

# Research of Electro-Explosive Iron Powder Using the Hydrolytic Adsorption Method

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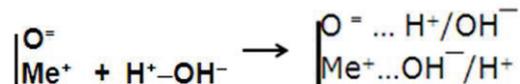
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**Abstract.** This work is aimed at solving the urgent problem associated with the diagnostic and forecasting of functional characteristics of finely dispersed materials. It considers the effect of primary acid-base center characteristics on the wetting process. The research of hydrolytic adsorption is carried out using the nano-dimensional iron powders. The powders were obtained by applying the method of electric explosion of conductors, after that they were passivated under different conditions. The identification of composition and structure of the passivating oxide film was carried out applying the method of transmission electron microscopy and X-ray diffraction analysis. The paper also describes the inhibition mechanism of hydrolytic adsorption on ferrioxide compounds with different composition and structure. The inhibition mechanism explains the hydrophilic / hydrophobic behavior of oxide compounds. The material of this article can be useful for its implementation in industrial, research and school laboratories.

## INTRODUCTION

The wide range of significant physical and chemical properties of metallic iron in nano-dispersed condition offers new areas of its application. To assess the efficient performance of finely dispersed iron in different media (liquid, gaseous) some special quality criteria are developed. Therefore, in the system “solid - liquid” it is essential to know the hydrophilic / hydrophobic behavior of powder surface. However, high reactive ability, small size and spherical shape of particles make difficulties for using traditional methods of the wetting process investigation [1]. Therefore, it necessitates the application of indirect methods based on the measurement of values associated with the wetting phenomenon.

One of these techniques is the hydrolytic adsorption. This technique has several options [2]. Each technique allows assessing quantitatively one of the fundamental characteristics of test specimen (the size of isoionic point, point of zero charge and the rate of exchange capacity) [3]. Using kinetic mode there is another chance to assess such features as hydrophilic /hydrophobic behavior of the surface [4-6]. By applying the kinetic mode it is possible to observe the pH change of aqueous suspension with time. This pH change is associated with the reaction behavior of acid-base interaction between the surface centers of a solid and water:



After differentiation of kinetic curves of pH-measurement a new parameter “the rate of pH change” is obtained. This parameter is an essential tool for analyzing the hydrophilization inhibition. The difference in the hydrophilization inhibition is predetermined initially by the composition and structure of the object and acid-base centers of its surface.

The study on the test specimen of ferric oxide in the solid state displays high sensitivity of the hydrolytic adsorption method to such objects [4-7]. Since the pyrophoric characteristic of nano-dimensional iron reduces the passivation in oxidizing medium, the nano-dimensional layer of ferrioxide compounds [8-10] is formed on the iron core. These ferrioxide compounds have various composition and structure with different acid and base centers. It can be supposed that the hydrolytic adsorption method is also sensitive to nano-dimensional oxide layer.

All the above mentioned makes the study of nano-dimensional structures employing the method of hydrolytic adsorption urgent and methodologically rigorous.

The purpose of this article is to study nano-dimensional iron obtained by the conductor electric burst applying the hydrolytic adsorption method.

## OBJECTS AND RESEARCH TECHNIQUES

The object of research is iron nanopowders obtained by the electric explosion of steel wire of St 3 type (Russian Standard 380-2005). The explosion was carried out in argon under gas pressure of 0.2 MPa [11]. The powders were passivated in different environment. Specimen 1 – the passivation process was as follows: the container with nanopowder was slowly filled with air and the process lasted 72 hours at 20°C in accordance with recommendations [12]. Specimen 2 – after being passivated in the container the nanopowder was additionally heated in the muffle furnace at temperature from 20°C to 180°C at rate 0.06°/min.

The composition and structure of the oxide film on the iron core were studied by applying the method of transmission electron microscopy (TEM) and X-ray diffraction analysis (XRDA). The transmission electron microscopy (TEM) was carried out on the equipment of TPU Nano-Center (JEOL “JEM - 2100F”) and diffractometer “Difray-401” was used for X-ray diffraction analysis (XRDA).

