Interface layer formed in a low-temperature plasma of hydrocarbons on iron

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Abstract. The method of uncovering the interphase layer in the systems “iron-nanosized polymer film” obtained in a low-temperature plasma on iron from hydrocarbons was used. A method of interface layer uncovering based on electrochemical dissolution of the iron substrate was proposed, which allowed one to achieve a high rate of metal. Ammonium sulfate solution was used as an electrolyte. A method of interface layer uncovering based on electrochemical dissolution of the iron substrate was proposed in the work. This allowed one to achieve a high rate of metal dissolution and make it possible to control the composition of the dissolution product. Salt solution was used as an electrolyte. Interface layer studies were carried out using the AFM and XPS methods, which allowed establishing the relief and chemical composition of the interphase boundary, as well as the location on the interphase surface of the metal-containing phase. The application of a double-layer iron substrate consisting of a plate of ⁵⁶Fe nonresonance isotope with a ⁵⁷Fe ultrafine layer deposited on its surface allowed one to use the Mössbauer spectroscopy for investigation of the chemical state of iron atoms in the interfacial region of “iron-nanoscale polymer film” systems.

1. Introduction.
The formation of nanoscale protective organic and polymer layers on metals to protect them from corrosion is an urgent problem. It is known that the protective effect of polymer coating is caused by both the isolating properties of the coating itself and the energy state of the interphase boundary of the “coating-substrate” system, which is especially important for nanoscale coatings. One method of coating thin protective organic layers is the plasma-chemical method. Earlier, we found [1, 2] that in the low-temperature plasma forming polymer coatings from hydrocarbons on iron, the chemical structure of the coating is due to the radical formed during the conversion of the hydrocarbon in the plasma. In this connection, the study of the chemical constitution of the interphase boundary and processes proceeding during its formation is quite important for understanding the action of the protective mechanism of such coatings.

The interfacial layer obtained by depositing a polymer coating from heptane on iron in a low-temperature low-pressure plasma was investigated.

2. Experimental
A plasma polymerization reactor had a working volume of 200 cm³ and the external arrangement of the electrodes. Low-temperature plasma was excited by a radiofrequency (40.68 MHz) field. Polymer films were deposited in the dynamic mode onto an insulated metal (iron) mounted at the center of the
reactor at equal distances from the electrodes. The heptane vapor pressure was 12 Pa, the discharge power was 40 W and plasma processing time 300 s.

The methods of investigations were used: X-ray photoelectron spectroscopy (XPS), atomic-force microscopy (AFM), and Mössbauer spectroscopy. XPS investigations were performed on an ES2401 spectrometer with a magnesium anode. The vacuum in analyzer chamber was $10^{-5}$ Pa. The spectrometer was calibrated with respect to the Au4f7/2 peak at bond energy $E_b$ equal 84.0 eV. Investigations by AFM methods were carried out on a Solver P47 microscope in a tapping mode. The Mössbauer investigations were performed at room temperature on a YaGRS-4M spectrometer operating in a regime of constant accelerations with a source of $\gamma$-radiation of $^{57}$Co in a Cr matrix. The Mössbauer spectra were mathematical treated in a discrete representation with the use of a Levenberg–Marquardt algorithm by the damped least-squares method. Samples on the side of plasma-polymerized film were isolated by epoxy adhesive. As was shown by X-ray photoelectron spectra of the film surface, the residual air in the reactor had no effect on the chemical composition of the films at these parameters. The substrates from both ARMCO-iron and double-layer substrate from $^{56}$Fe ($^{57}$Fe content is not more than 0.01%) and $^{57}$Fe with isotopic purity of 95% served as samples for development of production techniques for investigation of the interfacial region in “iron–nanoscale polymer film” systems. In all cases, the iron content in the substrates was 99.9%. Before coating of film, the ARMCO-iron surface was subjected to electrochemical polishing with immediate washing by water, acetone, and petroleum ether. The double layer substrates were washed in the same way after $^{57}$Fe deposition [3]. The substrates prepared in this way were immediately transferred into a reactor for plasma-treatment. The substrates were oxidized upon transfer into the reactor: according to XPS data, there were 5 at % of oxygen in the surface layer of iron substrates.

