The Structure of Surface Layers and Corrosion Stability of Fine Iron Obtained by Mechanical Grindingin Organic Media

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Abstract

The corrosion stability of finely dispersed iron powder obtained by grinding in heptane and in heptane with a surfactant added (oleinic acid) in a 0.85 % NaCl solution at a temperature of 37 °C is investigated. It is shown that corrosion stability increases with increasing grinding time; it also increases in the presence of the surfactants (SAS), in spite of the increase of powder dispersivity. The increase of corrosion stability is connected with the formation of a thin (up to 10 nm thick) protective surface layer containing graphite-like and oxide layers, as well as complex organic compounds. The composition and structure of these layers depend on grinding time and on the presence of SAS.

INTRODUCTION

Technological and medical application of fine iron is limited by its tendency to oxidize. Both the problem connected with obtaining fine iron particles and the possibility of their protection from corrosion are urgent. At present, mechanical grinding of materials remains the simplest method to prepare dispersed substances. Plastic metals can be ground only in the presence of adsorption-active media. On the other hand, it is known that one of the efficient methods to stabilize the properties of metal surfaces is to coat their surface with a film based on organic long-chain surface-active substances (SAS) [1]. Thus, grinding iron in the presence of SAS one may bring together obtaining fine metal particles and forming protective layers on their surfaces.

The goal of the present investigation is to reveal the interconnection between corrosion stability and the structure of the surface layers of fine iron powder obtained by mechanical grinding in organic media.

SAMPLES AND METHODS OF INVESTIGATION

Powders were obtained by grinding the carbonyl iron of specially pure reagent grade (och.ch. 13-2) with carbon mass fraction of less than 0.03 % and particle size up to 300 mm in a Pulverizette-7 ball planetary mill for (t_{grind}) 1–99 h in heptane (H powder); for some samples, SAS was added. It was oleininc acid at mass fraction of 0.3 % (H + SAS powder), according to the procedure described in [2]. Mean size of the particles obtained at t_{grind} = 24 h in heptane is 18 mm, in SAS solution 8 mm; at t_{grind} = 99 h, the size is 30 and 4 mm, respectively. The powders have nanocrystalline structure (after grinding for 1 h, grain size is 20 nm; after 99 h it decreases to 4 nm); the powders are solid solutions of C, O, H in the body-centred cubic (*bcc*) iron lattice with inclusions of carbide and oxide phases, their sources being the products of destruction of heptane and oleinic acid [2, 3].

Corrosion tests of the powders in physiological solution (NaCl 0.85 %, pH 6.13) at a temperature of (37 ± 0.5) °C were carried out

according to the procedure [4], its essence being the determination of the difference in hydrogen volumes evolved during the dissolution of a sample before and after exposing it to the corrosive medium. The evolved hydrogen volumes are equivalent to the mass of unoxidized metal in the sample; the difference of hydrogen volumes corresponds to the corrosion losses in the sample after exposure. Unlike [4], concentrated HCl was used to achieve satisfactory powder dissolution rate. In order to prevent the etching solution from absorbing oxygen, which can be consumed for side reactions (oxidation of iron and Fe^{2+} ions into Fe^{3+}) thus bringing errors to volumetric measurements between acid and air, a physical barrier made of undecane layer was created [5]. Corrosion tests were carried out with the samples kept in air for 3 years. The relative error of the determination of corrosion losses was not more than 20 %.

The structure of the surface layers was investigated by means of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). XP spectra were obtained with a ES-2401 spectrometer with Mg anode. Vacuum in the analyser chamber was 10^{-6} Pa. The spectrometer was calibrated using the Au $4f_{7/2}$ line (84.0 eV). Binding energy (E_b) of the line of C $1s$ electrons in the alkyl group was taken to be 285.0 eV. The accuracy of line position determinations was 0.1−0.2 eV. The spectra were decomposed according to the procedure described in [6]. The samples were placed in the chamber of spectrometer without contacting with air (under the undecane layer); besides, samples were investigated after they were kept in air for 2 h and 3 years. Auger spectra were recorded with a JAMP-10S spectrometer at the accelerating voltage of 10 keV, current 10^{-7} A, diameter of electron probe 300 nm. Vacuum in the chamber of the spectrometer was 10^{-7} Pa. Relative error of determining line intensities by means of XP and Auger spectroscopy was 10 %. The depth of layer analysed by means of electron microscopy did not exceed 10 nm [7].