The wettability of the specimen surface was studied by pH-measurement variation of hydrolytic absorption method [2]. The initial pH of water was 6.7÷6.9. The suspension was prepared in the ratio “water: powder = 50:1”. This ratio is determined for the achievement of value solid-state point of zero charge [2]. pH change of aqueous suspension was registered by pH-150M device every 5 seconds of contact within 90 minutes by continuous stirring of suspension using a magnetic stirrer (measurement accuracy was ± 0.03 un. pH). The obtained integral kinetic curve of pH change was differentiated with different stepping interval to get data about the rate of pH change ( $vpH = \Delta pH_i / \Delta \tau, \text{min}$ ).

## RESULTS AND DISCUSSION

The tasks of the given work are as follows:

1. The identification of ferric oxide film structure and composition at the surface of the iron particles.
2. The investigation of the process of the hydrolytic adsorption on EEP iron.
3. The mathematic treatment of kinetic curves of pH-metry and qualitative assessment of the specimen hydrophilic and hydrophobic behavior.

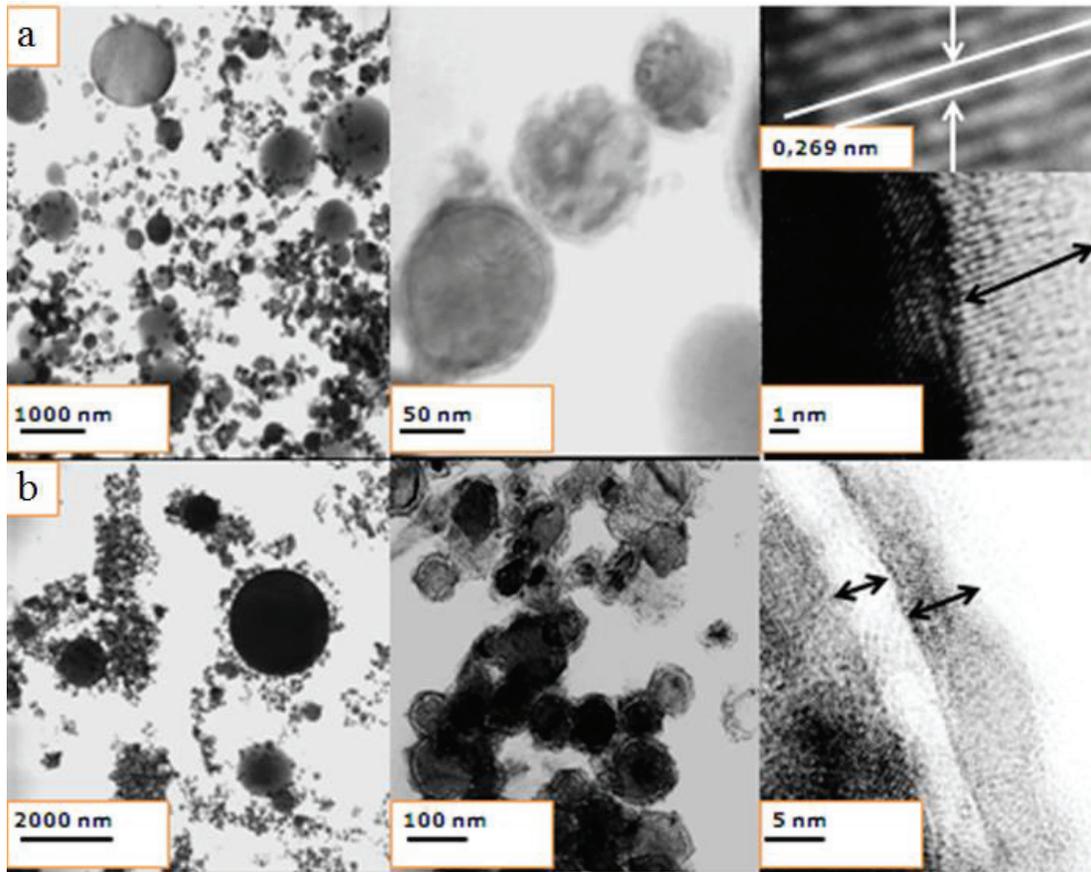
### The identification of structure and composition of ferric-oxide film on the EEP iron core

Iron oxide film by thermal steel oxidation has distinct laminated structure. At high temperatures and oxygen excess there is thermodynamically more likely the arrangement of layers with the increase of oxygen content in the composition being outward from the iron core center [13]: FeO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>. By variation of passivation conditions (oxidizing medium composition, temperature and time of oxidation) the oxide film can be formed with some certain composition and structure [14].

