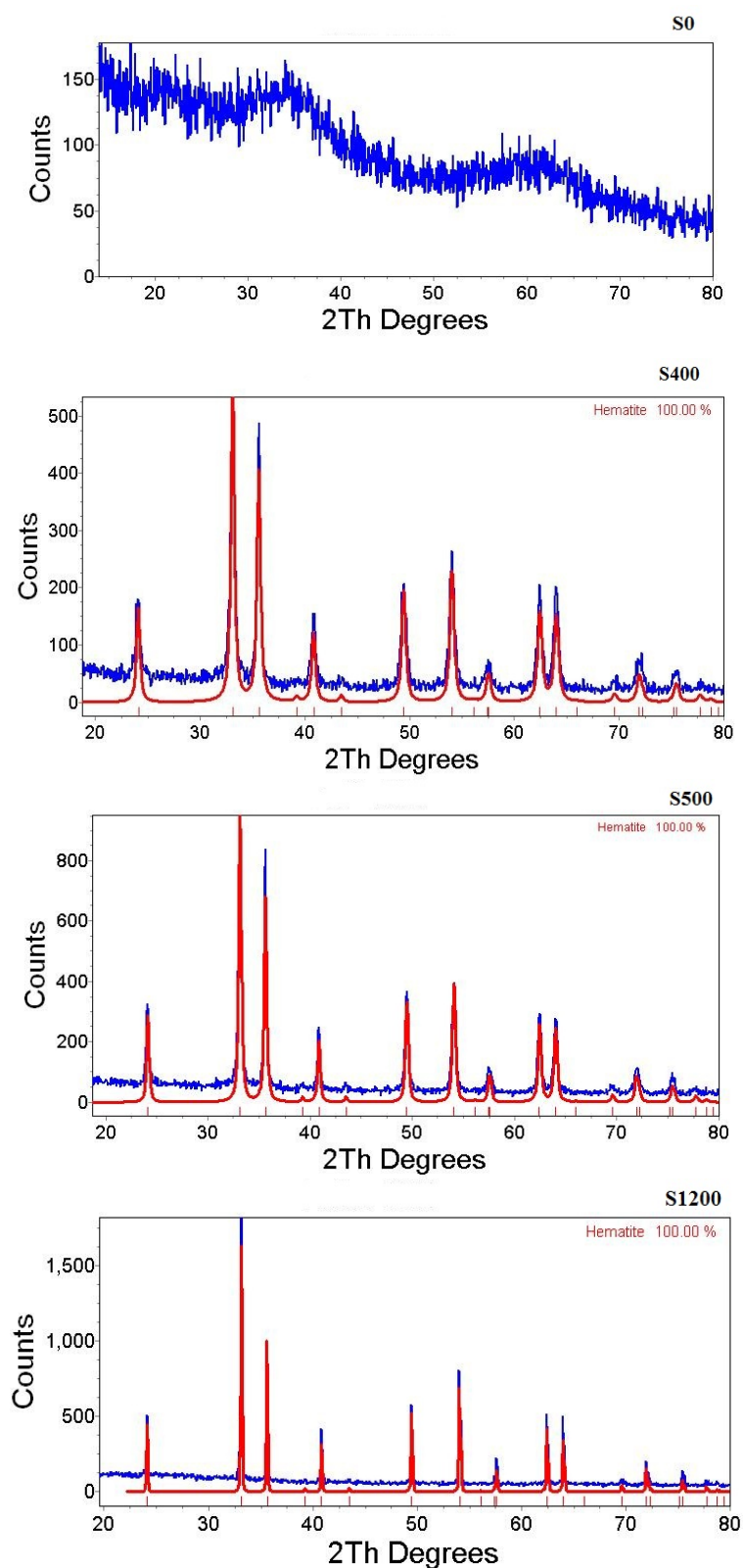


Fig.2. XRD result for NP, produced from iron nitrate solution (S0 – initial NP; S400, S500, S1200 – after annealing at the temperatures 400, 500 and 1200°C).

Table 1. Specific surface area and NP yield

Concentration, a. u.	SSA, m ² /g		Yield, mg	
	maghemite	hematite	maghemite	hematite
0.25	18.7		35.8	-
0.5	14.7	17.9	57.2	84.9
1.0	12.1	45.7	117	201.8
1.5	6.9	-	157	-
2	7.9	80.8	146	362.6
2.5	2.4	-	180	-

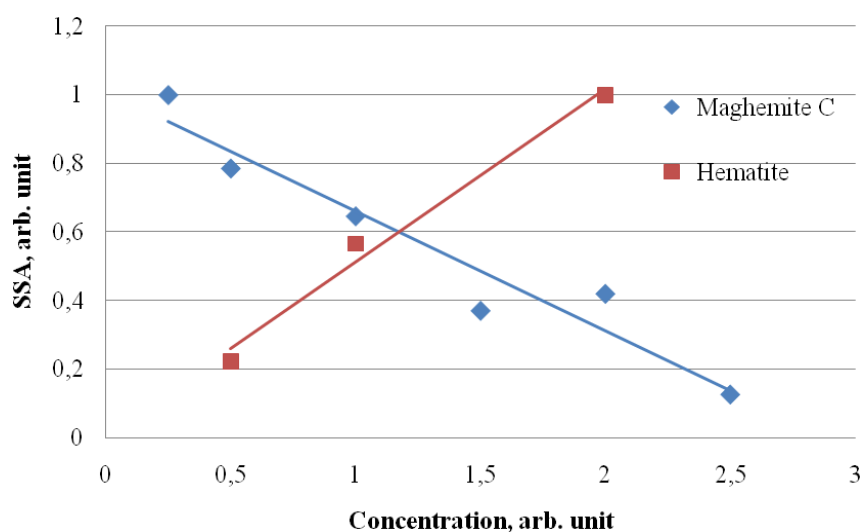


Fig.3. Specific surface of NP when changing the concentration of precursors.

