ВЛИЯНИЕ ДИСПЕРСИОННОЙ СРЕДЫ НА ПРОЦЕССЫ МЕХАНОХИМИЧЕСКОГО ОКИСЛЕНИЯ ЖЕЛЕЗА

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В теоретической части работы выполнен обзор способов получения оксидов железа, в частности, рассмотрены особенности методов осаждения из растворов, термического разложения солей железа и механохимического синтеза. В экспериментальной части работы с помощью методов рентгенофазового, рентгеноструктурного и синхронного термического анализа, мессбауэровской и ИК-спектроскопии, а также комплекса химических методов исследован процесс механохимического окисления крупнодисперсных порошков железа и чугуна. Показана возможность получения оксидов железа различного состава путем механической активации порошка железа марки ПЖР и чугуна марки СЧ 12-28 в ролико-кольцевой вибрационной мельнице в среде технического кислорода, паро-кислородной смеси с соотношением пар:газ=0,45, воды и растворов щавелевой кислоты концентрацией 5-30%. В работе приведены данные по фазовому составу получаемых продуктов на стадиях механической активации и термической обработки. Определены оптимальные параметры технологических процессов: время механической активации, температура и длительность термической обработки. Установлено влияние состава жидкой и газовой фаз на скорость и степень превращения железосодержащих порошков в оксиды. Проведен сравнительный анализ различных вариантов технологического процесса, на основе которого сделан вывод, что наиболее эффективным окислителем металлических порошков является 25%-ная щавелевая кислота. Использование этого окислителя позволяет, изменяя температуру термообработки от 240 до 450 °C, получать анионно-модифицированные оксиды железа с площадью поверхности от 70 до 120 м²/г, что на порядок выше, чем у оксидов, полученных по промышленной технологии, основанной на методах осаждения и термического разложения солей.

Ключевые слова: оксиды железа, механохимическое окисление, порошок железа, порошок чугуна, фазовый состав

INFLUENCE OF DISPERSION MEDIUM ON PROCESSES OF MECHANOCHEMICAL OXIDATION OF IRON

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The theoretical part of this paper is devoted to a review of the methods of iron oxides obtaining. In particular, features of methods of sedimentation from solutions, thermal decomposition of iron salts and mechanochemical synthesis are considered. In the experimental part of the paper the process of mechanochemical oxidation of coarse-dispersed iron and cast iron powders was studied using X-ray diffraction and synchronous thermal analysis, Mossbauer and IR-spectroscopies and a complex of chemical methods. The possibility of obtaining iron oxides with various structures by the mechanical activation of iron powder of PZhR grade and cast iron powder of SCh 12-28 grade in a roller-ring vibrating mill in the environment of technical oxygen, vapour-oxygen mixture with the vapour:gas ratio of 0.45, water and oxalic acid solutions with concentrations from 5 to 30% is shown. Data on phase structure of the products received in stages of mechanical activation and heat treatment are given. Optimal parameters of technological processes, among of which the time of mechanical activation, temperature and duration of a heat treatment, are determined. Influence of composition of fluid and gas phases on the rate and coefficient of conversion of ferriferous powders into oxides is established. The comparative analysis of various options of technological process is carried out. On its basis it is established that the most efficient oxidizer of metal powders is the 25% oxalic acid. Using this oxidizer and changing in a temperature of heat treatment from 240 to 450 °C it is possible to obtain anionically modified iron oxides with the specific surface area from 70 to 120 m^2/g that is 10 times more than that of iron oxides received by industrial technology based on the methods of sedimentation and thermal decomposition of salts.

Key words: iron oxides, mechanochemical oxidation, iron powder, cast iron powder, phase composition

INTRODUCTION

Presently iron oxides are one of the most widespread powder materials which are widely used by production of inorganic pigments and fillers, magnetic data carriers, catalysts and sorbents [1-7].

The most common methods of receiving disperse systems like hydroxides, oxyhydroxides and oxides of iron (III) are oxidation of compounds of iron (II) and hydrolysis of compounds of iron (III) [5-9].

Hydroxides, nitrates, carbonates, sulfates, alcoholates, oxalates and other iron compounds are used

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as raw materials for receiving iron oxides by thermal decomposition [7, 10-15]. The method of magnetite obtaining by joint annealing of powder mixture of metal iron and hematite (α-Fe₂O₃) at a temperature of 740-840°C with further cooling in the closed volume and inert environment and crushing of the received mixture is described in the patent [16]. Authors of work [17] suggest to synthesize ferrous oxide with controlled fractal dimension of a surface. This method is based on thermal decomposition of a product of ferrous-ammonium oxalate dehydrofreezing. Microwave synthesis is one of the heat treatment methods. The possibility of γ-Fe₂O₃ obtaining from ferrous nitrate both in the process of microwave influence and its combination with low-temperature processing is shown in the work [18].

Methods of sedimentation are based on liberation of iron compounds from water solutions of insoluble salts in the form of hydroxides, carbonates, hydrocarbonates with their further thermal decomposition [5, 8, 19-24]. The technology can be presented schematically as follows:

iron salt + precipitant → precipitate → precipitation ageing → flushing → drying → calcination

Sulfate or nitrate of iron are preferable raw materials for precipitation [19-22, 24-30]. Initial reagents for oxidic catalysts manufacturing should be available, well soluble in water and they must not contain harmful impurities. For example, iron chlorides and sulfates are avoided in catalysts production since chlorides and sulfates are poisons for the majority of catalysts. Presence of sodium is also undesirable as far as it may cause agglomeration of an end-product [25].

Ammonium, sodium and potassium hydroxides are usually used as precipitators. Ammonium and sodium carbonates are widely used as well. There are data on application for iron precipitation using gaseous ammonia which is bubbled through its salt solution [19-22, 24-31].

Authors of work [31] offered the method of iron oxides obtaining that is based on interaction of metal iron in the form of microspherical particles, scrap or cuttings with carbonic acids solutions up to formation of iron carboxylats and their thermal decomposition at 200-350 °C. The article [32] is devoted to the obtaining of iron oxide of high purity using technogenic raw materials by the method of liquid extraction.