The transmission electron microscopy analysis (Fig.1) has shown that specimens passivated in different conditions have differences in the structure of the oxide layer.

The particular features for specimen 1:

- particles have regular spherical shape and are not aggregated;
- thickness of oxide film is uniform and equals 4÷5 nanometers;
- lines of atomic rows are solid and have one direction. The distance between atomic rows is 0.269 nanometers. It corresponds to the maximum on the reflex intensity with  $d(104)=0.269$  nanometers, which is typical for ferric oxide with haematite structure ( $\alpha\text{-Fe}_2\text{O}_3$ ). The absence of aggregation of powder particles is also the evidence of  $\alpha\text{-Fe}_2\text{O}_3$  formation which magnetic susceptibility is low.



**FIGURE 1.** TEM images of the specimen of iron particles passivated in different conditions: a) upper series of images – specimen 1; b) lower series of images – specimen 2

As shown in the images of specimen 2 small particles with higher reactive capability ( $d < 100$  nm) are not spherical. Their shape is hexagonal cross-section (sometimes their shape is quadrangular). Double-layer oxide coating (its total thickness is 20 nm) is formed on the surface of particles with higher reactive capability. Oxide layers have the same thickness (10 nm), but they differ in by color and density. The outer layer is denser than the inner one. The aggregation of small particles is more clearly marked in specimen 2 than in specimen 1. It confirms that ferric oxides in specimen 2 are formed with strong magnetic properties. It means, that oxide film in specimen 2 differs from the oxide film in specimen 1.

The processing of the specimen in the muffle furnace (with haematite oxide film formed at  $20^{\circ}\text{C}$ ) and its smooth and prolonged heating up to  $180^{\circ}\text{C}$  (about 35 hours) do not lead to FeO formation (this oxide is resistant and steady at temperatures higher than  $570^{\circ}\text{C}$ ). However, some nonequilibrium conditions are created for the further oxidation. Opposite diffusion flows have different rate (oxygen flow is hindered by the presence of surface film, while the ion flow is facilitated by the temperature rise). Isostructural ferric oxides with defective spinel structure like magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) are formed in these conditions [15-16]. These oxides differ by the following indices: light refraction, the density of grain package and adhesion to iron core. Magnetite has better adhesion and is darker and denser ( $n=2.42$  and density  $\approx 5.3 \cdot 10^3$ ) compared with maghemite ( $n > 2.52$  and density  $\approx 4.9 \cdot 10^3$ ).

Hexagonal external image of nanoparticles (typical for magnetite) and gapping of inner layer to iron core (forming maghemite grains) indicate that the outer layer is represented by magnetite grains and inner layer by maghemite grains [17-18]. The temperature of oxide formation is evidence in favor of such arrangement of layers. The upper layer is formed by the reconstruction of phase transition from haematite to magnetite. The rearrangement of crystal lattice is accompanied by the occurrence of considerable inner tension. It also suffers from diffusion troubles and takes place at higher temperatures. The inner layer has maghemite structure which is formed at lower temperatures.

The same density of nanoparticle oxide film shows equal possibilities of magnetite and maghemite formation. The texture is formed before the formation of stable dislocation network (grid) which has stoppers.

The variant with temporarily stabilized dislocation network (grid) is typical for powders with high dispersion. Such structures started their recrystallization but did not complete it. They possess low thermal stability of their texture, which rearrangement is unpredictable.

The experimental findings correspond to the conclusions of other scientists. In the conditions of mild low temperature oxidation of iron the oxides of spinel structure are formed in the same proportion [19]. The ability of fine particles to aggregation (Fig.1, Row b) due to high magnetization of spinel structures points out the above mentioned fact [20].

The results of X-ray diffraction analysis confirm the emergence of phases with spinel structure (Fig.2) in specimen 2. There are only four distinct reflexes for specimen 1, their arrangement and intensity are typical for iron (table). Other phases are not found. It shows the X-ray amorphism of ferric oxide due to its small amount.

