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## Ferromagnetic Nanopowder Iron-Based Materials Synthesized from Iron Citrates for Medical Purposes

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In recent years, magnetic composite nanosize powder materials are increasingly used in medicine as a magnetic base for the transfer of a number of drugs. The undoubted advantage of using such composite medical systems is the maintenance of an appropriate level of local concentrations of therapeutic drugs in the affected area under conditions of a significant reduction in the volume of their total dosage and a reduction in side effects on the human body as a whole. As established, the method of low-temperature (350–400°C) decomposition/reduction of citrate salts in hydrogen medium allows obtaining nanosize ferromagnetic  $\alpha$ -Fe powder with a specific surface area of 31.4 m<sup>2</sup>/g. High specific surface area and magnetic characteristics allow us to recommend ferromagnetic  $\alpha$ -Fe powder as a magnetic base for the development of composite medical materials.

Останніми роками дедалі більше застосування у медицині в якості магнетної основи для перенесення низки лікарських препаратів знаходять магнетні композиційні нанорозмірні порошкові матеріали. Безперечною перевагою використання таких композиційних лікарських систем є підтримання належного рівня локальних концентрацій терапевтичних препаратів у зоні ураження за умов істотного пониження обсягу загального дозування їх і зменшення ефектів побічної дії на організм людини у цілому. В роботі встановлено, що методом низькотемпературного (350–400°C) розкладання/відновлення солей цитратів у середовищі водню одержано ферромагнетний нанодисперсний порошок  $\alpha$ -Fe з

питомою поверхнею у 31,4 м<sup>2</sup>/г. Високі питома поверхня та магнетні характеристики уможливають рекомендувати ферромагнетний порошок  $\alpha$ -Fe в якості магнетної основи для створення композиційних матеріалів медичного призначення.

**Key words:** ferromagnetic nanopowders, magnetic nanosize powder materials, composite medical systems, biologically active agents.

**Ключові слова:** ферромагнетні нанопорошки, магнетні нанорозмірні порошкові матеріали, композитні медичні системи, біологічно активні реагенти.

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## 1. INTRODUCTION

In recent years, composite magnetic nanosize powder materials are increasingly used in medicine as a magnetic base for the transfer of various drugs [1, 2]. The undoubted advantage of using such composite medical systems is the maintenance of an appropriate level of local concentrations of therapeutic drugs in the affected area under conditions of a significant reduction in the volume of their total dosage and a reduction in side effects on the human body as a whole [3].

More recent *in vivo* studies [4–6] have shown that the use of magnetic iron-based suspensions as a magnetic base for the localization and transport of chemotherapeutic agents in oncological practice provides the necessary concentration and prolonged action of drugs in the affected area.

It is known that nanosize iron particles are biologically active agents, which can activate or, conversely, suppress certain functions of vital organs, depending on their quantity, chemical composition and presence of impurities. Therefore, when a certain amount of iron powder is introduced into the body, first, it is necessary to have a clear idea of its behaviour in such bioenvironments as blood, tissues, and intercellular fluids and lymph.

The purpose of this work is to develop and produce ferromagnetic nanosize  $\alpha$ -Fe powder with a certain complex of physical and chemical properties (phase composition, high specific surface area, chemical purity) required for medical use.

## 2. MATERIALS AND METHODS

The main objects of research were iron powders with different phase compositions and sizes obtained by decomposition/reduction

of iron citrate salts under special technological conditions of synthesis.