THE RESULTS OF XPS AND AUGER STUDIES

The XP spectra of Fe $3p$, Fe $2p$, O$1s$, C$1s$ of H and H + SAS were obtained for diffe-

rent grinding times. Since the depth of Fe $3p$ electron escape is more than that of Fe $2p$, the analysis of Fe $2p$ lines gives additional information on the upper surface layer. Figure 1 shows the spectra of H and H + SAS samples obtained at t_{grind} = 24 h and kept in air for different time intervals.

The spectra of Fe $3p$ (see Fig. 1, *a*) contain three lines which can be assigned to unoxidized iron (E_b = 53.0 eV), iron oxide Fe_2O_3 (E_b = 55.7 eV), and organometallic complex of iron (E_b = 53.0 eV) [7−9]. The oxide constituent of the surface layer grows with increasing time of sample exposure to air, at the corresponding decrease of the fraction of unoxidized iron (Fig. 2). After a 2 h exposure to air, the fraction of unoxidized iron in H powders decreases by more than 20 % but remains unchanged in H + SAS powders, which points to different mechanisms of the formation of oxide layer. An increase of exposure to air causes the decrease of Fe^0 fraction in the layer under question due to the growth of the oxide film.

The content of the organic complex with iron as the central atom is approximately equal in all the samples. However, in the H + SAS sample transferred into the chamber of the spectrometer under the undecane layer the line corresponding to the organometallic complex is characterized by E_b = 57.7 eV, which is about 1 eV below the H and H + SAS samples kept in air (see Fig. 1). This means that organometallic complexes formed during grinding in heptane and in the presence of SAS are different from each other.

