UDC 538.95:544.47

SYNTHESIS OF MAGNETITE BY HOMOGENEOUS CHEMICAL DEPOSITION FOR PREPARING OF MAGNETIC FLUID ON ITS BASIS

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The magnetite synthesis by methods heterogeneous and homogeneous chemical deposition is conducted. The phase composition and magnetic properties of the samples are investigated. Revealed that magnetite synthesized by homogeneous chemical deposition has higher magnetic characteristics than magnetite obtained by heterogeneous precipitation method. It is shown that a homogeneous chemical deposition method possible to carry out the synthesis and stabilization of magnetite in a single step.
Keywords: Homogeneous chemical deposition, magnetite nanoparticles, stabilizer, oleic acid, the magnetic fluid.

Introduction. Magnetic fluids have a unique combination of fluidity and ability to significantly interact with the magnetic field. They possess properties of the ferromagnetic liquid, allowing them in new ways solve a variety scientific, technical and medical-biological problem [1-5]. Their properties are determined by the totality of characteristics, which they are consisting: solid magnetic phases, dispersion medium and stabilizer (varying by them may widely change the physical and chemical properties of magnetic fluids).

Basically, as solid phase in the magnetic fluid is used nanosized magnetite (Fe_3O_4). Methods for preparing magnetite nanoparticles include dispersion and condensation processes. Chemical deposition (relating to the condensation processes) is considered today as one of the simple and cheap methods. This method offer a low temperature alternative to conventional powder synthesis techniques in the production of nanoparticles, and the particles sizes can be well controlled addition of surfactants [6].

However, nanosized magnetite has a large specific surface area and therefore possesses high surface energies. Thus, they tend to aggregate so as to minimize the surface energies. Moreover, the naked magnetite has high chemical activity, and is easily oxidized in air, generally resulting in loss of magnetism and dispersibility. Therefore, it is important to provide proper surface coating and developing some effective protection strategies to keep the stability of magnetite [6].

Traditional method of chemical deposition, what include depositing ions Fe (II) and Fe (III) in a molar ratio 1:2 by alkalis (NaOH abo NH_4OH), cannot completely exclude the oxidation and aggregation of obtained magnetite nanoparticles [7-9]. For overcoming these drawbacks interesting there is applying homogeneous chemical deposition method using a urea which allows combining the steps of preparing magnetite and its stabilization in one process.

The aim of this work was the synthesis of magnetite by homogeneous chemical deposition, investigation its phase composition, magnetic properties and comparison with magnetite obtained by the traditional heterogeneous precipitation.

Objects and methods. For synthesis of magnetite the following reagents were used: iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) (chemically pure qualification), iron (III) chloride ($FeCl_3 \cdot 6H_2O$) (chemically pure qualification), hydrochloric acid (HCl) (qualifications pure for analysis), urea ($CO(NH_2)_2$) (qualifications pure for analysis), oleic acid ($C_{18}H_{34}O_2$) (qualifications pure for analysis).

Magnetite was prepared by two methods: heterogeneous and homogeneous deposition techniques in the aqueous phase.

The synthesis of magnetite by heterogeneous precipitation was performed by Elmore [1], where was used ammonia water as precipitants. Synthesis was conducted direct and inverse way.

The synthesis of magnetite by homogeneous chemical deposition was carried out as follows. To 100 cm^3 solution (1M $FeSO_4$ in 2M HCl and 0.5M $FeCl_3$ in 2M HCl) was added 10÷150 g of crystalline urea. The resulting solution was heated to 95^{o}C and maintained for 20÷120 min. As a result took place of urea hydrolysis with the formation of ammonia water by the reaction:

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4OH + CO_2. \qquad (1)$$

Ammonia water interacted with ions of iron (II), (III) and precipitated magnetite (Fe_3O_4) according to the general reaction:

$$FeSO_4 + 2FeCl_3 + 8NH_4OH \rightarrow Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 4H_2O. \qquad (2)$$

During synthesis added 5 cm^3 of oleic acid. The choice of oleic acid (as surfactants) was carried with following reasons. Oleic acid is a commonly used surfactant to stabilize the magnetic nanoparticles with strong chemical bond between the carboxylic acid and the amorphous iron oxide nanoparticles [10].

