Article

On the Mechanism of Formation of Conversion Titanium-Containing Coatings

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Abstract: The present work is devoted to the study of the mechanism of the process of formation of adhesive oxide-titanium coatings on steel, zinc, and aluminum surfaces. For the first time, the following hypothesis has been confirmed experimentally, namely, that nickel, being the first metal to be deposited on a steel substrate, creates active centers on which titanium oxides are formed, because the hydrolysis of hexafluorotitanic acid is adsorbed, which then form a continuous film. The data obtained, regarding the dependence of the coating thickness on the linear rate of the solution flow along the treated surface, indirectly confirm that the formation of insoluble titanium oxides occurs because of the alkalization of the solution adjacent to the surface. It has been established that in the presence of hexavalent molybdenum compounds in the solution as oxidizers, molybdenum is included in the coating in the form of oxides. It has been revealed that in the lower layers of the coating, molybdenum is contained in the form of compounds of molybdenum (V) and (VI), while in the upper layers, it is contained only in the form of the compound of molybdenum (VI).

Keywords: corrosion protection; titanium-containing coatings; conversion coatings; hexafluorotitanic acid; passivation of metals

1. Introduction

Modern technologies for painting steel surfaces include the preliminary formation of adhesive conversion coatings in order to ensure adhesion and increase the protective ability of the subsequent paint and varnish coating (PVC). Most often, before steel surfaces are painted, they are phosphated; galvanized and aluminum surfaces are chromated, although they are also phosphated when in the fabricated structure [1–3]. The disadvantages of the phosphating and chromating processes are known and have been repeatedly discussed in the literature [4–9].

High energy consumption caused by high operating temperatures (from 70 to 90 °C) is a known disadvantage of phosphating processes. In addition, the implementation of modern technologies of crystalline phosphating requires fairly complex equipment. Furthermore, the processes themselves require tight controls, because the properties of the coatings formed are highly dependent on parameters such as the total and free acidity, temperature, concentration of accelerators, etc.

Compounds of hexavalent chromium, which are contained both in chromating solutions and in chromate coatings, are rather toxic and carcinogenic.

In recent years, in some types of oxide-titanium adhesion coatings have been proposed as a replacement for the adhesive phosphate and chromate layers under PVC [7,9–17]. Among the advantages of the new coatings are their energy saving production technologies, ease of implementation and operation, and the low toxicity of the solutions used.

According to the literature to date, the solutions for the formation of these coatings must contain hexafluorotitanic acid; ions of heavy metals, such as nickel, copper, cobalt, silver, and chrome; and an oxidizer, which can be molybdates, hydroxylamine, nitrates, etc. [7,11,12]. Coatings are formed in such solutions after several at pH 4–5 and at room temperature (Figure 1).

Figure 1. Scheme of formation of coatings.

According to the hypotheses described in the literature, the mechanism of formation of oxide-titanium coatings on steel surfaces at pH values of 4.0–5.0 for the solution, includes the following reactions [7]:

It is assumed that hexafluorotitanic acid is hydrolyzed at pH 4–5 on the surface of the metal to be treated (steel, zinc, or aluminum) with the formation of titanium oxides. These are at first adsorbed on the surface of heavy metals (Ni, Cu, Co, and Cr), which are on a steel substrate during contact and then expand, forming a continuous coating.

It is believed that similar processes also occur on a zinc substrate, and the coatings formed in this case consist mainly of oxides of TiO_2 , Ti_2O_3 , and ZnO [9,18].

The mechanism of formation of titanium-containing coatings on aluminum and its alloys is somewhat different because of the presence of a thin oxide film on their surface. According to the literature data, initially the oxide film dissolves according to the reaction [15,19]:

Furthermore, hexafluorotitanic acid oxidizes aluminum as follows:

The oxyfluorides of aluminum and titanium that form as a result of these reactions are also initially adsorbed on the surface of the heavy metal that is deposited during contact, and they then form a continuous coating.

However, no experimental confirmations of the described hypotheses are given in the literature. Understanding the mechanism of formation of coatings is very important for improving existing technological processes and for developing new ones.

The present work is devoted to the study of the mechanism of the process of formation of adhesive oxide-titanium coatings on steel, zinc, and aluminum surfaces.