In the Fe $2p$ spectra (see Fig. 1, *b*), the shoulder with E_b = 707.0 eV corresponds to unoxidized iron; the maximum with E_b = (711 ± 0.2) eV may be related both to Fe_2O_3 and to FeOOH [1, 7−9]. After the samples are exposed to air, the decrease of the intensity of the shoulder with E_b = 707.0 eV corresponds o the growth of the oxide layer. Besides, in H powders, the fraction of hydrated oxides increases which is evidenced by the shift of the spectral maximum towards higher bond energies. In the spectrum of H + SAS powder, unlike the H powder transferred into the chamber of spectrometer under the undecane layer, there is a shoulder in the region of 709 eV corresponding to the compounds in which iron is present
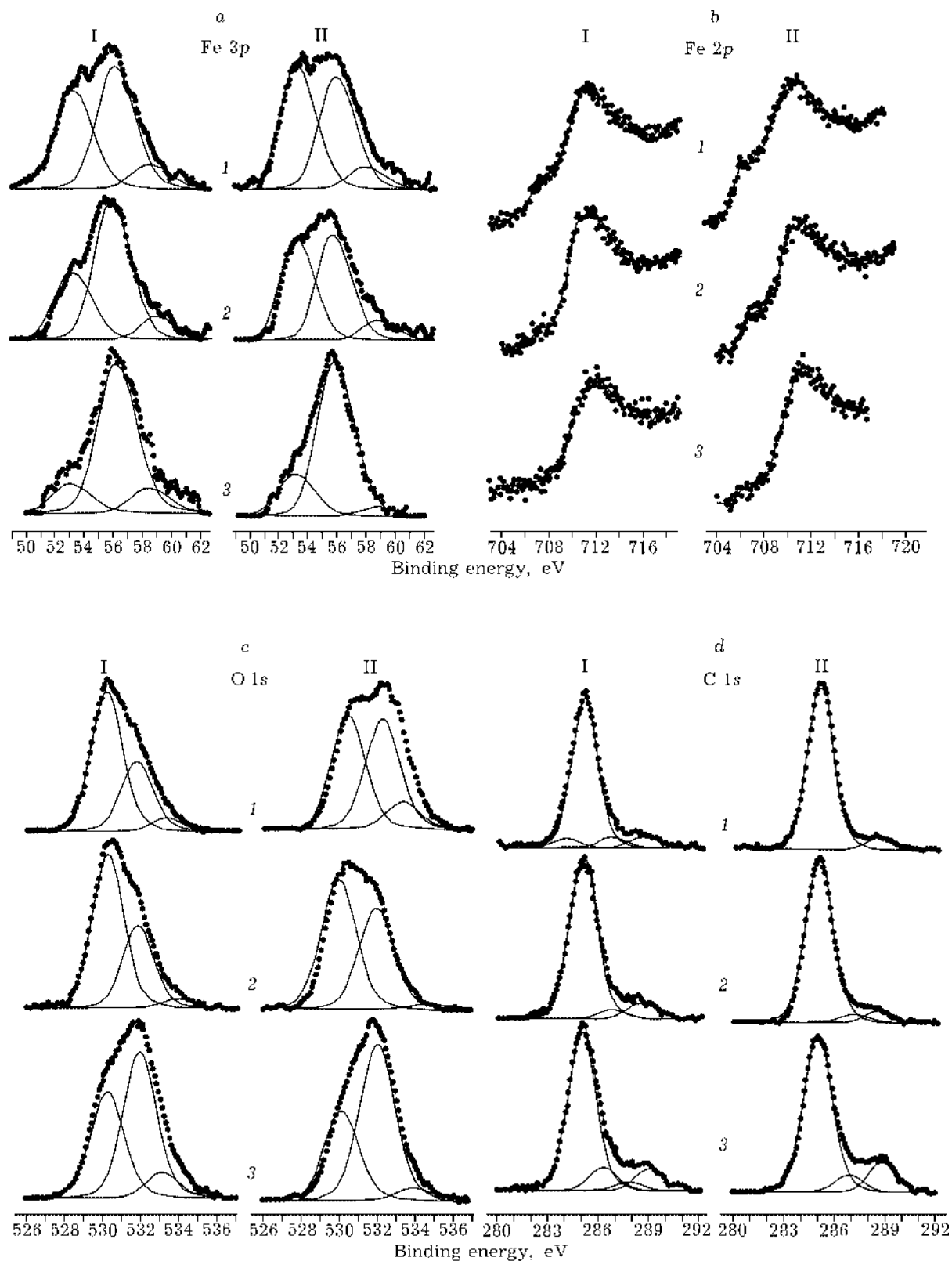
Fig. 1. XP spectra of powders obtained at t_{grind} = 24 h: 1 − samples transferred into the spectrometer chamber without contacting air; 2 and 3 − samples kept in air for 2 h and 3 years, respectively. Grinding medium: I − heptane, II − the solution of oleinic acid in heptane.
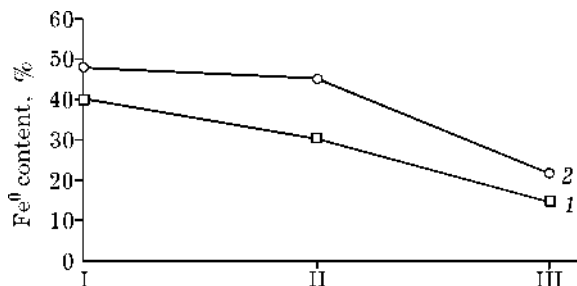
Fig. 2. Fe^0 content of the powder layer under investigation (t_{grind} = 24 h) depending on time of exposure to air (according to XPS data): *1* − grinding in heptane, *2* − heptane + SAS; I − without exposure to air, II, III − exposure for 2 h and 3 years, respectively.

in the oxidation states lower than that of Fe$_2$O$_3$. This shoulder disappears after the powder is exposed to air. The width of the low-energy part of the Fe 2p spectrum, measured at its half-height, decreases from 2.6 to 1.8 eV, the position of the maximum remaining unchanged; this is the evidence of the increase of the fraction of highly oxidized iron atoms, including hydroxides, in the oxide layer of the H + SAS powder.