The formed product is cooled and resulting suspension washed from ions Cl and residual oleic acid with distilled water by magnetic decantation. The presence of ions Cl tested by solution of silver nitrate ($AgNO_3$), and oleic acid – potassium permanganate ($KMnO_4$). The washed precipitate was dried at room temperature for 24 hours.

XRD and XRS analysis of samples were performed using an apparatus DRON-3M with Cu-radiation and a step scan 0.005 deg. Coercive force, specific magnetization and residual induction were measured on ballistic magnetometer of Steinberg.

Results and discussion. Conditions of obtaining magnetite samples by heterogeneous deposition are shown in Table 1, and produced by homogeneous deposition – in Table 2. All the samples were assayed on the presence of magnetic properties by a permanent magnet.

Table 1

Samples of magnetite obtained by heterogeneous chemical deposition

The sample	The precipitant	Type deposition	Magnetic properties
Sample 1´	concentrated NH_4OH	Direct	+
Sample 2´	concentrated NH_4OH	Inverse	+
Sample 3´	1 M NH_4OH	Direct	-
Sample 4´	1 M NH_4OH	Inverse	-

As seen from Table 1, the samples 1´ and 2´ have magnetic properties, samples 3´ and 4´ have not magnetic properties. These results are consistent with literature data according to which the formation of magnetite occurs when excess hydroxide ions is at least 1.5 times [1].

Among samples of magnetite induced in Table 2, magnetic properties possessed by all the samples except sample 1. Additionally sample 2 had poorly expressed magnetic properties; sample 3 was not technological by forming a gel upon cooling of the reaction mixture after synthesis.

Table 2

Samples of magnetite obtained by homogeneous chemical deposition

The sample	The urea mass, g/100 cm^3	The synthesis duration, min.	Magnetic properties
Sample 1	10 г	20	-
Sample 2	100	20	+ (poorly)
Sample 3	150	20	+
Sample 4	125	20	+
Sample 5	125	40	+
Sample 6	125	80	+
Sample 7	125	100	+
Sample 8	125	120	+

On Fig. 1 shows the diffraction patterns of samples 1´, 2´, 4÷8. According to given diffraction patterns in all samples magnetite and hematite phases are present.

The phase composition and crystallite size for all magnetite samples shows in Table 3. The crystallite size of magnetite samples 1´ and 2´ varies in the range 20÷25 nm and samples 4÷8 – 27÷40 nm. The highest content of magnetite phase was achieved with using homogeneous chemical deposition. At the same time, the content of magnetic phase increases with increasing of synthesis time.

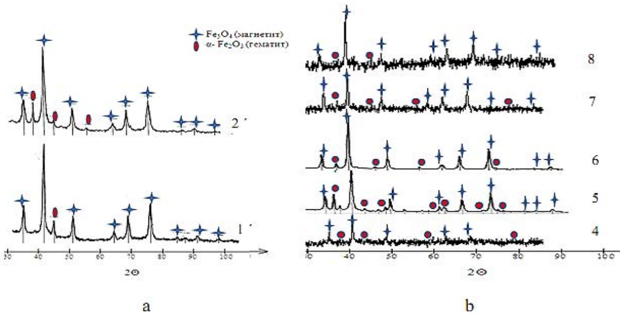

Fig. 1. Diffraction pattern the magnetite samples

Table 3

Phase composition and crystallite size of the magnetite samples

The sample	Phase composition,%		The crystallite size, nm
Sample 1´	Fe_3O_4	90	25
	α- Fe_2O_3	10	40
Sample 2´	Fe_3O_4	82	20
	α- Fe_2O_3	18	33
Sample 4	Fe_3O_4	67	40
	α- Fe_2O_3	33	55
Sample 5	Fe_3O_4	80	40
	α- Fe_2O_3	20	70
Sample 6	Fe_3O_4	94	40
	α- Fe_2O_3	6	130
Sample 7	Fe_3O_4	95	31
	α- Fe_2O_3	5	110
Sample 8	Fe_3O_4	96	27
	α- Fe_2O_3	4	100

Figure 2 shows the dependence of specific magnetization from tension of magnetic field for samples magnetite 1´, 2´, 4, 5, 6, 8. As seen in Fig. 2 and Table 3, the magnetic properties of magnetite samples depend not only on their phase composition, but also the crystallite size of the magnetic component.