Iron compounds are also found in nature. For example mineral ferrichydrate [33-35] is a natural oxohydroxide and its stoichiometric formula is Fe₅HO₈·4H₂O [33, 36]. The samples of a synthetic ferrichydrate are described in the literature [33, 34, 37, 38]. The size of

a two-way ferrichydrate is 1.6-2.0 nm, its specific surface area is 300-400 m²/g. Due to the nanodimension of ferrichydrate crystallites and their high specific surface area the special catalytic characteristics in comparison with well crystallized iron oxides such as hematite and getit (α-FeOOH) are expected. Unique properties of this compound open up the prospects of its use in catalysis. Instability of ferrichydrate limits its application [33, 34].

New, alternative methods of iron oxides obtaining are of great interest presently. One of them is mechanochemical synthesis (MCS). Mechanical treatment, as it is shown in the work [39], of Fe and Fe₂O₃ mixture in planetary-centrifugal mill leads to formation of a nanocrystal wustite with nonequilibrium structure Fe₀,₈₇O. Its further thermal decomposition in vacuum at 200 °C allows nanodimensional composite Fe/Fe₃O₄ to be received. In the article [40] the oxidation of powder of pentacarbonyl iron in water using planetary-centrifugal mill is considered.

MCS as a the method of obtaining oxidic materials allows to avoid pollution of a product to be synthesized, to reduce the number of power-intensive stages, to combine stages and to provide high economy of the technological process. Besides, the MCS makes it possible not to use solvents or use them in the minimum quantity that significantly simplifies ecological problems of chemical productions [41-45].

The purpose of the work is to research processes of mechanochemical synthesis of iron oxides from coarse dispersed powders of metal iron and cast iron in the roller-ring vibrating mill of average power tension using gaseous and liquid oxidizers. This requires researching of the physicochemical processes that occur when powder of metal iron is to be mechanochemical oxidized (MCO) and clarification of influence of the used oxidizer on the structure of obtained product.

MATERIALS AND METHODS

Coarse dispersed iron powders (IP) grade PZhR-3.450.26 with particle size up to 630 μm and cast iron powders (CIP) grade SCh 12-28 with particle size up to 1250 μm were used as the raw materials for obtaining iron oxides.

Mechanochemical oxidation using various oxidizers was carried out in the roller-ring vibrating mill VM-4. Roller and ring made of chemically resistant steel grade ShH15 were used as the grinding bodies. Their total mass is 1194 g and the mass of the material to be activated is 100 g.

MCO of metal powders in the oxygen and vapour-oxygen environment was carried out using special

facility (Fig. 1). The reactionary glass (8) of vibrating mill (7) is filled up with ferriferous powder. Oxygen or vapour-oxigen mixture made up by bubbling oxygen (1) through water (6) is fed through unions in reactor cover. Temperatures in the reactor and in the bubbler are registered with multifunctional temperature registrar and are brought to the personal computer display.
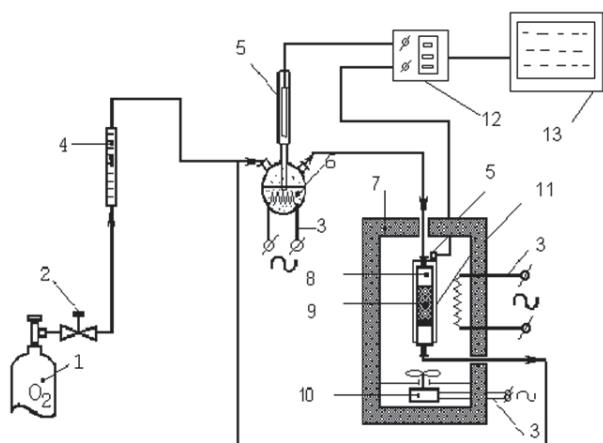

Fig. 1. Scheme of device for MCO of metal powders: 1 - balloon (O_2); 2 - valve; 3 - heating element; 4 - rotameter; 5 - thermometer; 6 - bubbler; 7 - vibration mill; 8 - reactor; 9 - sample; 10 - fan; 11 - thermal jacket; 12 - multifunctional temperature meter; 13 - PC
Рис. 1. Схема установки для МХО порошков металлов: 1 – баллон (O_2); 2 - вентиль; 3 - нагревательный элемент; 4 - ротаметр; 5 - термометры; 6 - барботер; 7 - вибромельница; 8 - реактор; 9 - образец; 10 - вентилятор; 11 - тепловая рубашка; 12 - многофункциональный регистратор температур; 13 - ПК

Gaseous oxygen with the flow of 15 ml/min, vapour-oxygen mixture with the vapour:gas ratio of 0.45, distilled water and oxalic acid solution with concentration of 5-30 mass % were used as oxidizing mediums.

The X-ray diffraction phase analysis (XRD) was carried out using diffractometer DRON-3M with Cu Kα – radiation ($\lambda = 0.15406$ nm, the Ni-filter). XRD analyzes data were identified with the help of Mincryst database. Broadening of X-ray diffraction profile allows to define how the area of coherent dispersion (ACD) and value of mean square microdeformations changes. Thermogravimetric analysis of mechanical activation products was carried out using synchronous thermal analysis facility STA 449 F3 Jupiter in the atmosphere of Ar-O_2 with heat rate of 5 °С·мин$^{-1}$. The composition of the obtained oxides and content of metal iron were determined by the method of differentiating dissolution that based on selective dissolution of iron from oxides mixture [46] and by the method of Mossbauer spectroscopy [47] that was executed using the YaGRS-4M spectrometer that was working in the permanent accelerations mode with the use of γ-radiation 57Co in Cr matrix at the room temperature.

The X-ray photoelectronic spectroscopy was chosen as the researching method of samples surface that was executed using ES-2403 facility with 5-channel energy analyzer PHOIBOS-100. The samples specific surface area was determined by the BET method using Sorbi MS device. The laser analysis of particle distribution by the sizes was carried out on the Analysette 22 Laser-Partikel-Sizer device that is the universal instrument for establishing particle dispersion of solids in liquid, gas (suspension, aerosol) or emulsion. The particle distribution of coarse dispersed powders was determined by the sieve method. IR spectra of powder materials were received using facility called Avatar 360 FT – IR ESP with wave number range of 400-4000 cm^{-1}. Powder to be analyzed was used in the form of tablets with potassium bromide. The element analysis was carried out with FlashEA 1112 CHNS-O Analyzer device. The amount of the brought energy in the course of the MA was calculated by the technique stated in work [48].

