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## **Hydrothermal Treatment of Electrochemically Synthesised Nanocrystalline Magnetic Iron Oxide Powder**

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### **Abstract:**

*Magnetic iron oxide nano-powders were synthesised electrochemically, using a low-carbon steel electrode immersed in a NaCl aqueous solution, at constant temperature of the electrolyte, pH and current density. In the second step, portions of the starting admixture were boiled at ~360 K during two hours and autoclaved at various temperatures. Both the starting powder and the treated ones were examined by a standard XRD method, then uniaxially pressed into pellets under 400 MPa, and their electric and magnetic behaviour during non isothermal heating was analysed.*

**Keywords:** *Magnetic iron oxides, Electrochemical synthesis, Hydrothermal treatment.*

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### **Introduction**

Development of nano-structured materials is a topic of a great current interest [1]. Quantum states in nanomaterials are size-dependent, leading to novel mesoscopic properties that are sometimes substantially different from those of their atomic and bulk counterparts [2]. Intensive studies [3] of the magnetic behaviour of ferro and ferrimagnetic nano-particles with sizes ranging from several to ~100 nm, have established that their magnetic properties strongly depend on surface effects, finite-size effects and interparticle interactions [4]. For example, nanomagnets exhibit unusual phenomena such as super-paramagnetism and quantum tunneling of magnetization [5]. Strong magnetic materials – ferri and ferromagnetic – are ordered microscopically in magnetic domains [6], regions of about  $10^7$  inter-atomic distances in size, separated by Bloch walls, formed to minimize the total energy of the system, including the exchange, anisotropy and domain wall contributions. The final energy balance determines the structure and shape of the domains. When the size of the crystal decreases, competition between the magneto-static energy and the domain-walls surface energy causes that below a certain limit of the crystal size, a single-domain structure appears. Typically, this single-domain limit is in the range of 20 to 800 nm [6].

Below the other critical diameter which is usually about 10-100 nm, sub-domain magnetic nano-particles can exhibit super-paramagnetic behaviour [7]. Due to reinforcement of the surface magnetic anisotropy, ferro- and ferri-magnetic nano-crystalline powders often

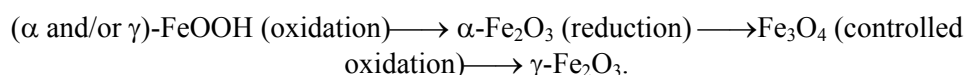
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have larger coercitivity than bulk materials [8], and the mechanism of reduction of the saturation magnetisation that occurs in them, is still unclear. Understanding of these phenomena and processes is crucial for their applications as components of ferro-fluids, catalysts, biomedical materials, printing, xerographic imaging, and the magnetic recording media [3, 4, 5, and 9]. Among magnetic iron oxides, magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) are of a particular interest [10]. Magnetite is an inverse spinel ferrite. The oxygen ions form a close-packed cubic lattice with the iron ions located at two different interstices between them, tetrahedral 8a (A) sites and octohedral 16d (B) sites [1]. Chemically, magnetite/maghemite can be represented by the formula [10]:



where  $y=0$  stays for pure magnetite and  $y=1$ , for pure maghemite (fully oxidized magnetite). In the temperature range from room (RT) to Curie temperature ( $T_c=860$  K) the A sites are populated by  $\text{Fe}^{3+}$  ions and the B sites equally by  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions. That way, twice as many sites are populated with  $\text{Fe}^{3+}$  than with  $\text{Fe}^{2+}$  ions. Although a simple dehydration of lepidocrocite ( $\gamma\text{-FeOOH}$ ) topotactically transforms into  $\gamma\text{-Fe}_2\text{O}_3$  [11], commercial manufacturing of maghemite follows the multistep process [5]:



because maghemite obtained in this way exhibits higher saturation magnetization values than the one obtained directly from FeOOH. This is enabled by an easy diffusion of  $\text{Fe}^{3+}$  ions through the spinel structure of magnetite, forming the well ordered vacancy structure in the as produced maghemite [12]. Unfortunately, pure nano-sized magnetite and/or maghemite powders are instable, especially at elevated temperatures. Nanosized maghemite transforms to  $\alpha\text{-Fe}_2\text{O}_3$  (hematite) at rather low temperatures ( $\sim 570$  K) [13], so knowledge of size-effects and thermal transformations of magnetite and maghemite [14] is very important for optimisation of their properties for various applications [15], and understanding of mechanisms of their formation and transformation in natural (biological, geophysical) and technological processes, such as corrosion at room and elevated temperatures [16]. These investigations include the influence of the degree of crystallinity and presence of dopants on the transformation characteristics of the starting materials [17].

Obviously, it is important to know how to prepare iron oxide powder with distinct morphological, crystallographic and physical properties, suitable for a particular technological application. To achieve this goal, various methods of synthesis have been developed. Chemical (direct precipitation, Copperas, Laux) processes of thermal decomposition of ferrous chloride are known to produce relatively large-sized particles magnetic iron oxide powders, with a relatively high impurity content [2], and a low coercive force [18]. In the attempt to overcome these miss drawings, the electrochemical (EC) preparation method, of ferric hydroxide [3] and magnetite [19], based on anodic iron dissolution in an aqueous NaCl solution has been developed.

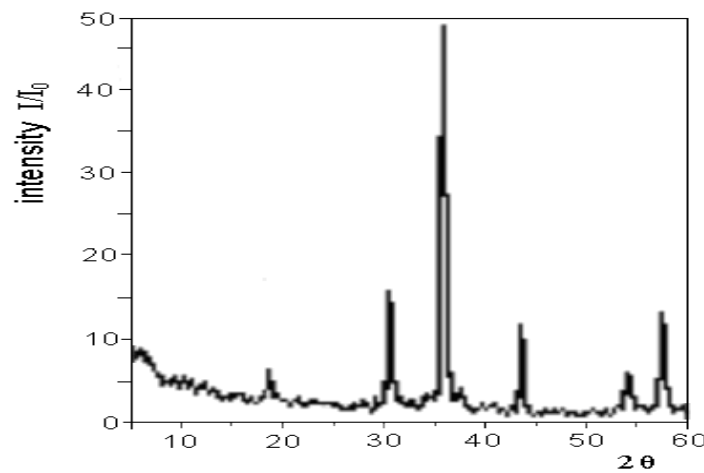
The present work aims to extend knowledge on the inter-dependence of conditions of the EC synthesis process and the properties of the so obtained nano-sized magnetic iron oxide powders. Also, the possibility of stabilization and/or optimization of electrical and magnetic characteristics of real systems with non-uniform particle volumes by succeeding thermal and hydrothermal treatment have been investigated.

## 2. Experiment

An optimal procedure has been derived through numerous preliminary experiments. Two low-carbon steel (99.6% Fe and up to 0.25% Mn, as the main impurity) plates, submerged within the ~0.04 molar NaCl aqueous solutions, were used as electrodes. A D.C. power supply provided the voltage at the electrodes for a period of time sufficient to produce an iron oxide phase(s), at the selected temperature ( $T = 313$  K), and current density ( $I = 1000$  mA/dm<sup>2</sup>). A portion of the admixture was then boiled at ~360 K during two hours, filtered and dried at room temperature. The two other parts of the starting powder were charged to a Teflon-lined autoclave of 50 cm<sup>3</sup> inside capacity, and heated at 433 K and 483 K, during two hours. After that, the contents were allowed to cool, removed from the autoclave, washed with water, and dried at room temperature. To prevent further aging, the as obtained green filter cake was washed with deionised water until the conductivity of the filtrate fell below 10  $\mu$ S/cm. After drying at room temperature, a part of synthesized powders was used for the phase content identification. Diffraction patterns were recorded using nickel-filtered CuK $\alpha$  radiation from a highly stabilized Phillips X-ray generator (PW 1130) operated at 40 kV coupled to a Phillips X-ray diffractometer with a PW 1710 controller. The rest of the powders were two-side uniaxially pressed into disks with a diameter of 8 mm, and mass of 10<sup>-5</sup> kg, at the pressure of 400 MPa. Temperature dependences of magnetic susceptibility under non isothermal (heating rate of 20 K/min) conditions were measured in the temperature range 300 K – 900 K, in argon and air atmosphere, using a modified Faraday method. The resistivity was measured under the same conditions by a home-built apparatus.

