

CONVERSION COATINGS

Two-Step Oxidation of Steel in Nitrate Solutions

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Received July 18, 2013

Abstract—The possibility of increasing the thickness of a magnetite coating (MC) and its heterogeneity due to successive oxidation of low-carbon steel in two baths based on ammonium nitrate solutions has been shown. Results are shown of a comparative corrosion test of steel with an MC obtained during single- or two-step oxidation in nitrate solutions, with further passivation by the IFKhAN-39U composition, which show the advantages of oxidation in two baths.

Keywords: low-carbon steel, corrosion, magnetite coatings, corrosion protection, passivation

DOI: 10.1134/S2070205116070169

INTRODUCTION

One methods for protection of items made of carbon steels from atmosphere corrosion is the formation of magnetite coatings (MCs) on their surface. In the studies that began at the Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, at the beginning of the 1990s [1], much attention was devoted to the preparation of MCs in weakly acidic solutions of ammonium nitrate. The oxidation in these baths favorably differs from the conventional alkali bluing in concentrated NaOH solutions in having a lower temperature of the process, as well as ecological parameters.

However, the obtained MCs possess weak protective properties; therefore, they are usually modified by various additives into the oxidizing solution, which change the structure of the surface. There are two methods for the improvement of the properties of MCs. In one of them, additives are used that decrease the defectiveness of MCs and improve their protective properties. As an example, they include some complexes of hydroxyethylidene diphosphonic acid [2], lithium [3] or aluminum [4] nitrates. The other method involves the formation of a thick porous MC, which is then impregnated with passivation solutions. One example is the use of ammonium persulfate additives, which increase the MC thickness and provide an increase in their anticorrosion properties only along with passivating treatment, for example, by an aqueous solution of IFKhAN-39 inhibitor [5].

In this method, development of the MC surface is important, because, the better the heterogeneity of the

coating, the better the initial adsorption of passivating agent proceeds. For this reason, we focused on the two-stage oxidation of steel, which was recently used upon alkali bluing in order to increase the MC thickness [6].

At the first stage of this process, a thin continuous MC is formed, which slows down the dissolution of steel. The second step is carried out in another oxidation bath, where this coating is partially dissolved, so that only the framework of the film remains, which consists of coarse crystals. These crystals act as new crystallization centers, during the growth of which a continuous, but a thicker, film is formed again.

EXPERIMENTAL

All studies were carried out on low-carbon steel of St3 brand. To prepare MCs, flat samples with sizes of $10 \times 15 \times 2$ mm were stripped by the polishing paper up to the mirror shine, degreased with ethanol, pickled in 15% HCl, and oxidized in ammonium nitrate solutions with and without and various additives at temperature $t = 96\text{--}98^\circ\text{C}$.

Oxidized samples were rinsed with water, dried with filter paper, and conditioned for at least 16 h in a desiccator over CaCl_2 . The MC thickness (per pore-free oxide) was evaluated from the weight loss of the sample after its removal in 2% acetone solution of HCl (30–40 s). For passivating treatment, 10% aqueous solution of IFKhAN-39U (10 min) was used [7].

For electrochemical studies, we used a cylindrical sample fixed in the Teflon holder in such a way that

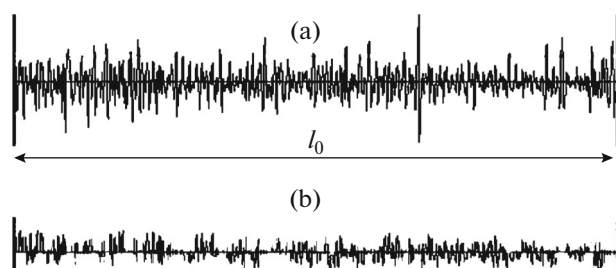


Fig. 1. Example of the profile of a steel sample with an MC: (a) full (maximum) profile and (b) minimum profile.

only the cylinder basis would be the working surface ($S = 0.785 \text{ cm}^2$). Stripping was performed by polishing papers up to no. 0; then, the sample was degreased by ethanol. To record chronopotentiometric curves, a glass thermostatted cell ($V = 0.05 \text{ L}$) with nonseparated cathodic and anodic compartments was used. Constant temperature ($t = 98^\circ\text{C}$) was maintained using a U5 ultrathermostat with the exactness of $\pm 0.5^\circ\text{C}$. The heat carrier was ethylene glycol (bp 197.8°C). The cell was filled with a working electrolyte that was heated to $t = 98^\circ\text{C}$, the electrode was fixed, and recording of the potential was started.

The electrode potentials (E) were measured relative to a saturated silver-chloride electrode and presented in the normal hydrogen scale. The potential of local depassivation E_{pt} was determined at room temperature in borate buffer solution with pH 7.4 containing 0.015 M NaCl.