2. Materials and Methods

The specimens were made of cold-rolled steel A622 grade, 5556 aluminum alloy, and zinc-coated steel.

To prepare the solutions, the chemical reagents of grades “pure”, “chemically pure”, and distilled water were used.

For an accelerated evaluation of the protective ability of coatings, a drop express method was used for the steel and aluminum substrates using Akimov’s reagent, with the solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 82 g/L, NaCl 33 g/L, and 13 mL/L 0.1N HCl, and for the zinc-coated substrate, the solution contained $\text{Pb}(\text{CH}_3\text{COO})_2$ 50 g/L. According to the drop method, the protective ability (PA) of the coating is evaluated in seconds as the color change time of the control area under the drop of the solution, from gray to red-brown (on steel) and to black (on zinc).

The composition of the surface layers was studied using X-ray photoelectron spectroscopy (Omicron, Taunusstein, Germany) (XPS) [20]. Coated samples were fixed in a holder and placed in the pre-evacuation chamber of an OMICRON ESCA+ XPS unit (Omicron). The samples were then transferred to the analyzer chamber, where the pressure was maintained at a level no higher than 8×10^{-10} mbar. $\text{MgK}\alpha$ radiation was used (1253.6 eV; power, 252 W). The pass energy of the analyzer was 20 eV. To allow for the charge of the samples, the position of the XPS peaks was standardized with respect to the C 1s peak of the hydrocarbon impurities from the atmosphere; the bonding energy (Eb) of the peak was assumed to be 285.0 eV. The spectra were decomposed after subtracting the background, determined using the Shirley method [21]. The peak position was determined with an accuracy of ± 0.1 eV. Component ratios were calculated using integrated intensities under the peaks, while allowing for photoionization cross sections (σ) of the respective electron shells [22]. Using the integrated intensity of the peaks and the MultiQuant software (version 7) program [23], the thicknesses of the layers formed on the surface were calculated, with allowance for the mean free path of electrons (λ), determined using the formula of Cumpson and Seah [24]. The panoramic spectra were also recorded after argon-ion etching of the coating in different depths. Thus, the composition of the coating at different distances from the substrate was determined. The pressure of the inert gas in the working chamber was maintained at this level, so that the ion energy and the ion current rate, and consequently, the etching rate, were constant. When analyzing the obtained spectra, it was considered that the analyzing beam penetrates the material to the depth of 5 nm, i.e., the resulting spectra correspond to a layer of material 5 nm thick.

The morphology of the surfaces of the coated specimens was studied using an MPLAPONLEXT 100 lens with the LEXT-OSL 4100 confocal laser microscope (OLYMPUS Corporation, Tokyo, Japan).

The thickness of the coatings was determined by an ellipsometric method using a spectroscopic ellipsometer by Sentech SENreasech (SENTECH Instruments GmbH, Krailling, Germany) 4.0 SER 800 with a high-speed monochromator. The measurements were carried out in the spectral range of wavelengths of 240–1000 nm [25].

The contact angle of the water in contact with the metal plates was determined with the Goniometer LK-1 apparatus (OpenScience, Krasnogorsk, Russia). When working with a goniometer with the camera Levenhuk C310 NG (Levenhuk, Tampa, FL, USA) photographs of the drops were obtained, and then the contact angle was calculated using DropShape software (developed by the Colloid Chemistry Department of the M.V. Lomonosov Moscow State University, Russia, version 3).

3. Results and Discussion

The present research was made with a solution that was developed by us previously [10,15]:

It should be noted that in the development of this composition, we studied hydroxylamine, nitrates, and molybdates as oxidizers. The best protective and adhesive coatings were formed in the presence of ammonium molybdate, so it was chosen as a component of the solution.

When the treated specimens were immersed in this solution at a temperature of 18–25 °C, conversion titanium-containing coatings formed on their surfaces. Formation of the coating on steel, galvanized, and aluminum substrates was completed within 30, 60, and 180 s, respectively. Ellipsometric measurements show that the differences in the thicknesses of the coatings formed during this time on steel, zinc-coated steel, and 5556 aluminum alloy were insignificant, at 70, 75, and 68 nm, respectively.

The panoramic X-ray photoelectron spectra revealed the presence of titanium, molybdenum, fluorine, and oxygen compounds, in addition to iron, in these coatings (Figure 2, curve 1), as well as zinc or aluminum, depending on the nature of the substrate.