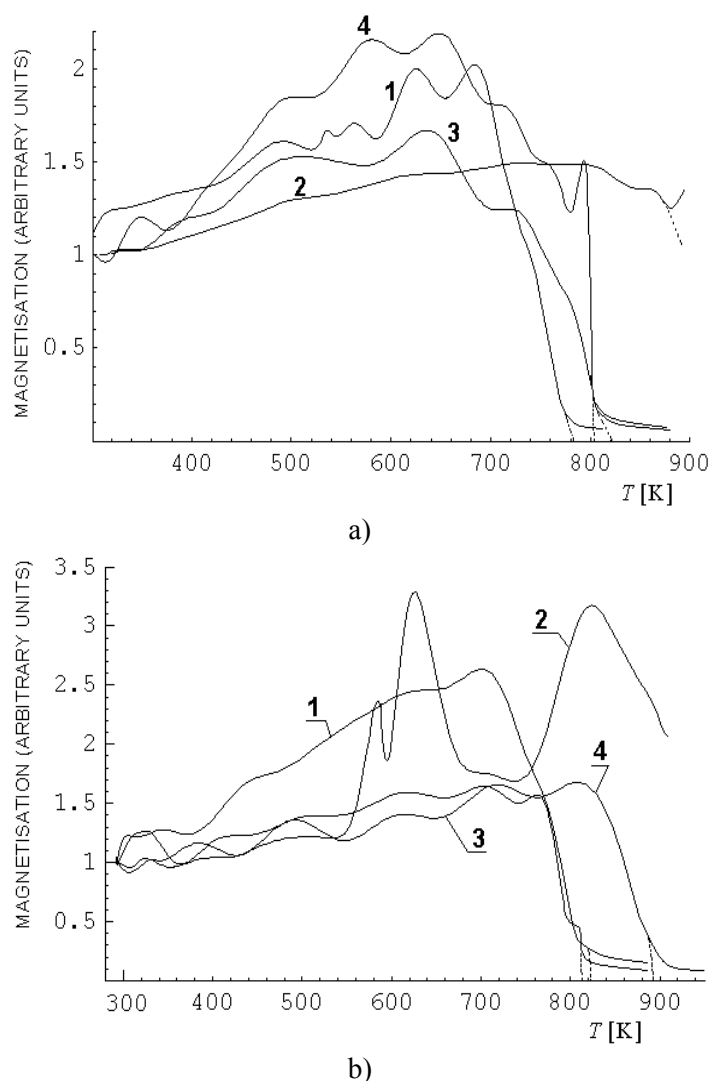
## 3. Results and discussion

Many efforts have been carried out to explain the various contributions to the behavior of iron oxide powder systems [20], establishing the framework for the EC process (current density, temperature, pH of the mother liquor, etc.) which should be considered in an attempt to produce powders of desired properties. Following it, we produced a pure magnetite phase, without impurities. The next step was to prepare maghemite (and/or cation deficient magnetite) with improved magneto-electric properties, by appropriate treatment of the as obtained magnetite [3], and to clarify the behavior of the powder systems during heating, using XRD, magnetization and resistivity measurements.



