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Analysis of the Possibility of Obtaining Super-Paramagnetic Powders Based on Ferrooxides as Precursor by MR Contrast Material Synthesis

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Abstract: "Contrast" materials have very great role in many medical areas. Considering modern medical diagnostic techniques and the significance of the solution to the therapy (or surgery) tasks, the questions on precise medical images of high resolution are very important. The high resolution (especially if the image serves further for the numerical processing and analysis is certainly of significances as well as the material for recording or other assisting tasks. The contrasts material for the processes of magnetic resonance (or NMR) and analysis of their performances in the form of initial powder material with super paramagnetic performances are presented in this paper.

1 Introduction

The contrast mediums are echo-substances, which can be used to increase the contrast in recording techniques. For example, depending of the contrast mediums the efficacy could be increased or decreased in Roentgen techniques. Also, by choosing the corresponding medium echo-amplitude can be changed in ultrasonic records. There are special contrast mediums for radiographic records, too [1].

In the present paper, attention will be devoted to analyzing conditions of the synthesis of various iron-oxide powders. Those materials can be used in synthesis of contrast medium for recording organic tissues data (signals) obtained by magnetic resonance (MR) or nuclear magnetic resonance (NMR) [2].

So-called iron oxi-hydroxides, goethite (α-FeOOH) and lepidocrocite (γ-FeOOH), can be used as intermedial products in processing of final powder based on iron-oxides with specific morphologic and (super) paramagnetic properties. The synthesis of goethite

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with specific properties is very interesting in analyzing of possibility to get mentioned contrast mediums [3].

The goetite (α-FeOOH) is a typical product of atmospheric corrosion on the steel's surface. It can be used to protect the steel from further corrosion [4]. In the last years detailed investigations of goethite application in super-paramagnetic powders are achieved. Those powders can be used in the synthesis of the contrast liquids in biomedicine. There is some indication of getting special structure, with nanometer particles, using goethite like intermedial product, too [4]. In the present paper will be shown that various conditions of the goethite synthesis can be influenced on properties of final product. The Fe^{2+}-oxides particles with desired crystal structure, morphologic and magnetic properties can be achieved on this way.

2 Experiment

The experiment was achieved by getting super-paramagnetic powders based on ferro-oxides from solutions of corresponding iron salt's, iron (II)-sulfate and iron (II)-chloride. These high pH basic solutions were treated on different temperatures.

The first experiment was performed by using iron (II)-sulfate salt. The sedimentation was achieved in NaOH solution on the temperature of 302 K. In this solution was added iron (II)-sulfate water solution. This iron (II)-sulfate solution was vacuumed on 105 Pa pressure before using. On this way solute oxygen was removed. Non-oxide atmosphere is realized with getting nitrogen through the suspension during the reaction of sedimentation and after aging iron (II)-hydroxide's sediment in basic solution. After that, the white sediment of iron (II)-hydroxide was converted gently in iron (III)-hydroxide through the aeration ring during six hours. During the process of aeration the temperature of suspension was increased to 305 K. (Note that the process of formation oxi-hydroxide is exothermic.) The sediment of goethite was elutriated until the negative reaction on corresponding ions was appeared. It means that specific electric conductance was smaller than 10 μS/cm.

All these processes to obtaining iron oxi-hydroxide were repeated on the temperature conditions for sedimentation/oxidation: 315 K / 318 K and 335 K / 338 K, respectively. Beside two last cases of experiment for precursor was used iron (II)-sulfate instead of iron (II)-chloride, but other conditions of experiment weren't changed.

By reason of stabilization and stopping of agglomeration of particles, powders are elutriated with the corresponding polar solvent with low boiling point. Then they are dried on room's temperature and pressed in disc shape with diameter of 6mm and thickness of 1.5 mm. Average-mass of starting powders was about 100 mg. Double-side one-axial pressing was made by pressure of 400 MPa. The density of probes is achieved 70 % of TD (TD-theoretical density).

The obtained specimens are examined on special device. The relative changes of mass and magnetic susceptibility of small specimens is measured in the same-time by modified Faraday method. This method is based on interaction of inhomogeneous magnetic field and magnetic materials. The measurement was done in temperature range from 293K to 873 K with heating rate of about 20 K/min. During the experiment electric

balance Sarthorius with sensibility of 10^{-7} kg was used. Magnetic field is formed by solenoid with DC from 0 A to 10 A, Fig. 1. For 7 A, intensity of magnetic field was 5440 A/m.

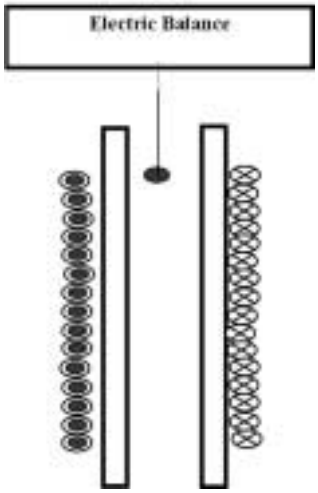

Fig. 1 - *Schematic of the devices for magnetics susceptibility measurement for small specimen by Faradey method.*

3 Results and Discussion

The goethite, α-FeOOH, is iron (II) oxihydrate with 89.86 % Fe_2O_3 and 10.14 % H_2O and crystallizes in rhombic lattice. The obtained prismatic crystals are with lattice's parameters: a=0.465 nm, b=1.002 nm and c=0.304 nm. The coordination number is Z=4 and the density is 4370 kg/m^3.