RESULTS AND THEIR DISCUSSION

1. *Mechanochemical oxidation of IP and CIP by oxygen*

Laser and sieve analyzes (Tab. 1) shown that cast iron predominantly consists of coarse particles with the size up to 1250 μm and the share of particles with the size less than 50 μm makes up about 0.1%.

Table 1
Dispersed composition of CIP
Таблица 1. **Дисперсный состав ПЧ**

Activation time, min	Fraction content, %							
	<50 μm	50-71 μm	71-100 μm	100-140 μm	140-250 μm	250-315 μm	315-630 μm	630-1250 μm
0	0.1	0.2	0.1	0.2	0.9	0.5	19	79
15	4.3	10.1	16.4	21.6	46.6	0.6	0.4	0
30	22.1	23.9	14.6	19.7	19.6	0.1	0	0
45	1.5	4.3	13.2	50.9	30.1	0	0	0

As a result of the MA within 30 min the share of particles with the size less than 50 μm increases up to 22.1%. When increasing the time of mechanical treatment up to 45 min the aggregation processes are dominating and the share of particles with the size less than 50 μm decreases to 1.5%. It shows that MA processes are dissimilar i.e. not only processes of amorphicity are take place but also there is an aggregation of fine particles in large agglomerates.

Element analysis data (Tab. 2) shows that the content of sulfur in cast iron is minimal and does not exceed 0.004%. The carbon and silicon which are con-

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tained in cast iron do not impair the qualities of the future catalyst but they can improve its molding capacity. The manganese which is contained in cast iron can exert positive impact on catalytic properties [20, 49].

Table 2

Data of elemental analysis of CIP

Таблица 2. Данные элементного анализа ПЧ

Element content, %			
C	H	S	O
3.903	0.017	0.003	0.596

By results of the laser and sieve analysis it is established that IP consists of coarse particles with the size up to 630 μm. The share of particles less than 50 μm makes 0.25% (Tab. 3).

Table 3

ΔG°₂₉₈ of reaction of iron oxides formation

Таблица 3. ΔG°₂₉₈ реакции образования оксидов железа

№ of reaction	Reaction	ΔG0298, MJ/mole
1	$Fe + 1/2O_2 = FeO$	-0.244
2	$3Fe + 2O_2 = Fe_3O_4$	-1015.0
3	$4Fe + 3O_2 = 2Fe_2O_3$	-741.65
4	$4Fe_2O_3 + Fe = 3Fe_3O_4$	-0.2355

It is known that iron forms three steady oxides: wustite FeO, hematite α-Fe_2O_3 and magnetite Fe_3O_4, that is depend on production conditions, precursor and temperature. Values of Gibbs energy for reactions of formation of different iron oxides are given in Tab. 3. It is shown that formation of Fe_3O_4 is thermodynamically the most probable. Thus any of these oxides can be formed but the first two are able to turn into the third. Besides during the reaction Fe_2O_3 will be formed on a surface and will interact with metal iron, the surface of grinding bodies and reactor walls.

As a result of the MA of metal iron powder in the environment of oxygen excess within 60 min in vibrating mill gradual reduction of phase reflexes of metal iron and formation of the X-ray amorphous product are observed. Heat treatment of the product at 450 °C leads to formation of magnetite – Fe_3O_4 that is confirmed also by results of IR-spectroscopy. Intensive absorption bands in the area of 450-500 cm⁻¹ which are characteristic for metal oxides are observed.

According to chemical and X-ray phase analyses conversion coefficient of iron was evaluated. It is established that the content of metal iron phase in the course of activation of CIP decreases and makes 10% during 60 min of MA and 7% in the oxidation process of IP (Fig. 2, curve 1,2). During MCO temperature in the reactor increased up to 61°C due to the fact that reaction of iron oxidation is exothermic. Friction and blowing of grinding bodies on the reactor walls also raise the temperature (Fig. 2, curve 3). The curve 4

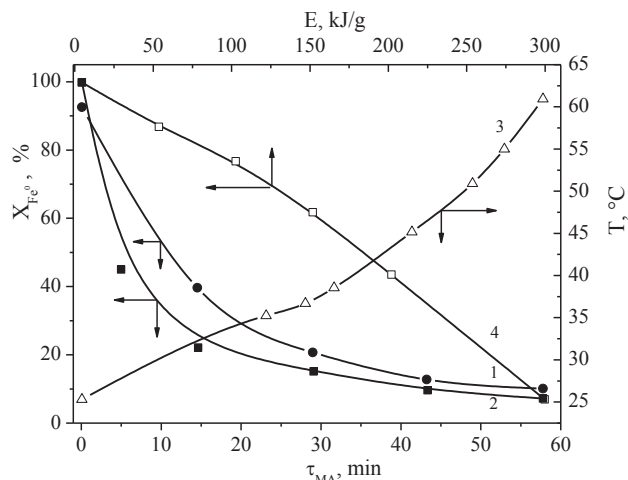shows influence of energy density on the process of oxidation of metal iron phase.

Fig. 2. Changing in temperature and content of Fe⁰ in the course of MA of CIP and IP in oxygen: 1-IP, 2-CIP, 3 - temperature line, 4 - Fe⁰ content in IP after 60 min. of MA

Рис. 2. Изменение температуры и содержания Fe⁰ в процессе МА ПЧ и ПЖ в кислороде: 1-ПЖ, 2 - ПЧ, 3 - линия температуры, 4 - содержание Fe⁰ ПЖ после 60 мин МА

Calculation of parameters of fine crystal structure shows that the sizes of CSR monotonously decrease both in case of oxidation of CIP and IP (Tab. 4). However, the sizes of CIP crystallites at bigger dispersion of initial powders have the smaller size than IP. After 5 minutes of the MA the size of CIP and IP makes 24.1 and 28.2 nm respectively. Obviously, it is connected with the fact that cast iron is more brittle material and under the influence of intensive mechanical treatment it collapses faster than iron. Also there is a growth of microdeformations of iron phase that is caused by increase of density of chaotically distributed dislocations and increase of lattice parameters connected with implementation of oxygen in it (Tab. 4).