Reduction and stabilization of particle size (crystallites) is achieved by introducing an oleic acid.

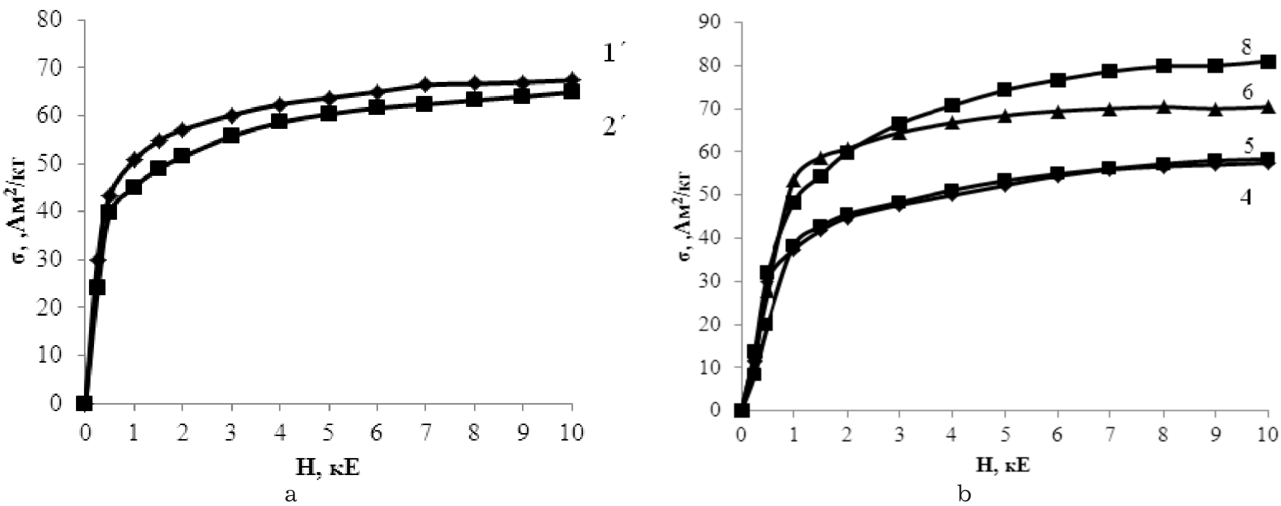

Fig. 2. The dependence of specific magnetization from tension of magnetic field for samples magnetite: a – heterogeneous and b – homogeneous deposition precipitation

However, the addition of oleic acid and its adsorption on the surfaces magnetite particle leads to a reduction in the magnetic properties. Figure 3 shows the dependence of specific magnetization from tension of magnetic field for samples magnetite unstabilized (samples 8) and with stabilized (samples 8*).

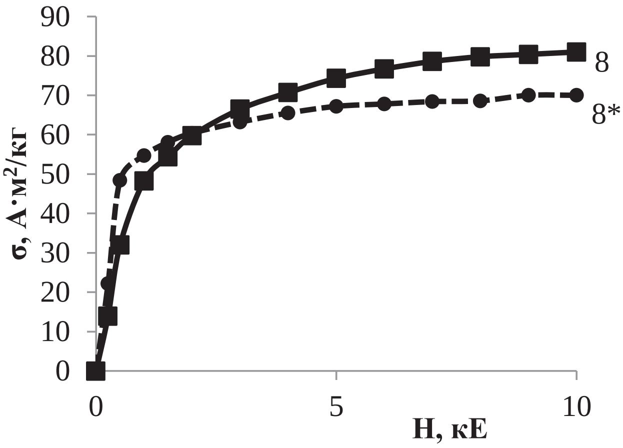

Fig. 3. The dependence of specific magnetization from tension of magnetic field for stabilized and unstabilized magnetite

Table 4

The basic magnetic properties of the synthesized magnetite samples

The sample	The method	σS, А·м²/кг	Hc, E	Br, Гс
Sample 1´	Heterogeneous deposition (direct)	67,4	25	251,5
Sample 2´	Heterogeneous deposition (inverse)	64,9	10	63,5
Sample 4	Homogeneous deposition	57,4	75	308
Sample 5		58,3	135	460
Sample 6		70,4	100	503
Sample 8		81	80	546,5
Sample 8*	Homogeneous deposition with stabilizer	70	2	22,6