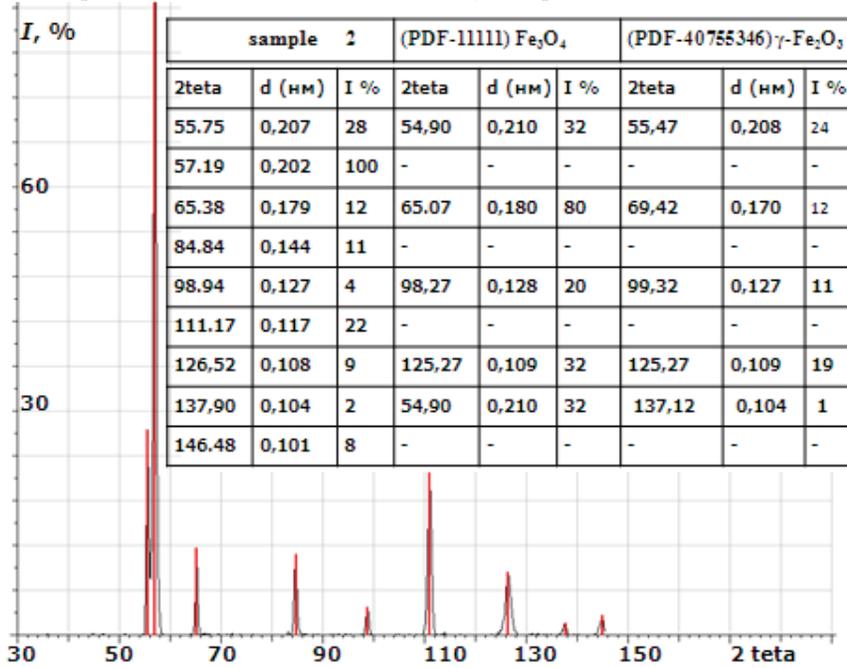


FIGURE 2. X-ray diffractogram of specimen 2 and the comparison table of interplanar spacing of reflexes with their standards.

There are four reflexes of iron in specimen 2 (Fig.2). There are also five additional (extra) extended weak reflexes, which arrangement and intensity are typical for both maghemite and magnetite. It can be explained by cooperative action of some range of factors: the similarity of magnetite and maghemite crystal structure, high dispersion and low rate of crystallinity of oxide structures. Crystallographic data of the determined phases correspond with the data of other scientific works [21].

TABLE. The comparison table of reflex interplanar spacing (d, nm) in roentgenogram

Test specimen 1			(PDF-60696) Iron. Fe Iron, syn.		
2teta	d (nm)	I %	2teta	d (nm)	I %
57.12	0.203	100	57.06	0.203	100
84.97	0.143	14	84.97	0.143	20
111.49	0.117	30	111.63	0.117	30
146.48	0.101	8	145.58	0.101	10

### The investigation of hydrolytic adsorption process on the EEP iron

The results of hydrolytic adsorption investigation have shown (Fig.3) that integral and differential kinetic curves illustrating pH changes of suspension have different directions for various specimens. The most distinctive differences are observed in the first five minute contact with water. Significant changes in pH observed in the first 10 minutes of contact for integrated kinetic curves. For differential kinetic curves - in the first 5 minutes of contact.