According to the equilibrium phase diagram of the Fe-O [50] system solubility of oxygen in α-Fe does not exceed 0.1 at. %. At the same time, solubility of oxygen in the deformed iron more than 10 times exceeds its solubility in casted form [50]. Increase of the oxygen content is followed by some increase in lattice parameters of α-Fe (Tab. 4). Thus if small (0.3 at. %) amounts of the dissolved oxygen lead to reduction of lattice parameter then on the contrary increasing of its content leads to the growth of lattice parameter [51].

It is known that brittle destruction of metal materials by the intergranular mechanism is connected with a segregation of impurity on high-angle boundaries of grains which can be considered as internal adsorption [53]. Apparently the mechanism of oxygen influence is the same. At increase of its concentration in

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iron there is a transition from intragranular to intergranular break [51-53]. Thus, presence of a significant amount of oxygen facilitates process of destruction of conglomerates by the intergranular mechanism at the MA. The increase in the general oxygen content in iron connected mainly with its segregation on high-angle boundaries of grains that is followed by approximately proportional growth of its concentration in a crystal lattice as is expressed in growth of its parameters. That is at forced capture of oxygen in the course of the MA supersaturation of its segregation on the formed high-angle boundary and corresponding emergence of a thermodynamic incentive for impurity diffusion deep into the crystal lattice is possible [54,55].

Table 4

Change in structural parameters of iron in the course of the MCO of CIP and IP in oxygen
Таблица 4. **Изменение структурных параметров железа в процессе МХО ПЧ и ПЖ в кислороде**

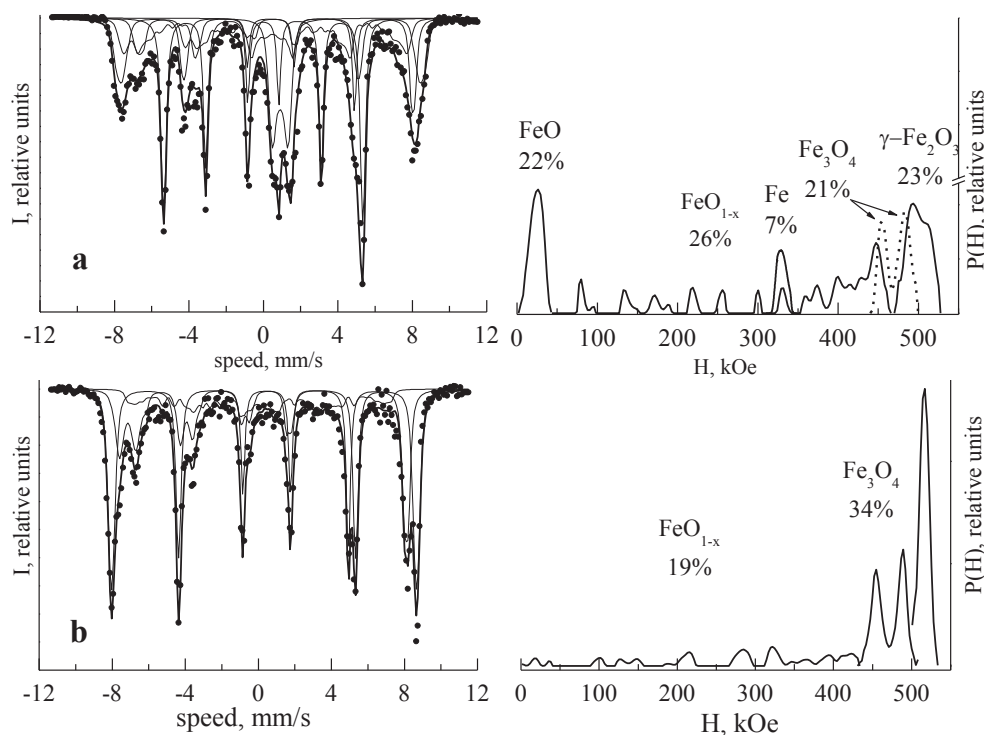| MA time, min	CIP			IP		
	Dcircle, nm	Value of microdeformations ξ, %	Lattice parameters (a, Å)	Dcircle, nm	Value of microdeformations ξ, %	Lattice parameters (a, Å)
5	24±1	0.27±0.02	2.866±0.003	28±1	0.24±0.02	2.866±0.003
15	21±1	0.28±0.02	2.872±0.003	28±1	0.25±0.02	2.881±0.003
30	20±1	0.29±0.02	2.883±0.003	25±1	0.26±0.02	2.884±0.003
45	19±1	0.31±0.02	2.886±0.003	24±1	0.27±0.02	2.889±0.003
60	18±1	0.33±0.02	2.887±0.003	23±1	0.28±0.02	2.900±0.003

Fig. 3. Mossbauer spectra of products of MCO of IP by oxygen (a) and heat treated at 450°C within 6 h at 450 °C (b)
Рис. 3. Мессбауэровские спектры продуктов МХО ПЖ кислородом (a) и подвергнутых термообработке при 450 °C в течение 6 ч при 450 °C (b)

By the method of X-ray diffraction it is impossible to divide phases of magnetite Fe_3O_4 and a maghemite γ-Fe_2O_3 as both phases have structure of spinel and close lattice parameters (8.35 and 8.39 Å for γ-Fe_2O_3 and Fe_3O_4 respectively), chemical analysis also does not give definite structure of the formed phases of oxides. Only the method of Mossbauer spectroscopy that is well proved for research of iron oxides composition allows to identify phases of γ-Fe_2O_3 and Fe_3O_4 [55-57].