Table 4 presents the basic magnetic properties of the samples 1´, 2´, 4, 5, 6, 8 and 8*. Magnetic properties of the samples there are different, that gives the basis their relating to various types magnetic materials. Samples 5 and 6 belong to hard magnetic materials, samples 1´, 2´, 4, 8 relate to average magnetic materials, and sample 8* is almost magnetically soft materials. The obtained results for all samples by magnetic properties correspond to data of X-ray diffraction and X-ray analysis.

The stable ferromagnetic fluid was synthesized using method of homogeneous chemical deposition according to the scheme in Fig 4. Magnetic fluid was stable for 2 months (continues observation until now).

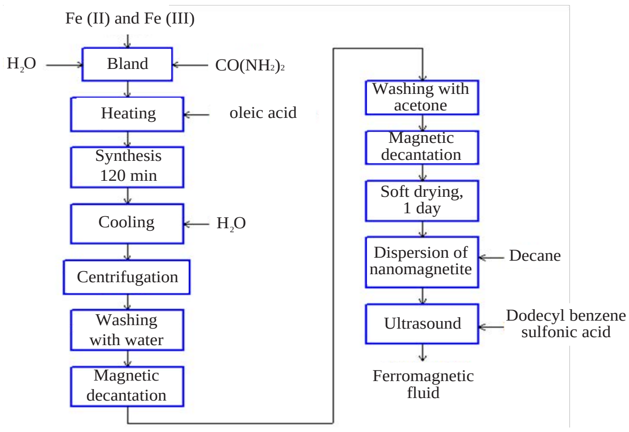

Fig. 4. The proposed scheme for obtaining a magnetic fluid using homogeneous chemical deposition

Conclusions. The use of the homogeneous precipitation method allows obtaining magnetite with the magnetic properties at 17% higher than the use of the traditional heterogeneous magnetite precipitation. Thus, this method can obtained chemically stable magnetite nanoparticles with high magnetic properties for build on their base magnetic fluid.

Preparation of a magnetic fluid using a homogeneous chemical deposition allows realizing the synthesis of magnetite and its stabilization in one step. It has been shown that the stabilization of the magnetic particles insignificantly reduces the magnetic properties of the magnetite particles and translates from the hard magnetic in soft magnetic materials.

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СИНТЕЗ МАГНЕТИТУ ГОМОГЕННИМ ХІМІЧНИМ ОСАДЖЕННЯМ ДЛЯ ПРИГОТУВАННЯ НА ЙОГО ОСНОВІ МАГНІТНОЇ РІДИНИ

Анотація
Проведено синтез магнетиту методами гетерогенного і гомогенного хімічного осадження. Досліджено фазовий склад отриманих зразків та їх магнітні властивості. Виявлено, що методом гомогенного хімічного осадження синтезується магнетит з більш високими магнітними характеристиками, ніж методом гетерогенного осадження. Показано, що методом гомогенного хімічного осадження можливо проведення синтезу та стабілізації магнетиту в одну стадію.
Ключові слова: Гомогенне хімічне осадження, магнетит, наночастинки, стабілізатор, олеїнова кислота, магнітна рідина.

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СИНТЕЗ МАГНЕТИТА ГОМОГЕННЫМ ХИМИЧЕСКИМ ОСАЖДЕНИЕМ ДЛЯ ПРИГОТОВЛЕНИЯ НА ЕГО ОСНОВЕ МАГНИТНОЙ ЖИДКОСТИ

Аннотация
Проведен синтез магнетита методами гетерогенного и гомогенного химического осаждения. Исследованы фазовый состав и магнитные свойства полученных образцов. Выявлено, что методом гомогенного химического осаждения синтезируется магнетит с более высокими магнитными характеристиками, чем методом гетерогенного осаждения. Показано, что методом гомогенного химического осаждения возможно проведение синтеза и стабилизации магнетита в одну стадию.
Ключевые слова: Гомогенное химическое осаждение, магнетит, наночастицы, стабилизатор, олеиновая кислота, магнитная жидкость.