Lepidocrokite, γ-FeOOH is iron (II) oxihydrate with 89.86 % Fe_2O_3 and 10.14 % H_2O. It crystallizes on the same way with lattice's parameters: a=0.388 nm, b=1.254 nm and c=0.306 nm. The coordination number is Z=4 and the density is 4000 kg/m^3 [6, 7].

Until the goethite's crystals have color from light to dark yellow, the crystals of lepidocrokite have color from ruby to dark red. Making one or the other iron oxi-hydrate's is very sensitive on the conditions of the synthesis (species and concentration of starting substances, pH value of solution, atmosphere and etc.). Very usually in the mixture of the goethite lepidocrokite, and other so-called hydrogoethites and hydrohematites sediment is placed. For this reasons the experiment was guided with very high precision. Especially, the crystal-chemical composite of the starting sediment is crucial for super-paramagnetic properties of final powders.

Magnetic susceptibility and gradient of magnetic field are related by relation

$$\chi_m = \frac{F_z}{m\mu_0 H \frac{\mathrm{d}H}{\mathrm{d}z}}, \qquad (1)$$

where:

F_z - force of inhomogeneous magnetic field on specimen;

m - mass of specimen;

H - intensity of magnetic field ; and

$\mathrm{d}H / \mathrm{d}z$ - gradient of magnetic field along solenoid axis.

The method of magnetic resonance (MR) is using the strong homogenous magnetic field and gradient fields for localization discontinuities in tissue. The MR technique has high resolution in 2D space with the satisfaction contrast effects. This technique can be used in 3D analyzing of tissue, too.

In Fig. 2 is the historical MR record of head is presented.

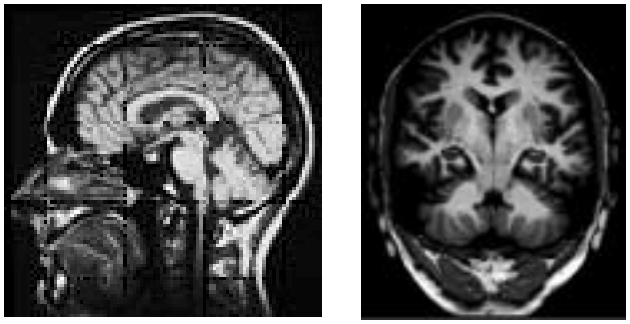

Fig. 2 - *The historical MR record of head [11] (R. R. Ernst, 1985.).*

The MR technique is also known as the NMR technique (nuclear magnetic resonance). This technique is based on interaction nucleus magnetic properties with different DC and AC magnetic fields. External RF pulses can change the nature of orientation of magnetic dipoles and pathogen variation is observed as disturbance. There are many variations of modern medical devices with corresponding programs for magnetic resonance. Analyzing the signals, which are depending of tissue's characteristics, the 3D record with high resolution can be achieved.

Times of relaxation T_1 and T_2 have big influence on the quality of MR records. The relaxation time T_1 is time for steady state longitudinal in magnetization M_z to its equilibrium value M_{z0}. The relaxation time T_2 is defined for transversal process of spin-spin relaxation [12, 13].

It is known that fine particles of ferrites ($Me^{2+}O{\cdot}Fe_2O_3$; Me^{2+} - ions of divalent metals) can be used as the contrast mediums in MR diagnostics. Many ions with paramagnetic characteristic (CO^{2+}, Cu^{2+}, Mn^{2+}, Gd^{3+}, Dy^{3+}, etc.) can be connected on bio-molecules. Fe^{3+} ions are the most wanted in formation intracellular and macromolecular MR

agents. The reasons for using these ions are theirs non-toxically and nature existing in many tissues [8].

The mentioned substances are shown considerable relaxation effects expressed by T_1. Difference between susceptibility of these substances and environment is reason of considerable oscillations of local magnetic field with T_2 relaxation processes. On this way the contrast in structure of organic tissue, in which were injected agents, is increased. For the contrast mediums iron (II) -oxide's particles with special structure (fine particles of super-paramagnetic iron (II) -oxides FSPMF) are used. Not less important are ultra-fine particles of super-paramagnetic iron (II)- oxides (UFSPMF). The UFSPMF are using in synthetic body's liquids and the FSPMF are using for recording tissues.

Super-paramagnetic particles or aggregates have one domain character and they can be easily connected on in-organic and organic substances on the special wanted place in tissue. These aggregates belong in diagnostics and/or pharmaceutical active substances. Average diameter of super-paramagnetic particles is between 3 nm and 50 nm and for degradable aggregate particles the average diameter is between 10 nm and 1000nm [10].