The Fig. 3 a, b shows Mossbauer spectra and corresponding distribution functions of ultrafine magnetic fields of initial and subjected to heat treatment at 450 °C IP. The spectrum of heat-treated sample is simpler and contains Fe_3O_4 and α-Fe_2O_3 oxides that is match literature data [55-58] judging by parameters which are given in Tab. 5. Except these two components in Mossbauer spectra there is one more component with wide distribution of ultrafine magnetic field. This component contains 19% of Fe atoms which can

be attributed to the oxide phase with non-periodic atomic structure [40].

Mossbauer spectrum of the sample exposed to MCA before calcination is more complex and it has five components (Tab. 5). 7% Of Fe atoms are in the phase of α-Fe and the doublet according to the characteristics corresponds to FeO [55-57]. The phase of Fe₃O₄ is defined unequivocally. Also as well as in previous case there is component with wide distribution of ultrafine magnetic field (50-450 kE) in which there is about 26% of Fe atoms. It is possible to assume that this phase represents the set of clusters of not stoichiometric iron oxides. The last fifth components have parameters close to γ-Fe₂O₃.

Calcination of samples at a temperature of 450 °C within 6 h leads to full oxidation of iron metal powder in case of use of IP as raw materials. When annealing the samples prepared from CIP under the same conditions metal iron remains in composition of the product. Characteristics of the oxides received by the MCO of IP and CIP in the environment of technical oxygen are given in Tab. 6.

Table 5

Phase composition of products of MCO of IP in oxygen before and after calcination

Таблица 5. **Фазовый состав продуктов МХО ПЖ в кислороде до и после прокаливания**

Phase	Share of Fe atoms in phase (in %)	H average (kE)	Isomer	Quadrupole
Before MCO				
α-Fe	7	333	0.0	-
FeO	22	24	0.9	0.8
Fe₃O₄	21	453 and 485	0.68 and 0.32	-
γ-Fe₂O₃	23	501	0.38	-
clusters of not stoichiometric composition	26	-	-	-
After calcination in air at 450 °C				
Fe₃O₄	34	455 and 489	0.6 and 0.3	-
α-Fe₂O₃	47	518	0.36	-0.1
clusters of not stoichiometric composition	19	300	0	0

Table 6

Characteristics of oxides obtained by the MCO of IP and CIP in oxygen

Таблица 6. **Характеристики оксидов, полученных путем МХО ПЖ и ПЧ в кислороде**

Indicators	Oxidation of CIP		Oxidation of IP	
	After MCA and drying at 100 °C	After calcination at 450 °C within 6/12 h	After MCA and drying at 100 °C	After calcination at 450 °C within 6 h
Conversion coefficient of Femet in oxides, %	90±1.5	95±1.5	93±1.5	100±1.5
Residual content of Femet phase, %	10	5/0	7	0
Phase composition	Fe, FeO, Fe3O4, γ-Fe2O3, FeO1-X	Fe3O4, FeO1-X, α-Fe2O3, Fe	Fe, FeO, Fe3O4, γ-Fe2O3, FeO1-X	α-Fe2O3, Fe3O4, FeO1-X
SSA, m²/g	12.0	-	10.0	-

2. *Mechanochemical oxidation of IP and CIP by vapour-oxygen mixture*

Earlier it was mentioned that process of MHO of ferriferous powders is followed both by crushing and secondary aggregation. Accordingly, for intensification of MCA and prevention of aggregation the vapour-oxygen mixture is offered.

It is established that application in the course of the MCA the vapour-oxygen mixture as the environment under the same conditions allows to increase conversion coefficient of metal iron powder and besides optimal vapour:gas ratio is 0.45. Increase in oxidation degree is connected with the fact that the water which is adsorbed on the surface of metal iron on the one hand complicates processes of their aggregation and with another actively participates in the oxidation process. The particle size of metal iron and composition of vapour-

oxygen mixture significantly influence the oxidation process as the conducted researches show. Data on conversion coefficient of iron to oxides (Fig. 4, curves 1-2) demonstrate that at the first stage of oxidation (5-15 min) sharp recession of curves of metal iron content is observed both in the case of using IP and CIP as the raw materials.

Further increase in time of the MA leads to delay of oxidation processes. Obviously, it is connected with the fact that the minimum particle size of the iron phase is reached and aggregation processes which complicate oxidation begin to prevail. Besides, the formed reaction products interfere with diffusion of an oxidizer to the iron surface. Calculation of lattice parameters of iron showed that, as well as in the previous case, there is implementation of oxygen in crystal structure (Fig. 4, curves 3-4).
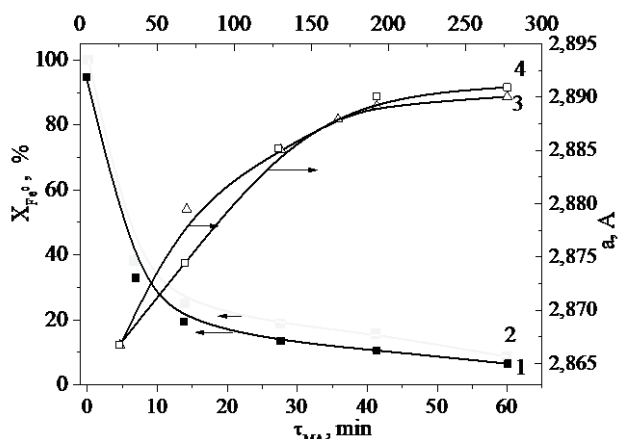
Fig. 4. Changing in iron lattice parameter and Fe^0 content in the course of MA of CIP and IP in vapour-oxygen mixture (vapour/gas=0.45) 1,3-IP, 2,4-CIP

Рис. 4. Изменение параметра решетки железа и содержания Fe^0 в процессе МА ПЧ и ПЖ в парокислородной смеси (пар/газ=0,45) 1,3-ПЖ, 2,4-ПЧ
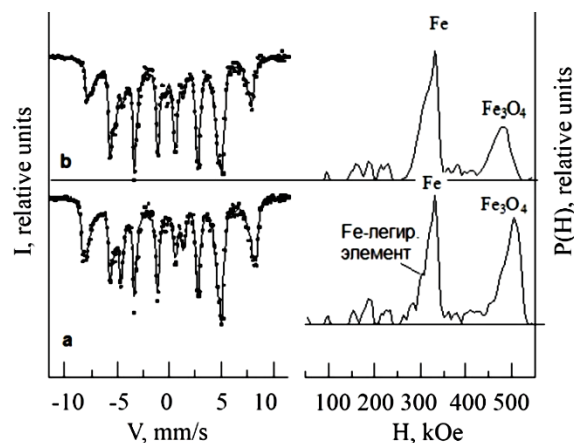