**Fig. 1** X-ray diffraction pattern of the EC obtained ( $I = 1000$  mA/dm<sup>2</sup>,  $T = 293$  K) iron oxide powder.

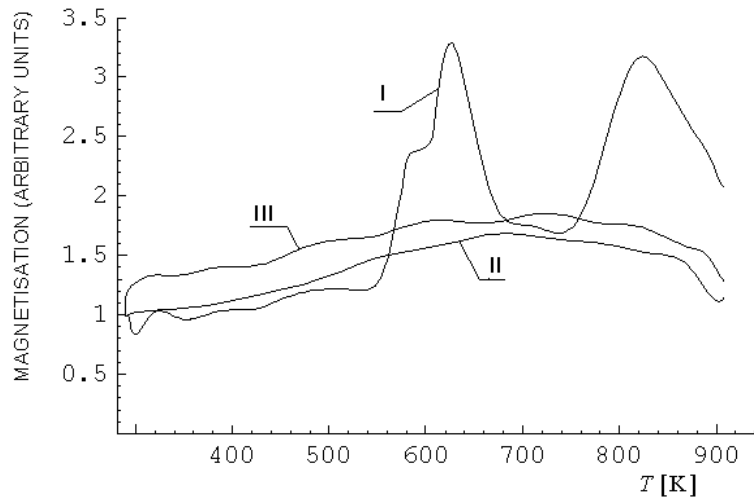
A comparative study of the thermomagnetic behaviour of the samples heated in argon and in air can provide interesting results. During heating in argon, only processes of magnetite phase stabilisation, grain growth, and redistribution of cation and vacancies, can be expected [21]. Two main peaks at different temperatures are visible in the temperature characteristics of samples N<sup>0</sup> 1, 3 and 4 heated in argon (Fig. 2). Their occurrence is frequently ascribed to relaxation processes followed by enhanced cation diffusion, and thermally induced domains reorientation [22].



**Fig. 2** Non isothermal (heating rate  $\sim 25$  K/min) temperature dependence of magnetisation of: 1- as obtained, 2-boiled in water, and hydrothermally treated at 3 -433 K, and 4 -483 K samples, in argon (a) and in air (b).

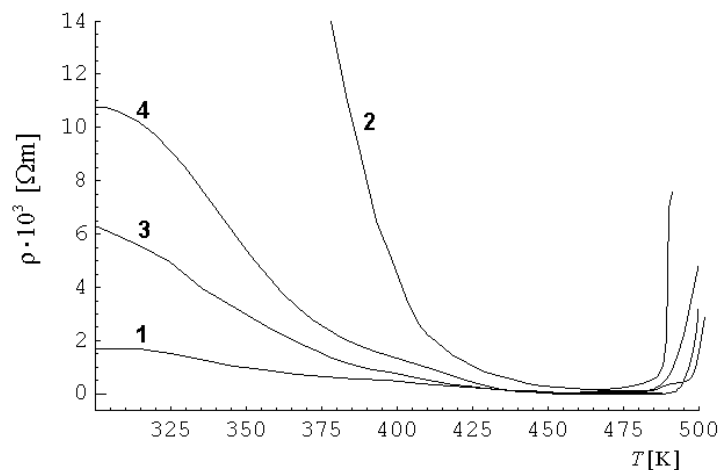
The remarkable decrease of magnetization observed below the Curie temperature of magnetite, is probably the consequence of the nano-crystalline structure of the samples [23]. The most prominent temperature dependence of magnetisation during heating in argon is observed in sample N<sup>0</sup>4. It seems that the sample has a high-defect magnetite structure close to the maghemite one (equation 1,  $y \approx 1$ ), which makes the cation diffusion and vacancy ordering that happens during heating. The boiled sample (N<sup>0</sup>2) is stable, with no peaks in the magnetisation temperature dependence, during heating in argon. It seems that boiling

stabilises the magnetic structure placing the  $\text{OH}^-$  ions in the iron-vacancy structure up to 930 K, high above the Curie temperature of magnetite  $T_c \approx 860$  K [24].



