Phase and structural conditions of low-temperature plasma interaction products with steel

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Abstract. Structural-phase research of low-temperature plasma interaction products with carbonaceous steel is conducted in the discharge between solid electrode and water. Such a discharge at a certain electric parameters leads to a powder formation of spherical particles with a diameter $10^{-6} - 10^{-3}$ m. A scale on surfaces of a steel electrode and the powder synthesized from it are subjected to a comparative analysis. Qualitative and quantitative phase characteristics of these products are different and depend on conditions of their formation. Their basic phase components are various ferric oxides: magnetite $\text{Fe}_3\text{O}_4$, wustite $\text{FeO}$, hematite $\alpha\text{-Fe}_2\text{O}_3$. Magnetite is contained in the powder synthesized at normal atmospheric conditions in the greatest quantity. Atmospheric pressure reduction and discharge implementation in a nitrogenous aerosphere considerably reduce quantity of magnetite in a formed powder. Diffusion speed in oxide layers and reaction temperature also influence electrode iron oxidation process. The formation mechanism of ferritic powder from steel under the influence of discharge plasma with a liquid electrode is offered on the basis of the gained results.

1. Introduction
The processes occurring at affecting on electric discharge plasma substance with use of liquids are the least known. The particular interest represents a case when solid electrode is taken out from an electrolyte, and the discharge occurs between solid and liquid electrodes [1]. Though recently there were the works devoted to studying of electrophysical characteristics of the similar discharge between metal and an electrolyte [2, 3, 4], plasma interaction with a solid body in the presence of erosion is a little investigated. Steel application as plasma machining object and its property modification is one of discharge use directions with a liquid electrode [5, 6]. The great value for physical and chemical processes understanding of low-temperature plasma interaction with a solid body surface has a structure and phase research of products formed.

2. Experiment
The discharge is carried out between an electrolyte and a solid electrode at constant voltage 1,3 kW and a current up to 1 A. A process water served as an electrolyte, and carbon steel is used as a solid electrode with a carbon content from 0,1 to 1,0 % and a cross-section diameter from 2 to 10 mm.

The structure and phase condition of solid products of plasma interaction with iron-carbon alloy is defined by methods of X-ray structure analysis and Mossbauer spectroscopy. X-ray phase analysis was

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based on difference of interplanar spacing and various phases lattice constant, Mossbauer spectroscopy is of isomer shift, quadrupole splitting and magnetic fields on iron cores. Application of Mossbauer Effect in various geometry allowed gaining the information, as by volume, and on a surface of investigated materials.

With a research objective of occurring processes in development, especially on a discharge initial stage, interaction product analysis was carried out stage by stage - depending on duration of discharge.

3. Results
At the very beginning of electric discharge there is visually defined layer on a narrow circle of its basis on a face surface of an electrode steel, a bit later - the first red-brown stains. In some seconds all face surface of steel becomes covered by a thin layer of rust. Then the electrode end heats up too much, the discharge occurs from all face surface of a steel, and it is covered by the black color layer which thickness gradually increases. Further there is a hemispherical drop on the electrode end, and its melt is spluttered in a liquid electrode where particles are intensively chilled and solidify in the spherical form, forming a powder.

The powder gained at current density on an electrode up to 10 A/cm², consists of black spherical particles with a diameter from 1 micron to 1 mm. Further increase in density of a current leads to instability of dispersion process and formation of balls with a diameter 1 – 2 mm. At current density above 20 A/cm² powder synthesis is stopped and the hollow particles are formed which transverse size reaches 5 mm.

The basic phase components of plasma interaction products with steel are various ferric oxides: magnetite Fe₃O₄, wustite FeO, hematite α-Fe₂O₃. However qualitative and quantitative phase compositions of these products (a scale on a steel electrode surface, powder and balls) are different and depend on conditions of their formation in an electric discharge with a liquid electrode. At the same time no ferric oxide gamma modification – maghemite γ-Fe₂O₃, is detected in each of them that follow from precision measurements of spinel structure and Mossbauer spectrum lattice spacing.

Originally appeared on a lateral surface of electrode steel the red-brown component is hematite α-Fe₂O₃. The scale formed on an electrode at much discharge times, basically consists of magnetite Fe₃O₄ and hematite α-Fe₂O₃ though it contains wustite FeO in insignificant quantity.

A dispersion powder is a mix of two ferric oxides Fe₃O₄ and FeO, though the magnetite phase considerably prevails and makes 80 – 90 % of volume. At the same time, as Mossbauer conversion spectra interpretation shows, the powder particles surface layer (about 0,1 µm) mainly consists of hematite α-Fe₂O₃.

The magnetite maintenance in a powder depends on many factors, including a discharge current, current density, carbon concentration in a steel electrode, and also a size of particles. At atmospheric pressure reduction the quantity of magnetite in a powder decreases and accordingly the wustite content increases. The same situation is also observed at synthesizing of particles in a nitrogenous aerosphere.

Precision measurements showed a little downgraded value of powder magnetite lattice parameter in comparison with stoichiometric Fe₃O₄. Intensiveness lines relation in synthesized particles magnetite Mossbauer spectrum that corresponds to ferric ions in tetrahedral and octahedral lattice points, also exceeds value, typical for a stoichiometric composition Fe₃O₄ [7]. The considerable broadening of FeO lines on diffractograms in comparison with equilibrium wustite is additionally revealed.