The present paper doesn't include concrete conclusion, but it gives some conditions and limitation for the super-paramagnetic powder synthesis. Those experiments can be very useful for future investigation of these materials as the non-invasion contrast mediums for MR technique.

The obtained powders were analyzed by electron and light microscopies as well as TD analyzes in non-isothermal conditions. Also, behavior of powders in modified Faraday's method was analyzed. The goethite powders (α-FeOOH) achieved from $FeSO_4$ as precursors in the temperature conditions T_s/T_{oxi}=29/35 (T_s - the temperature of sedimentation, T_{oxi} - the temperature of oxidation, both in ^{0}C) is shown in Fig. 3.

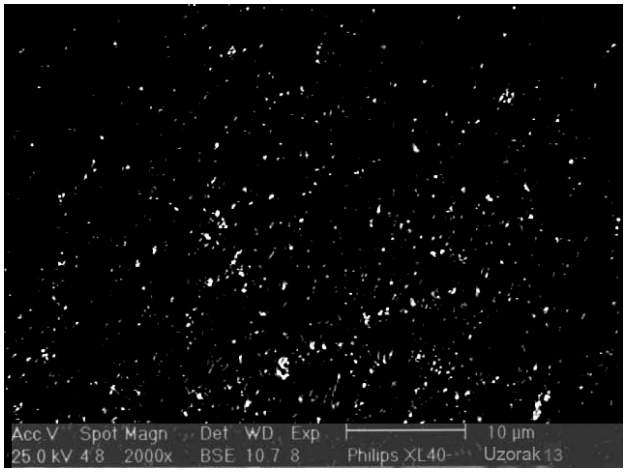

Fig. 3 - *TEM micrographs of goethite (α-FeOOH) obtained from $FeSO_4$ as precursors, T_s/T_{oxi}=29/35.*

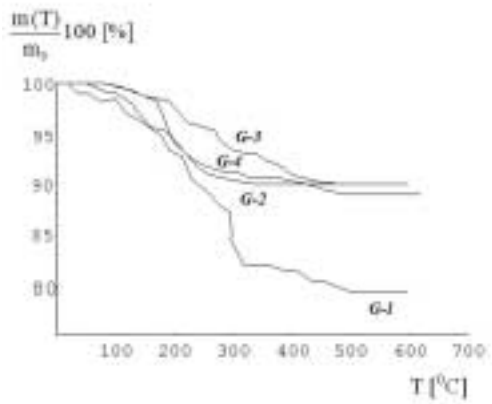

Fig. 4 - *TD curve of goethite synthesized from solutions under various starting precursor salt, temperature and pH*

G-1 - α-FeOOH chemically obtained from $FeSO_4$ as precursor T_t/T_{oxi} =29/35;

G-2 - α-FeOOH chemically obtained from $FeCl_2$ as precursor T_t/T_{oxi} =42/47;

G-3 - α-FeOOH chemically obtained from $FeCl_2$ as precursor T_t/T_{oxi} =60/65; and

G-4 - α-FeOOH chemically obtained from $FeSO_4$ as precursor T_t/T_{oxi} =46/46 Si is added in the TEOS form (tetra etil ortosilikata).

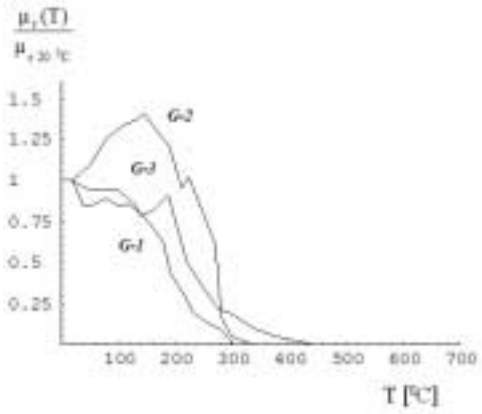

Fig. 5 - *Relative magnetic permeability versus temperature.*

G-1 - α-FeOOH chemically obtained from $FeSO_4$ as precursor T_t/T_{oxi} =29/35;

G-2 - α-FeOOH chemically obtained from $FeCl_2$ as precursor T_t/T_{oxi} =42/47; and

G-3 - α-FeOOH chemically obtained from $FeCl_2$ as precursor T_t/T_{oxi} =60/65.

TD curve of goethite synthesized from solutions under various starting precursor salt, temperature and pH is shown in Fig. 4.

The function of relative magnetic permeability ($\frac{\mu_r(T)}{\mu_{r\ 20\ ^0C}}$) versus the temperature is shown in Fig. 5.

4 Conclusion

In the present paper was analyzed the form of obtaining materials for diagnostic MR medical techniques. Some powders with potential super-paramagnetic properties were obtained. These powders were analyzed by electron and light microscope. Also changing their magnetic properties in function temperature increase and the synthesis's conditions of starting powders were analyzed by TD method. On this way it was achieved starting quantity indicator, which can be elaborated in the future.

5 References

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