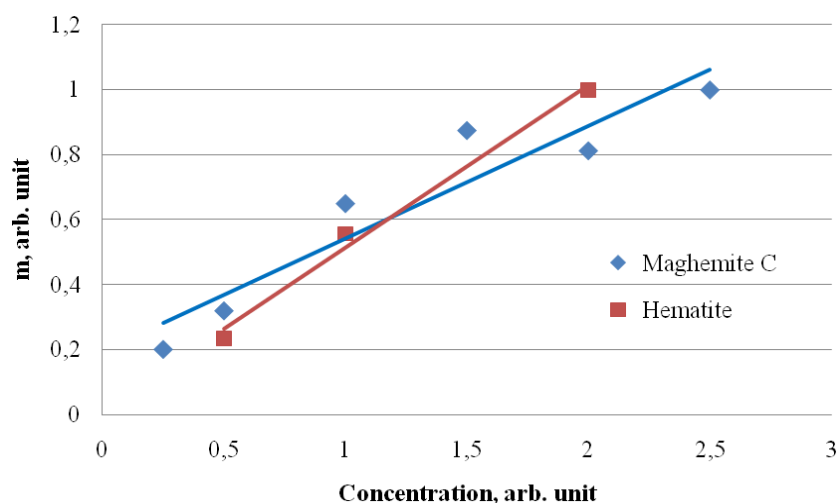


Fig.4. NP yield when changing the concentration of precursors.

4. Conclusion

Thus, it has been found that irradiation of an iron nitrate solution in isopropyl alcohol produces hematite particles Fe_2O_3 in an amorphous phase with high thermal resistance during annealing up to 1200°C . Changing the concentration of precursors in solutions at a constant dose and dose rate of an electron beam can control the size and output of the producing nanopowders.

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5. References

- [1] Cornell R.M., Schwertmann U., *The Iron Oxides*. (Weinheim: Wiley-VCH, 2003); doi: 10.1002/3527602097
- [2] Gubin S.P., Koksharov Yu.A., Khomutov G.B., Yurkov G.Yu., *Uspekhi khimii*, **74**(6), 539, 2005; doi: 10.1070/RC2005v074n06ABEH000897
- [3] Lu A.H., Salabas E.L., Schuth F., *Angew. Chem. Int. Ed.*, **46**, 1222, 2007; doi: 10.1002/anie.200602866
- [4] Shamim N., Hong L., Hidajat K., Uddin M.S., *Sep. Purif. Technol.*, **53**(2), 164, 2007; doi: 10.1016/j.seppur.2006.06.021
- [5] Nikitin A.A., Khramtsov M.A., Savchenko A.G., Abakumov M.A., Mazhuga A.G., *Pharm. Chem. J.*, **52**(3), 36, 2018; doi: 10.30906/0023-1134-2018-52-3-36-40
- [6] Hafeli, U. O., *Int. J. Pharm.*, **277**(1), 19, 2004; doi: 10.1016/j.ijpharm.2003.03.002
- [7] Ito A., Shinkai M., Honda H., Kobayashi T., *J. Biosci. Bioeng.*, **100**(1), 1, 2005; doi: 10.1263/jbb.100.1
- [8] Akgol S., Yasemin K., Denizli A., Arica M.Y., *Food Chem.*, **74**(3), 281, 2001; doi: 10.1016/S0308-8146(01)00150-9
- [9] Tolmacheva V.V., Apyari V.V., Kochuk E.V., Dmitrienko S.G., *J. Anal. Chem.*, **71**(4), 339, 2016; doi: 10.7868/S0044450216040071
- [10] Zhao D.-L., Zhang H.-L., Zeng X.-W., Xia Q.-S., Tang J.-T., *Biomed. mater.*, **1**(4), 198, 2006; doi: 10.1088/1748-6041/1/4/004
- [11] Degré G., Brunet E., Dodge A., Tabeling P., *Lab on a chip*, **5**(6), 691, 2005; doi: 10.1039/B501695A
- [12] Wang F., Li X., Li W., Bai H., Gao Y., Ma J., Xi G., *Mater. Sci. Eng.*, **90**, 46, 2018; doi: 10.1016/j.msec.2018.04.030
- [13] Ivanov V.V., Shkerin S.N., Rempel A.I., Khrustov V.R., Lipilin A.S., Nikonov A.V., *Reports of the Russian Academy of Sciences*, **433**(2), 206, 2010;
- [14] Minh N.Q., Takahashi T., *Science and technology of ceramic fuel cells*. (Amsterdam: Elsevier science, 1995); doi: 10.1016/B978-0-444-89568-4.X5001-4
- [15] Sokovnin S.Yu, Balezin M.E., *Ferroelectrics*, **436**(01), 108, 2012; doi: 10.1080/10584587.2012.731330
- [16] Kotov Yu. A., Sokovnin S.Yu., Balezin M.E., *Instrum. Exp. Tech.*, **1**, 112, 2000; doi: 10.1007/BF02759009
- [17] Balezin M.E., Sokovnin S.Yu., Uimin M.A., *J. Phys.: Conf. Ser.* **2064**, 012086, 2021; doi: 10.1088/1742-6596/2064/1/012086