The possibility of increasing the iron content was studied, while maintaining nanoscale size of powder is due to the use of low-temperature decomposition/reduction of citrate iron salt  $\text{Fe}_3\{\text{C}_3\text{H}_5(\text{O})(\text{COO})_3\}_2$  (instead of oxalate salts) in hydrogen atmosphere. With this aim, the processes of low-temperature iron synthesis from its citrate salts, which were decomposed with reduction in hydrogen in the temperature range of 250–450°C, were investigated. For the purposes of passivation and preservation of a high specific surface area of the powders obtained, a method for passivation of the surface of iron powder by a controlled gradual replacement of the reducing environment (hydrogen) by air for 5–8 hours was developed. In contrast to the traditional methods for the production of iron powders by thermal decomposition of iron salts [7], a combination of the methods of decomposition and reduction of iron citrate salt  $\text{Fe}_3\{\text{C}_3\text{H}_5(\text{O})(\text{COO})_3\}_2$  in a reducing hydrogen atmosphere and a modified technique for further prolonged passivation of iron powder surface by controlled substitution of protective hydrogen atmosphere with an air mixture was used.

X-ray diffraction studies of the obtained powders were carried out using a DRON-3.0 x-ray diffractometer in  $\text{CoK}_\alpha$  radiation. The dimensions of the coherent scattering regions ( $D_{\text{csr}}$ ) and, in particular, their diameters were calculated by line broadening in the diffractograms using the Scherrer equation [8].

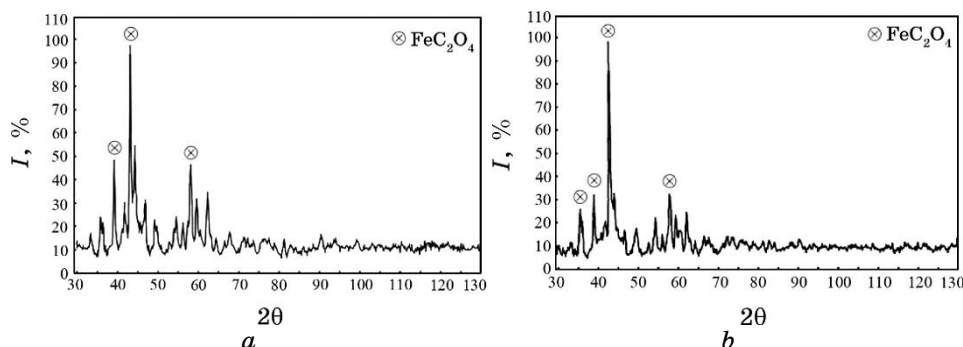
The magnetic characteristics of the powders (specific saturation magnetization  $\sigma_s$ , residual induction  $B_r$ , coercive force  $H_c$ ) were measured using a ballistic magnetometer in the fields up to 800 kA/m at room temperature [9].

Electron microscopy of the obtained powders was carried out at a scanning electron microscope JSM 6360 LA equipped with EDS microanalysis system JED-2200 with an accelerating voltage of 15 kV and an electron probe diameter of 4 nm.

### 3. RESULTS AND DISCUSSION

To monitor the phase composition and the powder size, the samples were examined after synthesis at temperatures of 250, 300, 325, 400, and 450°C. The temperature interval of 50°C was chosen with aim to accurately select and optimize the synthesis conditions for nanoscale iron powders, which (by their size, particle morphology, and phase and chemical compositions) could be used for medical purposes.

According to the x-ray phase analysis of the powders obtained in the temperature range of 250–450°C by decomposition/reduction of



**Fig. 1.** X-ray diffractograms of powders obtained by decomposition–reduction of iron citrate salt at temperatures: *a*—250°C; *b*—300°C.

citrate salts in hydrogen, the powders synthesized at 250 and 300°C contain only crystalline phase of iron oxycarbide  $\text{FeC}_2\text{O}_4$  (Fig. 1).

An increase in the synthesis temperature up to 350°C led to a decrease of the amount of crystalline phase of iron oxycarbide  $\text{FeC}_2\text{O}_4$  (Fig. 2).

According to x-ray diffraction analysis, the powders synthesized at 400 and 450°C consist only of the  $\alpha$ -Fe crystalline phase (Fig. 3).