Fig. 5. Mossbauer spectra of products of MCO of CIP by water (a) and heat treated at 450 °C within 6 h (b)

Рис. 5. Мессбауэровские спектры продуктов МХО ПЧ водой (a) и подвергнутых термообработке при 450 °C в течение 6 ч (b)

3. *Mechanochemical oxidation of IP and CIP by water*

The analysis of diffractograms of coarse dispersed IP and CIP activated in water within 5, 15, 45 and 60 min shows that before heat treatment at all samples there are widened reflexes of α-Fe and magnetite Fe_3O_4. By method of the differentiating dissolution it is shown that CIP in the presence of water in roller-ring vibrating mill within 60 min of MA is oxidized by 77.6% and IP is oxidized by 88%. Mossbauer spectra of samples with the corresponding distribution functions of ultrafine magnetic fields P(H) of initial (Fig. 5a) and annealed (Fig. 5b) products of the MCO of cast iron in water are shown in Fig. 5.

The type of functions is almost identical to both spectra. Peaks position unambiguously indicates the presence in samples of pure iron (333 kE), solid component (Fe as a doping element) with 1 atom of impurity

in the immediate environment of iron atom (~307 kE), iron oxide with fields on nuclei ~ 484 kE for "a" sample and 507 kE for "b" sample. In the first sample (Fig. 5a) (with discrete processing) the component form "rest" is close to a doublet that demonstrates presence of iron clusters at a paramagnetic state and by the structure those clusters are close to hydroxides. In this phase there is 4% of iron atoms. After calcination the quantity of Fe_3O_4 makes 68%, and about 10% of Fe_2O_3 (Tab. 7) appear. Considering the quantity determination error of the phase one may say that the oxygen which is in structure of hydroxide clusters passed into Fe_2O_3.

According to researches of the chemical composition of a surface of CIP sample activated in water within 60 min carried out by the method of X-ray photoelectronic spectroscopy (Fig. 6) it is established that iron on a surface is in the α-FeOOH form that corresponds to binding energy of 711.5 eV and is consistent with the reference data [58]. As it appears from models

Table 7

Phase composition of products of MCO of CIP in water before and after calcination
Таблица 7. **Фазовый состав продуктов МХО ПЧ в воде до и после прокаливания**

Phase	Share of Fe atoms (in %)	Average magnetic field on nucleus, H (kE)	Isomeric shift, d (mm/s)	Quadrupole splitting, Δ (mm/s)
After MCA				
α-Fe	27	333	0.0	-
Fe_3O_4	62	451 and 486	0.66 and 0.30	-
solid solution	7	307	0.03	0.05
other	4	-	-	-
After calcination at 450°C				
α-Fe	15	333	0.0	-
Fe_3O_4	68	456 and 489	0.66 and 0.33	-
solid solution	7	311	0.03	0.05
α -Fe_2O_3	10	517	0.37	0.10

oxygen has not less than 3 components (Fig. 6). The states which are characterized by O1s peaks with binding energy of 530.06 and 530.9 eV belong to O^{2-} and OH^- included in FeOOH. The oxygen form with binding energy of 532.46 eV can be rather reliably carried to the water [59] connected on a surface.

Lattice parameters of α-Fe were calculated (a = 0.287 nm) on the basis of the X-ray diffraction analysis that is consistent with the literature data. The value of parameter a does not change with increasing MA duration. Based on this it is possible to draw a conclusion that unlike results of work [60] in this case there is no implementation of significant amounts of oxygen atoms and hydrogen in the iron lattice. The data obtained are consistent with the work [40]. Calculation of fine crystal structure parameters of iron showed that in the course of the MA there is a decrease in the sizes of coherent dispersion areas for the samples prepared from CIP from 28 nm after 5 min. to 24 nm after 60 min and increase in size of microdeformations from 0.22 to 0.27% for the same time of the MA. For the samples prepared from IP the size of crystallites after 60 min of the MA makes 24 nm, and the size of microdeformations makes 0.32%. The sizes of magnetite crystallites at a final stage of the MA make 22 and 19 nm for the samples prepared from cast iron and iron, respectively.
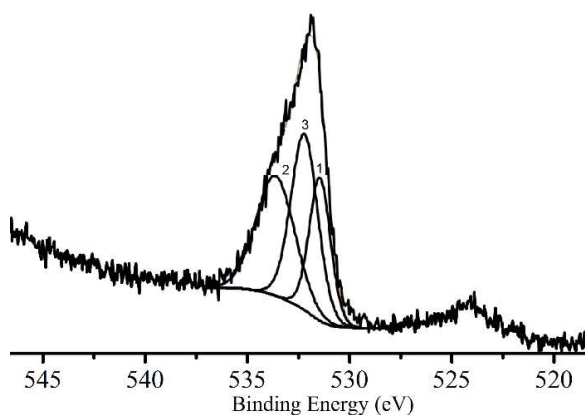

Fig. 6. X-ray photoelectronic O1s spectrum of products of MCO of CIP by water. Binding energies, eV: 1 - FeOOH-O – 530.06, 2 - O – 532.46, 3 - FeOOH-OH – 530.90
Рис. 6. Рентгенофотоэлектронный O1s спектр продуктов МХО ПЧ водой. Энергии связи, эВ: 1 - FeOOH-O - 530,06, 2 -O – 532,46, 3. FeOOH-OH – 530,90

The analysis of X-ray ray diffraction data shows that calcination of the samples prepared from cast iron at a temperature of 450 °C within 6 h leads to formation of the Fe_2O_3 phase and crystallization of magnetite and iron phases. During heat treatment of the samples prepared from IP total disappearance of reflexes of the metal iron phase and crystallization of the magnetite and hematite phases is observed. Oxidation of the samples prepared from cast iron demands more rigid conditions that is caused by presence of doping elements in it which slow down oxidation process. For full oxidation of cast iron it is necessary to increase time of heat treatment at 450 °C up to 14 h.