Figure 2. XPS spectra of a specimen with titanium-containing coating on steel prior to etching (1) and after 180 min etching of the coating (2).

The individual spectra of the elements in the coating on a steel substrate allowed us to make assumptions concerning the compounds containing these elements included in the coating. A wide oxygen peak can be interpreted as a mixture of iron, titanium, and molybdenum oxides (Figure 3a). Iron is presented as FeO–Fe₂O₃ oxide (710.8 eV) [26] (Figure 3b) and molybdenum is presented as MoO₃ oxide (232.7 eV) [27] (Figure 3c). The position of the peak intensity for titanium corresponds to TiO₂ (458.3 eV) [28] (Figure 3d).

The individual spectra of these elements in the coating on a zinc substrate indicate that in this case, in addition to the above compounds, a trivalent titanium oxide (456.8 eV) [29] (Figure 4) is present in the coating. Apparently, zinc, being a more electronegative metal, unlike iron, is able to reduce titanium (IV) to titanium (III) under the existing conditions.

Emission peaks of TiO₂ and Al₂O₃ were found in the spectra of the coatings on aluminum, as was expected.

In the panoramic spectra of coatings on the steel, zinc, and aluminum substrates, the emission peaks of nickel were practically absent. The nickel content in the coating did not exceed 0.2%, which is within the error of the determination. It should be considered that the analyzing beam penetrated the material to a depth of about 5 nm, that is, the spectra presented above correspond to a layer of material with a thickness of about 5 nm. The low intensity of the nickel emission in the panoramic spectra of coatings indicates that nickel was practically absent in the upper layers of the coating.

Figure 3. Individual XPS spectra of oxygen (a), iron (b), molybdenum (c), and titanium (d) in the coating on a steel substrate.

Figure 4. Individual XPS spectra of titanium in a coating on a zinc substrate.

In order to detect nickel in the lower layers of the coating, a layer-by-layer etching of the coatings in the chamber of the X-ray photoelectron spectrometer was carried out, followed by the spectra recordings.

As can be seen from Figure 2 of the panoramic spectrum of the coating on steel substrate after etching the coating for 180 min (Figure 2, curve 2), the intensity of the emissions of nickel, molybdenum, and iron increased and the intensity of titanium emissions decreased significantly.

The individual spectra of nickel (Figure 5a) indicate that after 20 min of etching of the coating, a peak of metallic nickel (853.5 eV) [30] emission appeared in the spectrum, whose height increased within the interval from 20 to 110 min. At the same time, the emission intensity of Ni^{2+} decreased practically to zero in the coating spectrum after 50 min of etching. Thus, the metal nickel in the coating was found only adjacent to the substrate layers of the coating.

The individual iron spectra (Figure 5b) also varied depending on the thickness of the coating: the peak of the emission of metal iron (707.4 eV) [31] appeared in the spectrum after 80 min of etching of the coating, and, as expected, increased as it approached the steel substrate. In addition, the content of iron oxides in the coating also increased as it approached the substrate.

Figure 5. Individual XPS spectra of nickel (a) and iron (b) in the coating on a steel substrate, depending on the duration of etching.

Similar dependencies were obtained for the zinc and aluminum substrates. Metallic nickel was found in the coating layers that lay directly adjacent to both the aluminum and zinc bases.

The results obtained were consistent with the assumption about the contact deposition of nickel at the initial stage of coating formation, as described in the literature. Then, the insoluble titanium oxides, of which the conversion coating mainly consisted, were adsorbed on the deposited metal. It can be assumed that the formation of insoluble titanium compounds due to the displacement of Equation (3) to the right becomes possible because of the alkalization of the boundary layer of the solution, in accordance with Equation (2).

In order to confirm this assumption, the dependence of the thickness of the coating formed during 3 min on the linear rate of the solution flow on the surface to be treated was studied.

As can be seen from the results in Figure 6, the thickness of the conversion coating increased as the flow rate of the liquid increased from 70 (without mixing) to 140 nm (at 100 m/min), which is most likely explained by the elimination of diffusion limitations. Reducing the thickness of the coating at high velocities of the solution (more than 100 m/min) is explained by the elimination of the

alkalization of the solution layer adjacent to the surface, and, consequently, the absence of conditions for the formation of titanium oxides.