A method of interface layer uncovering based on electrochemical dissolution of the iron substrate was proposed, which allowed one to achieve a high rate of metal dissolution and make it possible to control the composition of the dissolution product. Ammonium sulfate solution was used as an electrolyte. To preserve the interfacial layer and properly nanoscale film, the sample on the side of film was sealed with epoxy resin. We gave up on application of an electrochemical cell in which the cathode and anode spaces are not separated. The natural mixing of anode and cathode space content leads to the formation of iron (II) hydroxide, the suspension of which fills the whole volume of the cell and settles on the sample surface.

Application of a wedge-shaped substrate (Figure 1) allowed one to completely dissolve iron and, thus, prepare the “metal-plasmapolymerized film” interface layer for tests. Hereafter, complete dissolution was achieved with the use of substrate with a square shape by progressive dipping of it into electrolyte during dissolution.

![Figure 1](image-url). Dissolution scheme of wedge-shaped iron substrate and photographs of sample at different time of dissolution $\tau$, h: (1) 0.5, (2) 4, and (3) 8.
3. Results and discussion
The investigation of the sample after the iron-substrate dissolution by the X-ray photoelectron spectroscopy showed the absence of iron atoms on the external side of sample (epoxy resin surface) (Figure 2a) that testifies the qualitative washing of sample after the substrate dissolution.

At the same time, the investigation of the interface layer that remained on film revealed the signal of Fe atoms (Figure 2b) forming part of the interface layer. The low intensity of the Fe2p-electron spectrum at a rather high level of noise did not allow one to decompose it correctly into components; however, the range of the bond energy maximum of 707…712 eV allows one to assume the presence of metallic iron or its carbide and iron in higher degrees of oxidation [4] in the analyzed layer, which is confirmed by the intense O1s- electron line. There are a low-intensity line with Eb = 283.5 eV (carbides) and line with Eb = 289.0 eV characteristic of metal carboxylates in the C1s- spectrum along with the main line with Eb = 285.0 eV [4].

![Figure 2. X-ray photoelectron spectra: (a) free side of auxiliary film; (b) interface layer.](image)

Investigation of interface layer by atomic-force microscopy showed that the distribution of Fe-containing components is uniform, which is confirmed by a phase-contrast map (Figure 3).

To investigate the interface layer by the “volume” method of Mössbauer spectroscopy, double-layer substrates consisting of substrate of $^{56}$Fe nonresonance isotope with a $^{57}$Fe ultrafine layer where the polymer coating was deposited obtained on its surface [3]. This allowed one to increase the signal fraction of $^{57}$Fe atoms of the interfacial layer. In this case, the chemical compositions of the interface layer obtained with the use of substrates from both ARMCO-iron and $^{57}$Fe are identical.

![Figure 3. AFM images of interfacial region obtained after dissolution of iron substrate: (a) relief; (b) map of phase contrast.](image)
Before the deposition of $^{57}$Fe, the substrate of $^{56}$Fe0 representing a foil of 30 μm thickness was annealed in vacuum of 100 Pa at 700°C for 1 h. $^{57}$Fe was deposited by an electrolytic method from $^{57}$FeSO$_4$·(NH$_4$)$_2$SO$_4$ solution. $^{57}$FeSO$_4$·(NH$_4$)$_2$SO$_4$ solution was obtained at anode dissolution of $^{57}$Fe plate in (NH$_4$)$_2$SO$_4$ at room temperature. The electrolytic deposition of $^{57}$Fe on the substrate was performed under conditions of natural aeration (pH 2.5–3.5) at room temperature.

Mathematical treatment of the Mössbauer spectra of the samples under investigation showed that the spectra consist of two sextets (Figure 4) corresponding to local atomic configuration of Fe with the parameters characteristic for the α-Fe phase (intensity of ultrafine magnetic field $H = 330$ kOe) and Fe carbide phase ($H = 202$ kOe) [5] with a phase ratio of 0.86 : 0.14. The signals of α-FeOOH, Fe$_3$O$_4$, γ-Fe$_2$O$_3$, and α-Fe$_2$O$_3$ iron compounds with $H$ parameters equal to 356, 454, 503, and 511 kOe, respectively [6], can be also revealed in the Mössbauer spectra, but the intensities of these lines are negligibly small.

4. Conclusions

The investigation of an “iron-nanoscale polymer film” system obtained in low-temperature plasma of hydrocarbons showed that the interfacial layer consists of iron carbides and oxygen- and carbon-containing compounds of iron. The efficiency of the combination of the techniques proposed for investigation of the interface layer providing more complete information on the layer chemical composition was shown.

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