The obtained data indicate that the amount of oxycarbide phase  $\text{FeC}_2\text{O}_4$  is decreased, whereas the amount of  $\alpha$ -Fe phase is increased with the synthesis temperature; this is explained by the intensification of diffuse processes that lead to the formation of the mentioned crystalline phases (Table 1).

The specific surface area of the powders synthesized at different temperatures was determined by the gas chromatography method using thermal desorption of nitrogen [10].

As can be seen from the data obtained (Table 2), the specific surface area of the powders is increased with increasing decomposition temperature with the formation of several phases and is decreased insignificantly with the transition to a single-phase system at 400 and 450°C.

The dependence of the specific magnetization of powders obtained by decomposition/reduction of iron citrate salts at the temperatures of 250, 300, 325, 400, and 450°C on the magnetic field strength is shown in Fig. 4.

The obtained curves have the shape peculiar to the ferromagnetic materials, with the exception of powders synthesized at 250 and 300°C (Fig. 4, curves 2 and 3) which do not contain ferromagnetic phases. It should be noted that, as the synthesis temperature increases, the curves of the specific magnetization shift to higher absolute values (that also corresponds to an increase in the specific

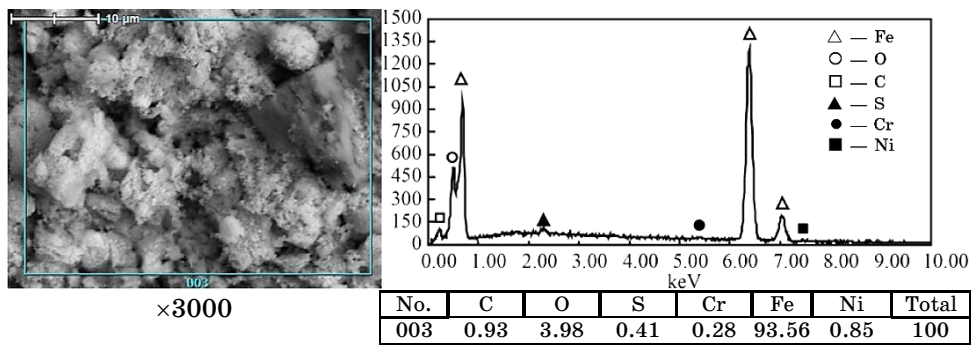


Fig. 2. Micrographs and chemical composition at randomly chosen areas of a sample of iron powder obtained by synthesis from iron citrate salts at 350°C (×3000).

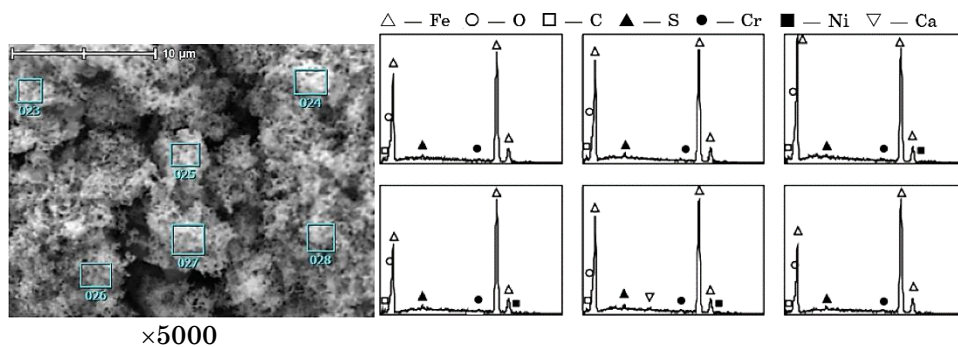


Fig. 3. Micrographs and chemical composition at randomly chosen areas of a sample of iron powder obtained by synthesis from iron citrate salts at 450°C (×5000).

magnetization of the powders).