**Fig. 3** Non isothermal (heating rate  $\sim 25$  K/min) temperature dependence of magnetisation of the samples, boiled in water during 2h after: first (I), second (II) and third (III) heat treatment in air.

One can generally expect that heating in air will increase  $T_c$  [24], which is indeed observed. In all cases  $T_c$  rises to  $T_c \sim 920$  K, the Curie temperature of maghemite. Also, it seems that oxidation of magnetite suppresses processes which, during heating in argon, produce the two peaks in samples  $N^0$  1, 3, and 4, but introduce them prominently in the boiled sample ( $N^0$  2), in which they were not observed during heating in argon. The processes are complex, accompanying the loss of a small amount of water, redistribution of vacancies, reorientation of magnetic domains, and external oxidation.



**Fig. 4** Non isothermal (heating rate  $\sim 25$  K/min) temperature dependences of resistivity ( $\rho$ ) of the samples: 1- as obtained, 2- boiled in water, and hydro thermally treated at 3 -433 K, and 4 -483 K.

Temperature dependences of resistivity ( $\rho$ ) of samples  $N^0$  1, 2, 3, and 4, are presented in Fig. 4. They are very sensitive to subsequent treatment of the initial powder. The initial resistivity is lowest for the untreated (green) sample  $N^0$  1. Higher initial resistivity is noticed for hydro-thermally treated samples,  $N^0$  3, and 4, and the highest one is for the boiled sample,

N<sup>o</sup> 2. These results are in agreement with the results of magnetic measurements where the most significant changes upon heating were observed in the boiled sample. The reason could be diffusion of H<sup>+</sup> ions into so called "lithium sites". Namely, the cation vacancies ("□") are distributed mainly in the octahedral cation sites. In maghemite, the vacancy structure is similar to that of LiFe<sub>5</sub>O<sub>8</sub>, where vacancies and/or H<sup>+</sup> ions go to Li<sup>+</sup> sites [16]. Having in mind that the crystal structure of the nonstoichiometric magnetite is similar to the maghemite one, similar behavior of H<sup>+</sup> diffusion can be expected in them. During boiling of a defect magnetite structure, H<sup>+</sup> ions diffuse into octahedral sites [25], and from the electro-neutrality law, the composition can be established as Fe<sub>2,6</sub>H<sub>0,2</sub>□<sub>0,2</sub>O<sub>4</sub>.

In all cases, the decrease of electrical resistivity with rising of the temperature, till 440-480 K (magnetite-maghemite phase transformation) was noted. Formation of the maghemite phase caused rapid increasing of the electrical resistivity. By repeating of the heating/cooling cycle the samples preserved the maghemite phase structure, as well as their high resistivity values.

#### 4. Conclusion

An electrochemical synthesis process of nano-powder magnetic iron oxides is established and complemented by additional hydrothermal treating of the as obtained powders. Hydrothermal treatment enables obtaining of very stable magnetic iron oxide powders, with an elevated Curie temperature, T<sub>c</sub>=920 K, instead of T<sub>c</sub>=860 K. The process of subsequent boiling has an especially strong influence on the powders electrochemically formed in water. It is supposed that stabilisation of the magnetic structure can be ascribed to incorporation of H<sup>+</sup> ions into thermally induced vacancies formed in the initially disordered, nonstoichiometric magnetite phase. Non isothermal heating of the as prepared samples significantly raises their initial magnetisation.