The surface profile was recorded using a 130.001-PS profilometer (OAO Zavod PROTON-MIET, Zelenograd) connected to a computer. The surface roughness (σ) was calculated according to the following equation:

$$\sigma = l/l_0,$$

where l is the path of the contact needle along the sample surface and l_0 is the run out length. In this case, the maximum roughness was referred to as the full path and the minimum as the path without the assumption of peaks on the plot of profile (Fig. 1).

Protective properties of coatings were evaluated with time until the appearance of corrosion damage in tests both in the G-4 thermal moisture chamber with the cyclic change of t corresponding to 8 h at 40°C and 16 h at 25°C and in the salt spray chamber at $t = 35^\circ\text{C}$ with the following cycle: 15 min of chloride spraying and 45-min conditioning.

RESULTS AND DISCUSSION

A solution based on ammonium nitrate with a zinc nitrate additive, which possesses inhibiting action with respect to the dissolution of iron, was used as the first oxidation bath [8]. In the second bath, there was the

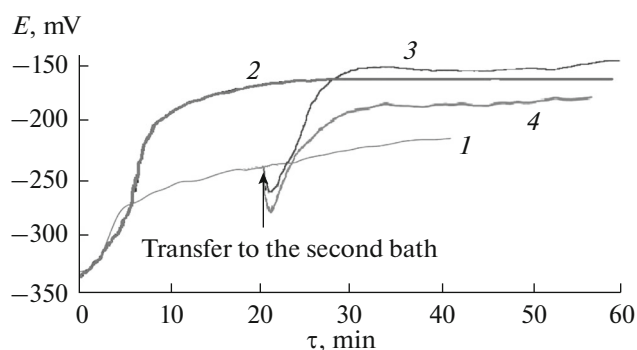


Fig. 2. Dependence of the potential of free corrosion on the time of oxidation of St3 steel (98°C) in (1, 2) one or (3, 4) two baths: (1) 25 g/L NH_4NO_3 + 0.2 g/L $\text{Zn}(\text{NO}_3)_2$, (2) 25 g/L NH_4NO_3 , (3) the first bath is 25 g/L NH_4NO_3 + 0.2 g/L $\text{Zn}(\text{NO}_3)_2$ and the second bath is 25 g/L NH_4NO_3 , and (4) the first bath is 25 g/L NH_4NO_3 + 0.2 g/L $\text{Zn}(\text{NO}_3)_2$ and the second bath is 25 g/L NH_4NO_3 + 0.15 g/L $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

solution of ammonium nitrate without or with the additive of known MC growth accelerators, namely, aluminum nitrate [4] and ammonium persulfate [5].

To evaluate the degree of extension of surface, we recently used flicker–noise spectroscopy, using which one can evaluate the degree of surface nonuniformity of coating and its corrosion ability [9]. It used the results of the measurements, which were performed using atomic force microscopy (AFM), which shows the roughness at the particular surface area of the sample. However, AFM does not allow qualitative determination of the roughness value above $1 \mu\text{m}$; therefore, in this work, the heterogeneity of the surface was evaluated by the two-dimensional profile, an example of which is given in Fig. 1.

One can suggest that, the higher the difference between the values of maximum and minimum roughnesses ($\Delta\sigma$), the higher the heterogeneity of the MC surface. As follows from the table, the maximum value $\Delta\sigma$ is in the case of MCs, which were prepared upon two-stage oxidation by the solution of ammonium nitrate with or without the additive of ammonium persulfate in the second bath. The thicknesses of MCs prepared in these cases are similar.

Chronopotentiograms, which were recorded in oxidizing solutions, show (Fig. 2) that, while the final potential of the formation of MCs is less than in the usual solution of ammonium nitrate in the first bath containing the additives of zinc nitrate, the transfer of the sample to the second bath increases it by several times. Consequently, one can anticipate an increase in the protective ability of MCs. When there is ammonium persulfate in solution, the final potential of steel is lower due to the higher porosity of the coating [5].

To evaluate the corrosion strength of steel with MCs after the end of oxidation, the anodic polarization curves were recorded in borate buffer solution

containing aggressive chlorides. As follows from the results of the measurement of the potential of steel during oxidation (Fig. 2), its value in the second bath reaches a plateau after 20 min; therefore, MCs, which were obtained after 40 min in a single bath and oxidized for 20 min in the first one and 20 min in the second bath, were compared.

As follows from Fig. 3, for the coatings obtained in single bathes, the current starts to grow rapidly already in the range of potentials $E = 0-0.02$ V. This can be the consequence of that MC is very porous and, thus, weakly protects against corrosion. The use of two-stage oxidation increases the potential of the current growth by 0.05–0.10 V, and these results weakly depend both on the composition of the second bath and the period of oxidation. In contrast, an increase in the time of treatment in the second bath (curve I'') and the use of ammonium persulfate additive (curve $2'$) decrease anode current, which may be related to the increase in the thickness of MC.