This experimental fact fully agrees with the results of x-ray phase analysis, and it is explained by the increasing amount of the ferromagnetic phase in powders with the synthesis temperature (Table 1). It was shown that an increase in the synthesis temperature also leads to an increase in the level of residual induction  $B_r$  (Table 3) due to the same reasons [11]. The coercive force  $H_c$  associated with the particle size of the powders is increased to a synthesis temperature of 350°C ( $D_{csr} = 150$  nm) and is reached a maximum value of 120 Oe; at 400°C, with an insignificant increase in the particle size ( $D_{csr} = 180$  nm), it began to decrease (65 Oe). The residual induction  $B_r$  was the highest at 400°C, when the system is consisted only of nanosize particles of  $\alpha$ -Fe.

With further increase of the synthesis temperature up to 450°C,

**TABLE 1.** Phase composition and size of the coherent scattering (Dock) regions ( $D_{\text{csr}}$ ) of powders obtained by synthesis of iron citrates.

Synthesis regime (in the course of 2 h)	Phase composition, wt. %	Phase fraction, %	$D_{\text{csr}}$ , nm
250°C	FeC <sub>2</sub> O <sub>4</sub>	100	50
300°C	FeC <sub>2</sub> O <sub>4</sub>	100	50
325°C	FeC <sub>2</sub> O <sub>4</sub>	70	60
	$\alpha$ -Fe	10	50
	Fe <sub>3</sub> O <sub>4</sub>	20	—
350°C	$\alpha$ -Fe	98	150
	Fe <sub>3</sub> O <sub>4</sub>	2	—
400°C	$\alpha$ -Fe	100	180
450°C	$\alpha$ -Fe	100	1100

**TABLE 2.** Dependence of the specific surface area of iron powders on the synthesis temperature.

Temperature, °C	250	300	325	350	400	450
Specific surface area, m <sup>2</sup> /g	9.88	15.07	28.0	30.8	31.4	30.7

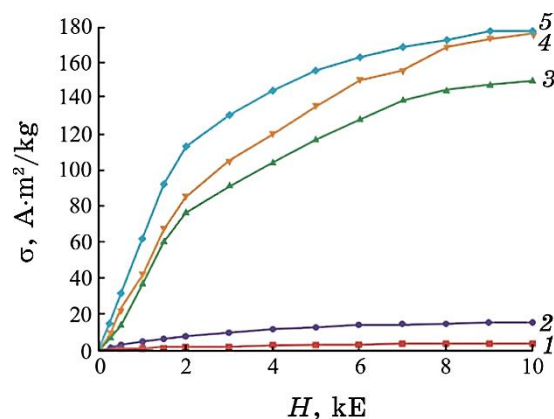
the specific magnetization  $\sigma_s$  and the residual induction  $B_r$  of synthesized powders associated with the content of the ferromagnetic phase remain practically unchanged, and the coercive force  $H_c$  continues to decrease due to the increase in the particle size. Thus, the powder obtained at 400°C had the highest magnetic properties (Table 3).

The nanosize iron powder synthesized at 400°C consists of ferromagnetic  $\alpha$ -Fe phase, has an optimum specific surface of 31.7 m<sup>2</sup>/g and high magnetic characteristics ( $\sigma_s = 177.6$  A·m<sup>2</sup>/kg,  $H_c = 100$  Oe,  $B_r = 1522$  G). It is a promising powder material for using in the chemical industry, medicine, and food industry.

#### 4. CONCLUSION

It is proved that the low-temperature decomposition of iron citrate salt  $\text{Fe}_3\{\text{C}_3\text{H}_5(\text{O})(\text{COO})_3\}_2$  in reducing hydrogen atmosphere under certain technological conditions allows to obtain nanosize iron powder. During the synthesis of powders in the temperature range of 250–450°C, the amount of ferromagnetic  $\alpha$ -Fe phase increases with temperature.