At high current densities metal balls are formed, and a main phase in them is, as in electrode steel itself, a solid solution on the basis of an alpha iron. Though the initial electrode steel had the equilibrium structure containing ferrite (a carbon solid solution in α-Fe) and the insignificant quantity of cementite (Fe₃C chemical compound), in composition of the above mentioned balls, except α-Fe, an austenite is available (a carbon solid solution in γ-Fe). The surface of these balls is covered by oxide crust which has phase composition qualitatively similar to a powder: Fe₃O₄ and FeO.
4. Discussion

Originally appeared on a surface of an electrode steel poorly reinforced layer on a narrow circle of its basis is a result of its heat treatment. However the discharge between a steel electrode and process water at the accepted modes practically does not allow reinforcing steel thermally: high temperatures developing in plasma promote further active interacting of ions being in excited state and electrons with formation of various compounds of iron with oxygen.

Oxidation process consists not only in a chemical compound of oxygen and iron, but also in diffusion of their atoms through the multiphase oxygenated layer. As the iron oxidizing reaction goes faster than diffusion through a scale layer, so at dense oxide film a speed of a scale build-up is defined by diffusion speed of atoms through its thickness that in turn depends on temperature and a oxide film structure. Magnetite and hematite have difficult cubic and rhombohedric crystal structure. Wustite crystallizes as a penetration phase, and it has vacant sites on a place of missing ions of iron that causes the big factor of diffusion in it. Thus it is necessary to mean that wustite formation in comparison with other ferric oxides is favorable thermodynamically only at higher temperatures [8].

At second discharge time the energy density on a face surface of an electrode is strongly non-uniform, and almost all energy is necessary on an external circle of the basis. Therefore the temperature of all surfaces of steel poorly raises, these can explain the absence of wustite in the oxygenated film at little discharge time. At increase in duration of plasma action the steel strongly heats up, the discharge is supported by all face surface of an electrode, and it oxidizes at such temperatures, forming Fe$_3$O$_4$ and FeO. The scale layer build-up on a steel surface is sharply sped up because of formation loose oxide FeO instead of dense oxide Fe$_3$O$_4$, and α-Fe$_2$O$_3$. The different concentration relationship of iron and oxygen atoms on the depth, caused by limiting diffusion, leads to decrease of magnetite content in a scale on depth.

The temperature, apparently, is a major factor causing difference in phase compositions of a powder and a scale on a surface of an electrode. Oxide ratio share in scale structure depends on temperature at which there is an oxidation of iron [9]. A characteristic point is eutectoid temperature (570°C under equilibrium conditions) below which the oxygenated layer consists only of hematite and magnetite, and above - among all three oxide types, however thus the hematite α-Fe$_2$O$_3$ content in comparison with magnetite Fe$_3$O$_4$ and wustite FeO is not enough. Indirectly this fact allows assuming range of temperature values at which there are processes of powder formation and the oxygenated layer on an electrode under the plasma action.

The additional factor of magnetite quantity raise in an oxide mixture, formed at plasma action on steel in the discharge with water, is ability of iron to react directly with its steams with Fe$_3$O$_4$ formation [10].

Oxide ratio share in the gained product is largely defined by concentration of oxygen in the dispersion environment. It decrease quantity of magnetite and accordingly increases the content of poorer oxygen wustite phase at atmospheric pressure reduction and at powder synthesizing in a nitrogenous atmosphere. The oxygen deficiency also leads to lack of hematite in powder particles.

The concentrated energy flows create special conditions of product synthesizing that explains formation in the discharge of non-equilibrium structures. A deviation of magnetite and wustite content from equilibrium, vacancies in their crystal lattices are developing process of these plasma interaction features with substance. Formation of unstable austenite in metal balls also explains a high speed cooling of steel particles in water (liquid electrode) from a liquid state.

The gained results allow to present synthesizing process of ferritic powder from steel under discharge plasma action with a liquid electrode. High-energy plasma action on a steel leads to formation on its face surface of a hemispherical drop of molten metal. High temperatures and water vapors cause presence of a magnetite and wustite mixture on an external surface of this drop with predominance of the first. The inner shell represents the molten metal kept by a surface tension force on the end of an electrode. When gaseous impurities burst out, they carry away material parts. A surface tension force gives them the spherical form, and extra fast cooling in a liquid electrode fixes their form.
Because the body-section phase composition of a drop is defined by diffusion of atoms at iron oxidation (magnetite predominates on a surface, deeper is wustite, metal is inside) its phase composition depends on volume of a material carried away by a particle. Oxidation proceeds before full cooling of a particle, however it already occurs at lower temperatures when thermodynamically favorable is $\alpha$-Fe$_2$O$_3$ formation, owing to that the particle surface becomes covered by a thin hematite layer.

5. Conclusions
At constant voltage above 1 kW and a current up to 1 A the electric discharge between a steel electrode and process water leads to formation of a spherical particles powder with sizes from micron to millimetric values. Sphericity of particles is provided with a surface tension force and high speeds of their cooling in a liquid electrode.

Process is accompanied by iron oxidation and its oxide Fe$_3$O$_4$, FeO and $\alpha$-Fe$_2$O$_3$ formation, except $\gamma$-Fe$_2$O$_3$. Major factors defining qualitative and quantitative phase content of plasma interaction products with steel are the temperature of their formation and diffusion speed of their elements.

Iron oxidation level decreases from a surface to the centre of particles of the synthesized powder, thus their surface is covered by a thin $\alpha$-Fe$_2$O$_3$ layer. Its quantity practically does not influence volume phase powder content which basically consists of Fe$_3$O$_4$ and FeO. A prevailing component of this mixture is Fe$_3$O$_4$ which content decreases at reduction of oxygen concentration in discharge environment.

The high substance content in a composition of a powder including into ferrite group with spinel structure, represents practical interest for magnetic materials powder metallurgy. Special value thus has magnetite powder particle form sphericity which can be an important condition of isotropy of its magnetic properties.

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