Assuming that a standard MC possesses weak protective properties, even slight (by standard measurements) increase in E_{pt} indicates growth of the protective effect for MC, which was prepared during two-stage oxidation and allows us to consider it to be highly effective after the passivating treatment by aqueous solution of corrosion inhibitors, which is usually used for oxidized steel. Indeed, the passivating treatment of single-stage MC by the composition IFKhAN-39U increases E_{pt} to 1.7 V, whereas the analogous treatment of MC formed upon two-stage oxidation increases it up to 1.9 V.

Corrosion tests according to GOST (State Standard) 9054–75 in a G-4 thermal moisture chamber confirmed the advantages of two-stage oxidation after impregnation of an MC with the inhibitor solution. The samples with an MC obtained upon two-stage oxidation (the first bath is the solution of ammonium nitrate with the additives of zinc nitrates, and the second bath is the ammonium nitrate solution with or without the additive of ammonium persulfate) were not exposed to corrosion damage within at least 120 days after passivation by aqueous solution of IFKhAN-39U (tests are continuing). Under analogous tests of the

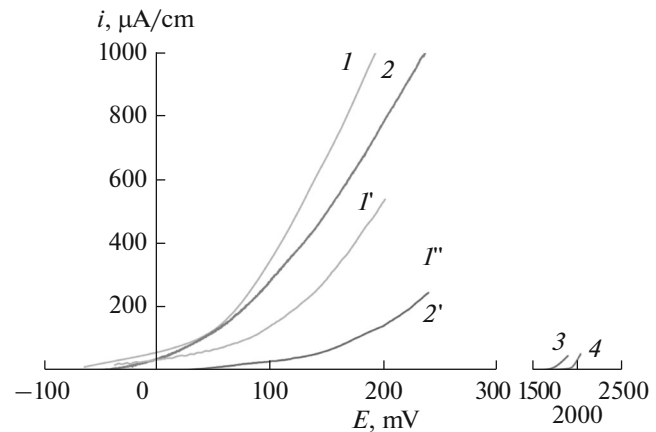


Fig. 3. Anode polarization curves of oxidized St3 steel in borate buffer solution (pH 7.4) containing 0.15 M NaCl. Oxidizing solutions are as follows (98°C, pH 5.0–5.5): (1) 25 g/L NH_4NO_3 (40 min), (2) 25 g/L NH_4NO_3 + 0.15 g/L $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (40 min), ($1'$) first bath is 25 g/L NH_4NO_3 + 0.2 g/L $\text{Zn}(\text{NO}_3)_2$ (20 min) and the second bath is 25 g/L NH_4NO_3 (20 min), ($1''$) the first bath is 25 g/L NH_4NO_3 + 0.2 g/L $\text{Zn}(\text{NO}_3)_2$ (20 min) and the second bath is 25 g/L NH_4NO_3 (40 min), ($2'$) the first bath is 25 g/L NH_4NO_3 + 0.2 g/L $\text{Zn}(\text{NO}_3)_2$ (20 min) and the second bath is 25 g/L NH_4NO_3 + 0.15 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (40 min), ($3'$) the steel oxidized in the solution (1) after impregnation with 10% IFKhAN-39U solution, ($4'$) the steel oxidized in the solution ($1''$) after impregnation with 10% IFKhAN-39U solution.

samples oxidized in one bath and passivated in the same solution, the first traces of corrosion appeared after 58 days.

Tests under more rigid conditions, namely, in the salt spray chamber, showed that two-stage oxidation followed by passivation increases the time of protection of steel by four to six times as compared to the single-stage process. In the latter case, corrosion damage appears already after 8 h of exposure of the sample and then develops rapidly along the surface. The period of full protection of steel after two-stage oxidation and passivation by the same inhibitor solution is as high as 36–48 h, while further development of damaged sections occurs more slowly than in the previous case.

Parameters of minimum (σ_{\min}) and maximum (σ_{\max}) roughness and thickness of an MC obtained upon oxidation in two bathes depending on the composition of the second bath (40 min). The first bath is 25 g/L NH_4NO_3 + 0.2 $\text{Zn}(\text{NO}_3)_2$ (98°C, 20 min)

Solution	Minimum roughness σ_{\min}	Maximum roughness σ_{\max}	Thickness d , μm
Without 2nd bath	0.8	1.7	1.1
2nd bath: 25 g/L NH_4NO_3 + 0.15 g/L $(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.8	2.4	1.5
2nd bath: 25 g/L NH_4NO_3 + 0.3 g/L $\text{Al}(\text{NO}_3)_3$	1.2	2.5	1.2
2nd bath: 25 g/L NH_4NO_3	1.4	2.9	1.4

CONCLUSIONS

1. Two-stage oxidation of steel in neutral nitrate solutions allows obtaining thicker MCs than those within a single stage and increases the extension of the surface.

2. Passivation of this MC by the IFKhAN-39U composition decreases its corrosion ability as compared to the single-step process.

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Translated by A. Muravev