Calcination process is followed both by loss of weight, and its increase (Fig. 7). It is shown that the mass of the calcined sample decreases in the temperature range of 20-150 °C by 1.2% that is caused by removal of the adsorbed moisture and CO_2 adsorbed from air and further temperature increase leads to increase of mass of samples. When calcinating from 450 to 1000 °C the mass of a sample increases by 24% that it is caused by oxidation of Fe^{2+} ions which are located in magnetite, its transition to hematite and also by oxidation of metal iron. Calcination process is followed by one endothermic and one exothermic effects.
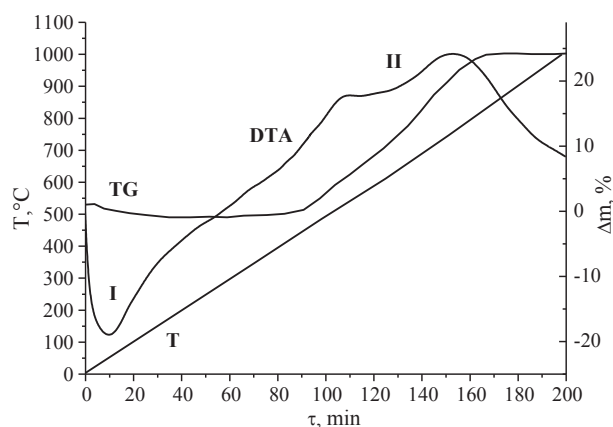

Fig. 7. Thermogram of products of MCO of CIP by water
Рис. 7. Термограмма продуктов МХО ПЧ водой

The effect I lying in the temperature range of 20-150 °C is caused by removal of the moisture adsorbed from the environment. In the temperature range of 500-1000 °C the exothermic effect II is observed that is connected with final oxidation of iron compounds. The analysis of gaseous products of decomposition by the method of IR spectroscopy shows that in the gas phase at the temperatures of 20-250 °C there is water and carbon dioxide, at the temperatures of 250-310 °C there is predominantly CO_2 which quantity sharply decreases with a further growth of temperature.
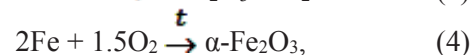
Thus it was found out that at initial stages of the MA of ferriferous powders in water there is a crushing with formation of an amorphous phase and accumulation of defects in the iron structure, along with it parallel processes of formation on a surface of iron hydroxides particles proceed according to the reaction:

$$Fe + 2H_2O \xrightarrow{MA} FeOOH + 1.5H_2 \qquad (1)$$
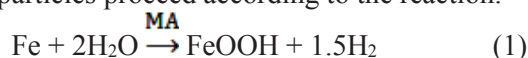
and the formation of magnetite phase

$$3Fe + 4H_2O \xrightarrow{MA} Fe_3O_4 + 8H_2, \qquad (2)$$
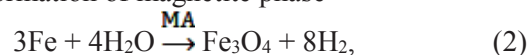
that is confirmed by the data of X-ray photoelectronic and Mossbauer spectroscopy. Heat treatment of samples leads to dehydration of hydroxides and final oxidation of metal iron phase with formation of hematite α-Fe$_2$O$_3$.

$$2FeOOH \xrightarrow{t} \alpha\text{-Fe}_2O_3 + H_2O \qquad (3)$$

$$2Fe + 1.5O_2 \xrightarrow{t} \alpha\text{-Fe}_2O_3, \qquad (4)$$
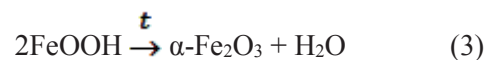
The characteristics of obtained oxides are given in Tab. 8.

Table 8

Characteristics of oxides obtained by the MCO of IP and CIP by water
Таблица 8. **Характеристики оксидов, полученных путем МХО ПЖ и ПЧ водой**

Indicators	Oxidation of CIP		Oxidation of IP	
	After MCA and drying	After calcination at 450 °C within 6/12 h	After MCA and drying	After calcination at 450 °C within 6/14 h
Conversion coefficient of Femet in oxides, %	73	85/100	88	93/100
Residual content of Femet phase, %	27	15/0	12	7/0
Phase composition	Fe, Fe$_3$O$_4$, FeOOH, solid solution Fe-doping element	Fe, α-Fe$_2$O$_3$, Fe$_3$O$_4$, solid solution Fe-doping element	Fe, Fe$_3$O$_4$, FeOOH,	Fe, α-Fe$_2$O$_3$, Fe$_3$O$_4$,
SSA, m^2/g	34	-	30	-

It should be noted that the specific surface area of the received oxides makes 30-34 m^2/g that by 2-3 times exceeds the surface of the oxides received by traditional methods of sedimentation and thermal decomposition of salts. The oxides received using this method can successfully be used for preparation of highly active iron oxide catalysts.

4. *Mechanochemical oxidation of IP and CIP by oxalic acid solutions*

Analysis of samples roentgenograms received after the MA of iron with oxalic acid solutions within 30 min. shows that when using solutions of acids with concentration of 5, 10, 15 and 20% the full oxidation of the metal iron phase does not occur both in the case of using IP and CIP. Increase in acid concentration up to 25% leads to total disappearance of characteristic re