The O 1s spectra of all the samples (see Fig. 1, *c*) exhibit two intensive lines at E_b = 530.2 and 531.9 eV, which confirms the presence of both iron oxides and hydroxides in the layer under investigation [1, 7−9]. The increase of the relative intensity of the line with E_b = 531.9 eV in powders exposed to air for a long time is connected with the increase of the fraction of hydroxides in the surface layer. The spectrum of the H + SAS sample transferred into the chamber of the spectrometer under the undecane layer exhibits a line at E_b = 532.6 eV, which can be related to oxygen in organometallic complex. Besides, the O 1s spectra of all the samples contain low-intensi-
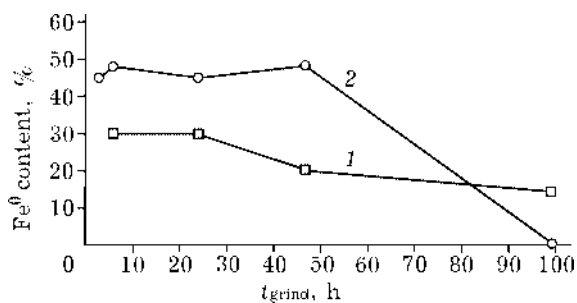
ty lines with E_b = 533.6 eV related to chemosorbed water [7].

The basic line in the C 1s spectra (see Fig. 1, *d*), with E_b = 285.0 eV, is characteristic of C−H and C−C bonds (including unsaturated ones). There is also a series of lines with E_b > 286.0 eV corresponding to carbon atoms in different oxidation states [10]. After the powders are exposed to air, the amount of the oxidized carbon atoms and their oxidation extent increase. The C 1s spectrum of the H sample transferred into the spectrometer chamber under the undecane layer contains a line with E_b = 284.0 eV which may be related to graphite-like structures [11]. After exposure to air, this constituent fo the surface layer is no more detected in the layer under investigation. It should be noted that the C 1s spectra do not contain a line characteristic of the acid group (E_b = 289.5 eV) [10]. This means that oleinic acid is decomposed during grinding.

XP spectra of the powders obtained at other t_{grind} are similar to those described above.

On the basis of the analysis of Fe 3p spectra of powders kept in air for 2 h, we obtained the dependence of the fraction of unoxidized iron in the layer under investigation on t_{grind} (Fig. 3). For H powders, a gradual decrease of Fe^0 content with increasing t_{grind} is observed. For H + SAS powders, this dependence is different in character. Till t_{grind} = 47 h, the Fe^0 content of the layer under investigation changes only insignificantly. For grinding times longer than 47 h, Fe^0 content decreases and comes to zero by t_{grind} = 99 h. This character of the dependencies is most likely conditioned by different rates and conditions for oxide layer growth on powders.
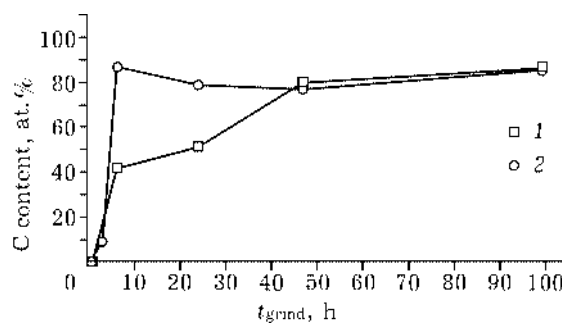

Fig. 3. Fe^0 content of the powder layer under investigation depending on t_{grind} (according to XPS data): *1* − grinding in heptane, *2* − in heptane + SAS.

Fig. 4. The fraction of graphite-like structures in the analyzed layer (according to Auger spectroscopic data): *1* − grinding in heptane, *2* − in heptane + SAS.
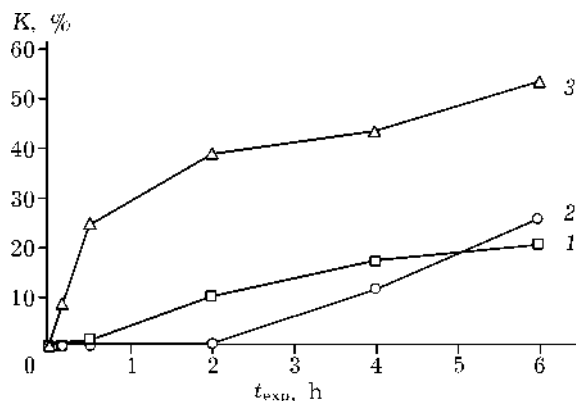
Fig. 5. Dependence of corrosion losses of powders (t_{grind} = 24 h) on time of exposure in corrosive solution: *1* – grinding in heptane, *2* – in heptane + SAS; *3* – carbonyl iron.