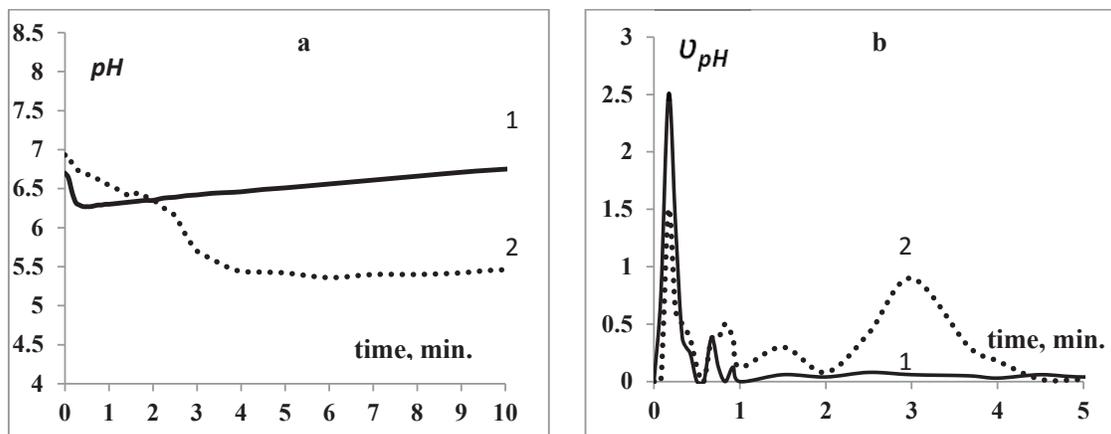


FIGURE 3. Integral (a) and differential (b) kinetic curves of suspension pH change for the tested specimens: 1) – specimen 1, 2) – specimen 2

The rate variation of hydrolytic adsorption in specimen 1 (there is ferric oxide with  $\alpha$ - $\text{Fe}_2\text{O}_3$  structure on the surface, Fig.3b, curve 1) stops in 2 minute contact with water. Such behavior is typical for hydrophobic surfaces and is caused by the processes of outer diffusion resistance. The outer diffusion resistance of hydrolytic adsorption reaction can be explained by the following facts:

1. The primary active centers of  $\alpha$ - $\text{Fe}_2\text{O}_3$  surface are  $\text{Fe}^{3+}$  cations of octahedral coordination with oxygen. In this case there is increased density of negative charge on the surface. The adsorption of water molecules from air forms secondary base centers of Brondsted type ( $\text{O}^{2-} \dots \text{H}^+/\text{OH}^-$ ) on the primary base Lewis centers;
2. Two-dimensional shielding film is formed due to hydrogen bonds between base Brondsted centers. It resists to further moistening. The surface is hydrophobic [4-6].

The pH change for specimen 2 (there are ferric oxides of spinel structure on the surface) is discrete and longer (up to 5 minutes of contact, Fig.3b, curve 2). Such behavior is caused by the processes of inner diffusion resistance and characterizes the hydrophilic behavior of the surface. The inner diffusion resistance can be explained by the following facts:

1. Spinel-like oxides belong to the class of coordinating crystals containing atoms of a transition metal in two different oxidation states:  $\text{Fe}^{3+}[\text{Fe}^{2+}\text{Fe}^{3+}]\text{O}_4$ . The primary active centers of the surface of spinel-like oxides are  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  cations. These cations are in tetrahedral coordination. In this case the density of positive charge of the surface increases. In this case there is increased density of positive charge on the surface and primary acid Lewis centers are formed.
2. The adsorption of water molecules from air forms secondary acid centers of Brondsted type ( $\text{Fe}^{2+} \dots \text{OH}^-/\text{H}^+$ ) on the primary acid Lewis centers;
3. Two-dimensional hydrogen-bond nets between acid Brondsted centers is not formed. There is no resistance to wetting. By reaching the critical concentration two-dimensional hydrate-hydroxyl coating is exposed to phase transition. A group of three-dimensional islands of liquid phase is formed on the surface. The islands of liquid phase flow together forming continuous layer, where the hydration wetting takes place. The hydrolytic adsorption process transfers to the depth of the loose oxide film and its rate changes discretely. Discreteness is caused by the process behavior at different in depth parts. Therefore, hydration is in different phases of its development and has different rate. Such sequence of rate decrease corresponds to the volumetric filling mechanism of porous space of the adsorbent by adsorbate solution (inner diffusion resistance mechanism) accepted in literature [22] and characterizes the hydrophilic behavior of solid surfaces.

## CONCLUSION

It was shown that kinetic variation of the hydrolytic adsorption method allows assessing wetting of finely dispersed powders (hydrophilic / hydrophobic behavior). The wetting diagnostic is based on the differences between rate acceleration and decrease of pH change of aqueous suspension in unit time. The drop of wetting rate for  $\alpha$ - $\text{Fe}_2\text{O}_3$  haematite is fast. This is caused by external diffuse inhibition and characterizes the surface hydrophobic behaviour of the specimen 1. For spinel-like structures the acceleration of mass transfer is abrupt, while the deceleration is slow and discrete. This is caused by inner diffusion resistance and is characterized by

the hydrophilic behavior of surface. The use of the results of pH-measurement allows making a rapid diagnosis of surface wetting.

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