According to x-ray phase analysis, the powders synthesized at 350, 400, and 450°C consist only of the crystalline  $\alpha$ -Fe phase. Synthesis of iron powders at higher temperatures leads to an increase



**Fig. 4.** Dependence of the specific magnetization of powders obtained by the synthesis of iron citrate salts on the magnetic-field strength at temperatures [°C]: 1—250; 2—300; 3—325; 4—400; 5—450.

**TABLE 3.** Magnetic properties of powders obtained by decomposition–reduction of iron citrates.

Synthesis regime (during 2 h)	$\sigma_s$ , A·m <sup>2</sup> /kg	$H_c$ , Oe	$B_r$ , G
250°C	0.5	—	—
300°C	4.1	—	—
325°C	15.8	20	58.8
350°C	150	120	666
400°C	177.6	100	1522
450°C	179.6	65	1599

in their specific magnetization and residual induction due to an increase in the amount of ferromagnetic  $\alpha$ -Fe phase.

It is found that a low-temperature (400°C) decomposition–reduction of citrate salts in hydrogen atmosphere allows obtaining ferromagnetic nanosize  $\alpha$ -Fe powder with a specific surface area of 31.4 m<sup>2</sup>/g. High specific surface area and magnetic characteristics allow us to recommend the ferromagnetic  $\alpha$ -Fe powder as a magnetic base for composite materials for medical applications.

## REFERENCES

1. Y. Shi, Y. Xing, S. Deng, B. Zhao, Y. Fu, and Z. Liu, *Chem. Phys. Lett.*, **753**: Article 137600 (2020); doi:10.1016/j.cplett.2020.137600
2. V. F. Cardoso, A. Francesko, C. Ribeiro, M. Banobre-Lopez, P. Martins, and S. Lanceros-Mendez, *Adv. Healthc. Mater.*, **7**: 1700845 (2017); doi:10.1002/adhm.201700845

3. *Nanotekhnologiya v Blizhaishem Desyatiletii. Prognoz Napravleniya Issledovaniy* [Nanotechnology in the Next Decade. Research Direction Forecast] (Eds. M. C. Roco, R. S. Williams, and P. Alivisatos) (Moscow: Mir: 2002) (Russian translation).
4. Is Fatimah, Ganjar Fadillah, and Septian P. Yudha, *Arab. J. of Chem.*, **14**, Iss. 8: 103301 (2021); <https://doi.org/10.1016/j.arabjc.2021.103301>
5. S. Andreas, M. Lubbe, C. Alexiou, and C. Bergemann, *Journal of Surgical Research*, **95**, No. 2: 200 (2001); <https://doi.org/10.1006/jsre.2000.6030>
6. P. Singh and C. Upadhyay, *J. Magn. Magn. Mater.*, **458**: 39 (2018); [doi:10.1016/j.jmmm.2018.02.075](https://doi.org/10.1016/j.jmmm.2018.02.075)
7. B. Shapiro, R. Probst, H. Potts, D. Diver, and A. Lubbe, *Proceeding of 46<sup>th</sup> IEEE Conference on Decision and Control* (New Orleans, LA: 2007), p. 3.
8. M. Rabiei, A. Palevicius, A. Monshi, S. Nasiri, A. Vilkauskas, and G. Janusas, *Nanomaterials (Basel)*, **10**, No. 9: 1627 (2020); [doi:10.3390/nano10091627](https://doi.org/10.3390/nano10091627)
9. Fausto Fiorillo, *Metrologia*, **47**, No. 2: S114 (2010); [doi:10.1088/0026-1394/47/2/S11](https://doi.org/10.1088/0026-1394/47/2/S11)
10. N. D. Zvezdina, L. E. Martynova, and K. A. Zvezdin, *Nanotekhnika*, **2**, No. 10: 33 (2007) (in Russian).
11. O. V. Tolochko, D.-V. Lee, C.-J. Choi, D. Kim, and Mohammad Arif, *Pis'ma v ZhTF*, **31**, Iss. 18: 30 (2005) (in Russian); <http://www.journals4free.com/link.jsp?l=15091549>