According to the data of Auger analysis (Fig. 4), the amount of graphite-like structures in the surface layer is also dependent on the environment and grinding time. For the H + SAS powder, a sharp increase of the amount of graphite-like structures is observed even within 6 h of grinding; further on, it remains practically unchanged with increasing t_{grind}. In H powder, the layer of graphite-like structures grows slower; only by t_{grind} = 47 h, their amount in the layer under investigation becomes equal to that of the H + SAS powder.

RESULTS OF CORROSION TESTS

The investigation of corrosion losses (C) in powders (t_{grind} = 24 h), pH changes and con-
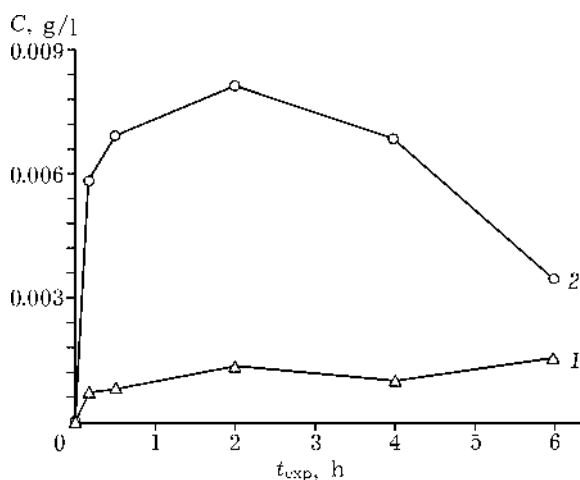

Fig. 7. The dependence of total iron ion content in the corrosion medium on the duration of corrosion test: *1* – carbonyl iron, *2* – H + SAS.
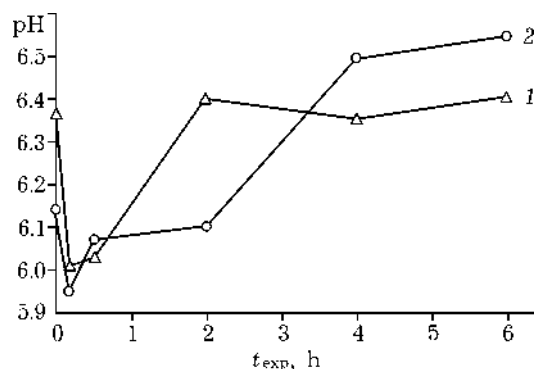

Fig. 6. Change of pH of the corrosive medium with the duration of corrosion test: *1* – carbonyl iron, *2* – H + SAS.

centration of iron ions in the corrosive medium versus exposure time t_{exp} in laminar flow (Re = 1700) is illustrated in Figs. 5–7, respectively. Corrosion stability of the H and H + SAS powders is higher than that of the initial carbonyl iron. For carbonyl iron, C is substantial even during the first minutes of exposure in corrosion medium; then the process slows down, which may be due to the decrease of the area of contacts between the powder and the medium because of iron powder dissolution. There is an induction period for ground powders; it is ~30 min for H powder and 2 h for H + SAS powder. After the induction period, the corrosion rates of both samples are approximately the same until saturation occurs. The measurements of pH and iron ion concentration in the corrosive medium during the tests of H + SAS showed that acidifying of the solution occurs during the induction period; then it becomes more basic.

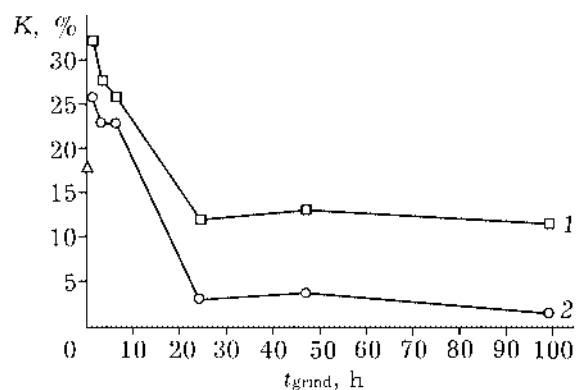Figure 8 shows the results of H and H + SAS powder investigations depending on t_{grind}

Fig. 8. The dependence of corrosion losses on grinding time: *1* – grinding in heptane, *2* – H + SAS.