Figure 6. The dependence of the coating thickness on the linear rate of the solution flow along the treated surface.

The high content of molybdenum in the lower layers of the coating (Figure 2, curve 2) can be explained by the partial reduction of hexavalent molybdenum by the substrate metal in order to form the oxides of a lower valency that were included in the coating along with the hexavalent molybdenum oxides. In the upper layers of the coating, molybdenum was presented only in the form of Mo^{6+} compounds which was confirmed by the individual molybdenum spectrum (Figure 3c).

It was found in the course of the experiments that, with an increase in the duration of coating formation of up to 8 min or more, an Mo^{5+} emission peak appeared again in the spectrum of the coating (231.8 eV) [32] (Figure 7). The inclusion of oxides of pentavalent molybdenum in the coating composition led to an increase in the thickness in the process of the deposition duration (Figure 8a). At the same time, the discontinuity of the coatings occurred (Figure 9a,b), which led to a significant decrease in their protective ability (Figure 8b).

Figure 7. Individual XPS spectra of molybdenum in the coating on a steel substrate (duration of the process (τ) = 8 min).

Figure 8. The dependence of the thickness (a) and the protective ability (b) of coatings on the duration of the process (1. H_2TiF_6 : 2 g/L; $\text{Ni}(\text{NO}_3)_2$: 0.4 g/L; pH 4.6–5.0; T : 20 °C) (2. H_2TiF_6 : 2 g/L; $\text{Ni}(\text{NO}_3)_2$: 0.4 g/L; $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$: 0.3 g/L pH: 4.6–5.0; T : 20 °C).

Figure 9. Photographs of the surface of coatings: (a) $\tau = 3$ min, (b) $\tau = 8$ min (H_2TiF_6 : 2 g/L; $\text{Ni}(\text{NO}_3)_2$: 0.4 g/L; $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$: 0.3 g/L; pH: 4.6–5.0; T : 20 °C).

The presence of the compounds of pentavalent molybdenum in the coating at an increased duration of its formation is apparently due to the fact that the discontinuity of the coatings associated with its prolonged residence in the solution increases the ability of reduction from Mo^{6+} to Mo^{5+} by a metal of substrate, as confirmed by the spectrum shown in Figure 7.

The results show that it is the presence of molybdenum compounds in the coating that provide coatings with their high protective ability. Despite the fact that the thicknesses of the coatings formed during the optimal time (3 min), in a solution containing no molybdenum compounds and in their presence differ insignificantly (Figure 8a), the protective ability in the second case was much higher (Figure 8b).

In addition, molybdenum-containing coatings are characterized by greater hydrophilicity: the contact angle of these coatings is equal to 29° compared with the 52° for coatings that do not contain molybdenum oxides. The hydrophilicity of the adhesive layer under the PVC is a positive factor contributing to the adhesion strength of water-soluble paint-and-varnish materials.

4. Conclusions

Thus, the fact of contact precipitation of nickel onto metal substrates, and the further formation of a titanium-containing film, are experimentally confirmed for the first time in the present study. It has also been shown that the coatings consist mainly of titanium oxides and metals of the substrate.

The data obtained regarding the dependence of the coating thickness on the linear rate of the solution flow relative to the surface being treated confirm indirectly that the formation of insoluble titanium oxides occurs due to the alkalization of the solution layer adjacent to the surface.

It has been established that coatings on a steel substrate contain only titanium (IV) oxides, and on zinc and aluminum substrates, coatings contain the oxides of titanium (IV) and titanium (III).

It has also been shown that in the presence of hexavalent molybdenum compounds in the solution as oxidizers, molybdenum is included in the coating in the form of oxides. Findings reveal that in the lower layers of the coating, molybdenum is contained in the form of the compounds of molybdenum (V) and (VI), while in the upper layers, it is contained only in the form of the compounds of molybdenum (VI).

Based on the results of this experimental study, we propose the following mechanism of the formation of coatings:

When the treated metal makes contact with the solution, Reactions (1) and (2) start to proceed, leading to the alkalization of the solution at the surface. As a result, conditions are created for the displacement of the equilibria, as follows:

towards the formation of insoluble oxides, which are first adsorbed on the surface of the heavy metal (Ni) deposited on the treated substrate by contact reduction, and further expand, forming a continuous coating.

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