flexes of the iron phase. As a result of interpretation of X-ray diffraction analysis data in the composition of samples iron oxalate FeC$_2$O$_4$·2H$_2$O is found. After analysis of IR spectra it should be concluded that the state of C$_2$O$_4$-groups in the compound is close to that of the chelate oxalate groups (bidentate-connected). In particular, the IR spectrum of not calcined sample shows the absorption band with frequency of 1633 cm^{-1} related to stretching vibrations of double bonds C=O. Besides on IR spectra the absorption bands with frequencies range of 1360-1317 cm^{-1} characterize valent antisymmetric and symmetric vibrations of single bonds C-O. Quite intensive bands in the area of 1009-821 cm^{-1} can be attributed to deformation vibrations of C$_2$O$_4$-group. Absorption bands in the range of 531-492 cm^{-1} are connected preferential with vibrations of Fe-O(C$_2$O$_4$). Particle size of reaction products does not exceed 18 μm (Fig. 8a).
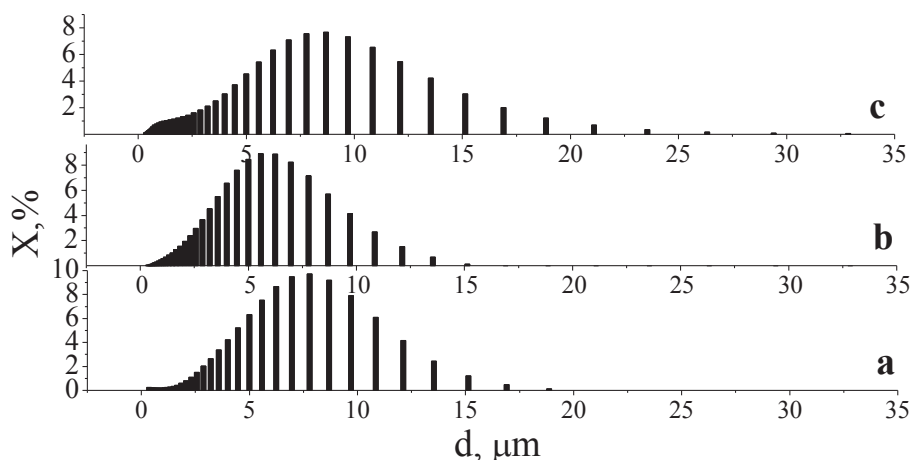

Рис. 8. Results of IP laser analysis: a – initial sample, b – sample heat treated in air at 240 °C, c - sample heat treated in air at 400 °C, d- Average particle size, μm, X - Particle fraction, %

Рис. 8. Результаты лазерного анализа ПЖ: a - исходный образец, b – образец прокаленный в среде воздуха при 240 °C, c - образец прокаленный в среде воздуха при 400 °C, d - средний размер частиц, мкм, X - доля частиц, %

Calcination of samples on air at the temperature of 240 °C within 1 h leads to formation of oxide γ-Fe_2O_3 with a particle size less than 15 μm (Fig. 8b). csr By method of the X-ray diffraction analysis it is established that the increase in calcination temperature that the CSR size of the formed oxides changes in the range from 12 to 27 nm in the temperature range of 240-450 °C, the specific surface area at the same time decreases from 120 to 70 m^2/g and the maximum size of secondary particles increases from 15 to 28 μm (Fig. 8c). Along with it recrystallization of γ-Fe_2O_3 to α-Fe_2O_3 occurs.

IR spectra of the calcined samples rather strongly change and indicate formation of the anionically modified oxides. On spectra of the samples calcined at the temperature of 450 °C the characteristic absorption band with the frequency of 1633 cm^{-1} characterizing valent vibrations of carbonate-ions is observed. Besides, there is an absorption band with the frequency of 3438 cm^{-1} characterizing existence of OH-groups.

The characteristics of obtained oxides are given in Tab. 9.

Thus, comparative analysis of different methods of iron oxides obtaining is presented in Tab. 10. The analysis of the received results shows that use of oxygen and vapour-oxygen mixture as the oxidizing atmosphere considerably complicates technological process and allows to receive iron oxides with the surface area of 10-14 m^2/g. However, heat treatment at the temperature of 450°C is necessary for minimization of impurity content in metal iron. Application of water as the dispersion medium leads to increase in quantity of metal iron phase in samples up to 12-27%. Using the aqueous solution of 25% oxalic acid in the course of Fe_2O_3 synthesis allows to carry out the thermolysis in the temperature range from 240 to 450 °C and to obtain both γ-Fe_2O_3 and α-Fe_2O_3 with the specific surface area from 70 to 120 m^2/g which is an order of magnitude greater than that of oxides obtained by the method of thermal decomposition of ferric chloride.

Table 9

Characteristics of oxides obtained by the MCO of IP and CIP by 25% solution of oxalic acid
Таблица 9. **Характеристики оксидов, полученных путем МХО ПЖ и ПЧ 25%-м раствором щавелевой кислоты**

Indicators	Oxidation of CIP		Oxidation of IP	
	After MCA and drying	After calcination	After MCA and drying	After calcination
Conversion coefficient of F_{emet} in oxides, %	100	100	100	100
Residual content of F_{emet} phase, %	0	0	0	0
SSA γ-Fe_2O_3, (Ttr = 240 °C) α-Fe_2O_3, (Ttr = 450 °C)	-	120 70	-	123 77

Table 10

Composition and characteristics of iron oxides
Таблица 10. **Состав и характеристика оксидов железа**

Oxidation medium	Raw materials							
	CIP				IP			
	MCO time, min	Femet content, %	Temperature of heat treatment, °C	SSA, m^2/g	MCO time, min	Femet content, %	Temperature of heat treatment, °C	SSA, m^2/g
Oxygen	60	10.0	450	12.0	60	7.0	450	10.0
Vapour-oxygen mixture	60	7.3	450	14.0	60	5.0	450	12
Water	60	27.0	450	24	45	12.0	450	20
25% solution of oxalic acid	30	0	240	125	30	0	240	119

CONCLUSION

In this paper the complex of researches directed to studying of physical and chemical basis of obtaining iron oxides from technogenic raw materials that are necessary for catalysts production is conducted. Besides, it was shown that iron oxides with different structure can be obtained by the MA of iron powder of PZhR grade and cast iron of 12-28 grade SCh in a vibration mill in the environment of technical oxygen, vapour-oxygen mixture with the vapour:gas ratio of 0.45, water and oxalic acid solutions with concentrations from 5 to 30%. It was established that the most effective oxidizer of metal powders is 25% oxalic acid. Using this method and changing temperature of heat treatment from 240 to 450 °C it is possible to obtain anionically modified γ-Fe_2O_3 and α-Fe_2O_3 with the surface area from 70 to 120 m^2/g that is 10 times more than that of iron oxides received by industrial technology.

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