in immobile corrosive medium at $t_{exp} = 6$ h. The C for initial carbonyl iron is lower than that for the powders obtained at $t_{grind} = 1$ h. At further increase of grinding time, K decreases; at $t_{grind} = 24$ h, K of both powders become lower than that of the initial carbonyl iron. It should be noted that the corrosion stability of powders increases with increasing grinding time, in spite of the substantial increase of dispersivity; finer dispersed H + SAS powders are more stable that H powders. For carbonyl iron, K is 18 %; for H powder obtained at $t_{grind} = 99$ h it is 12 %; for H + SAS powder it is 1.5 %, which corresponds to the decrease of corrosion rate not less than 15 and 900 times, respectively (calculation was performed without taking account of the changes of particle shapes and powder density).

DISCUSSION OF RESULTS

The analysis of all the results described above allows assuming the structure of the particle. The nucleus of the particle has nanocrystalline structure (bcc iron) with disperse inclusions of carbide phases (H powder), as well as carbide and oxide phases (H + SAS powder). Surface layers include three main constituents, namely, graphite-like layer, oxide layer and organic complex compounds.

The formation of graphite-like layer occurs since the start of grinding as a result of the destruction of organic medium; this process is more intensive in the presence of SAS. Under mechanical strain, numerous physicochemical processes accompanied by the rupture of molecular chains occur in organic compounds [12−15]. Besides, during dispersion and renewal of fresh surfaces, metals act as catalysts of the dissociation of organic compounds. The surface layers of particles activated during mechanical destruction interact intensively with the molecules of environment; the fragments of mechanically destroyed molecules sorbed on surface get chemically bonded to the surface layers of particles and penetrate them deeply. A constant amount of graphite-like structures in the layer under investigation after $t_{grind} = 47$ h is explained by the fact that carbon diffuses intensively from the surface

layer into the particle volume (into the near-boundary regions of nano-grains as the solid solution in iron and carbide phases [2, 3]). In the presence of SAS, due to the decrease of surface energy of the freshly formed metal surface, the volume gets saturated with destruction products with higher intensity.

The oxide constituent of the surface layer in H + SAS powders is formed directly during grinding with the participation of oxygen, which is a product of the decomposition of oleinic acid. Till $t_{grind} = 47$ h, the thickness of the oxide layer remains unchanged, which is connected with oxygen diffusion into the particle volume (see Fig. 3). During further treatment, a sharp increase of the fraction of oxide constituent occurs in the layer under question, which can be due either to the growth of oxide film or to the increase of powder dispersivity.

Unlike H + SAS powders, the oxide layer of H powders is formed when the powders are exposed to air. The presence of iron oxides in the surface layer of samples transferred to the chamber of spectrometer under the undecane layer (see Fig. 1) is likely to be due to the oxidation of iron by the residual gases in the spectrometer chamber, or by oxygen present in heptane and/or in the materials of the ball mill. It should be noted that the thickness of the oxide layer, fraction of hydrated oxides, and the amount of water adsorbed on powders are smaller for the H + SAS powders than for H ones, which is the evidence of differences in the structure of oxide layers. The layer is likely to be more friable on H powders. Exposure to air leads to further growth of the oxide constituent on all the powders (see Fig. 2); the oxide layer growing in air is formed above the layers formed during grinding.

Organic complex compounds are formed during grinding. The complex formed in heptane is not very stable; it may be oxidized even by oxygen present in the chamber of the spectrometer. In the presence of SAS, the formed complex has another chemical structure, which is evidenced by the presence of lines with $E_b = 532.6$ eV in the spectrum of O $1s$ and with $E_b = 57.7$ eV in the spectrum of Fe $3p$. Absence of oxidation in the spectrometer chamber is the evidence of its stability.

An increase of the number of oxidized carbon atoms in powder after contact with air (exposure in air for 2 h) is explained by the interaction of free radicals formed during grinding with the oxygen of the air. A substantial increase of the amount of oxygen-containing groups in the organic constituent of the surface layer after long exposure to air is connected with its oxidative destruction.