#### Literature

1. P. Jena, Nanostructured Materials, Nova Science, New York, 1996.
2. R. M. Cornell, and U. Schwertmann, The Iron Oxides, VCH mbH, Weinheim, Germany, 1996.
3. Patent, A. P. Toma, Romanian patent RO N<sup>o</sup> 93974, February, 29, 1988.
4. J. L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys., 98 (1997) 283.
5. S. Mørup, in: "Magnetic Properties of Fine Particles", eds. J. L. Dormann and D. Fiorani, North Holland, Amsterdam, 1992, pp. 125-190.
6. K. S. Rane, V. M. S. Vernekar, R. M. Pednekar, P. Y. Sawant, J. of Mat. Science: Materials in Electronics 10 (1999) 121.
7. F. Bødker, and S. Mørup, Europhys. Lett., 52 (2000) 217.
8. E. DeBiasi, C.A. Ramos, R.D. Zysler, and H. Romero, Phys. Rev. B, 65 (2002) 144.
9. Ž. Tomić, P. Jovanić, A. Bugarinović, S. Vardić, A. Maričić, Lj. Vulićević, G. Gligorić, Serbian Journal of Electrical Engineering, 13 (2004) 29.
10. Patent, K. Hayashi, et al, USP N<sup>o</sup> 6,638,675, Oct., 28, 2003.
11. Y. Cudennec, A. Lecerf, Solid State Sciences 7 (2005) 520.
12. Z. Somogyvari, E. Szeb, G. Moszoros, K. Krezhov, I. Nedkov, I. Sajo., F. Boure, Appl. Phys., A 74, (2002) 1077.
13. L. Neel, Ann. De Phys., 3 (1948) 137.

14. R. Dieckmann, H. Schmalzried, E. Schmidbauer, R. Keller: J. Magn. Magn. Mater., 152 (1996) 99.
15. Lj. Vulićević, S. Vardić, A. Maričić, Lj. Novaković, Yucomat 2004, H. Novi, Abs. Book P.S.C.10, p.100.
16. R. H. Kodama, J. Magn. Magn. Mat., 200 (1999) 359.
17. K. Przepiera and A. Przepiera, Journal of Thermal Analysis and Calorimetry, 65 (2001) 497.
18. S. G. Marhetti and R. C. Mercader, Hyperfine Interactions, 148/149 (2003) 275.
19. Patent, T. Souris et al., USP N<sup>o</sup> 6,197,179, January, 30, 2001.
20. D. Predoi, V. Kuncser, and G. Filoti, Romanian Reports in Physics, 56 3 (2004) 373.
21. J. L. Dormann, L. Bessais, and D. Fiorani, J. Phys. C, 21 (1988) 2015.
22. S. Music, S. Krehula, S. Popovic, Materials Letters 58 (2004) 444.
23. E. Tronc, A. Ezzir, R. Cherkaoui, C. Chanéac, M. Noguès, H. Kachkachi, D. Fiorani, M. Testa, J. M. Grenèche, and J. P. Jolivet, J. Magn. Magn. Mat. 221 (2000) 63.
24. F. Bødker, S. Mørup, M. S. Pedersen, P. Svendlindh, G. T. Jonsson, J. L. García-Palacios, and F. J. Lazaro, J. Magn. Magn. Mat. 117 (1998) 925.
25. R. H. Kodama, A.E. Berkowitz: Phys. Rev. B 59, (1999) 6321.

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**Садржај:** Нано-прахови магнетних оксида гвожђа су синтетизовани електрохемијским поступком, уз коришћење електрода од нискоугљеничног челика уроњених у водени раствор NaCl при константној температури електролита, рН и густине струје. У другој фази експеримента, један део добијене суспензије је загреван при ~360К током два сата а други је хидротермално обрађен под различитим условима притиска и температуре. Полазни и накнадно хидротермално обрађени узорци су подвргнути стандардној рендгенској дифракционој анализи. Пресовањем прахова при 400 МПа добијени су цилиндрични компакти који су даље коришћени за испитивање промене електричних и магнетних особина синтетизованих узорака оксида гвожђа током њиховог неизотермског загревања.

**Кључне речи:** Магнетни оксиди гвожђа; електрохемијска синтеза; хидротермална обрада.

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