The appearance of the induction period on the curves plotting the corrosion losses *versus* time of exposure in corrosive solution (see Fig. 5) allows assuming that a substantial increase of the corrosion stability of powders kept in air for 3 h, in comparison with the initial carbonyl iron, is connected with the surface layer possessing protective properties. It should be noted that the thickness of the protective layer is not more than 10 nm, which is confirmed by the presence of a line corresponding to the metal core of the particle (Fe^0) in the spectra of Fe $3p$. In spite of very small thickness of this layer in comparison with the particle size, it provides effective protection from corrosive destruction. The difference between induction periods for H and H + SAS powders is determined by the difference in the composition and structure of this protective layer, most probably by the difference in oxide constituents. In spite of smaller thickness of the oxide layer in H + SAS powders, its increased protective properties are explained by larger fraction of Fe_2O_3 and larger density. Parallel behaviour of $K - t_{exp}$ plots for H and H + SAS powders after induction period shows that corrosion rate is only insignificantly dependent on the difference in the volume composition of powders. Since non-metal inclusions are present in powder volume, the rate of their corrosion after induction period is lower than that of the initial carbonyl iron.

Similarly to carbonyl iron, pH of corrosive medium decreases during the initial period (10 min) in the case of H + SAS powder (see Fig. 6), which is explained by the formation of saturated solution of corrosion products, *i. e.* hydrated iron(II, III) oxides. Subsequent increase of pH does not lead to the decrease of the total iron ion content in the corrosion medium (see Fig. 7), which can be connected with the increase of the fraction of hydrated iron(II) oxides which are better soluble and have larger pH of saturated solution that iron(III) oxides do [16]. For H + SAS powder, pH increases slower during the induction period, which is connected with lower corrosion rate during this period. Much higher iron ion content in the corrosion medium after H + SAS powder test in comparison with carbonyl iron at comparable pH of solution can be connected with the decomposition of the organometallic layer of the surface. This decomposition results in the formation of organic ligands in the solution; they form water-soluble complex compounds with iron ions, which hinders deposition and increases their total content in solution.

Corrosion losses of samples (see Fig. 8) after $t_{grind} = 1$ h increase in comparison with carbonyl iron powder due to the increase of dispersivity. With increasing t_{grind}, corrosion losses decrease in spite of the continuous increase of dispersivity, corrosion losses being larger for finer dispersed H + SAS powders.

The increase of corrosion stability can be connected with the change of surface layer composition. A similar behaviour of the curves of corrosion losses (see Fig. 8) allows assuming that the reason of increased corrosion stability is the same in both cases. It follows from the analysis of the behaviour of curves (in Figs. 3, 4) that the major role in the increase of the corrosion stability with increasing t_{grind} is played by graphite-like layer, since the increase of the amount of graphite-like structures correlates with the increase of corrosion stability. An increased corrosion stability of the H + SAS powders in comparison with H powders is mainly connected not with the thickness of oxide layer but with differences in the structure of the oxide and organometallic constituents of the surface layer.

CONCLUSION

The corrosion stability of fine iron powder obtained by grinding in heptane without and with SAS additives (oleinic acid) in 0.85 % NaCl solution at 37 °C is investigated. It is demonstrated that the corrosion stability increases with increasing grinding time and in the presence of SAS, in spite of the increase of powder

dispersivity. Induction period is discovered; its appearance is connected with the surface protective layer.

The X-ray photoelectron and Auger spectroscopic analysis of layers formed on surface in different media and at different stages of grinding, as well as after exposure to air demonstrated that the surface layers include three constituents, *i. e.*, graphite-like and oxide layers (Fe_2O_3, hydroxides) and organic complex compounds. The thickness of the protective layer does not exceed 10 nm.

Graphite-like layer is formed as a result of mechanical destruction of heptane on freshly formed metal surface, the thickness of the layer being increased with increasing grinding time. This layer mainly provides the increase of corrosion stability of powders with increasing grinding time.

The composition and structure of oxide layers and organometallic complexes depend on grinding media. In the presence of SAS, the oxide layer starts to form directly during grinding with the participation of oxygen, the source of which is oleinic acid; its thickness increases with increasing grinding time. The formation of oxide layer on powders ground in heptane occurs mainly after the powders are transferred from the grinding medium into air; its thickness is insignificantly dependent on grinding time. Differences in the structure of oxide layers and organometallic complexes provide increased corrosion stability of powders obtained in the presence of SAS.

Acknowledgements

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