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Using cyclic voltammetry to determine the protective ability of phosphate coatings

***V.Statsyuk*[1], *A.Bold*[1,2], *M.Zhurinov*[1], *L.Fogel*[1], *L.Sassykova*[2], *T.Vagramyan*[3], *A.Abrashov*[3]**

[1]D.Sokolsky Institute of Fuel, Catalysis and Electrochemistry, JSC, 142 Kunaev Str., 050010 Almaty, Kazakhstan
[2]Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, 71 Al-Farabi Ave., 050040 Almaty, Kazakhstan
[3]D.Mendeleev University of Chemical Technology of Russia, 9 Miusskaya Sq., 125047 Moscow, Russia

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The paper presents experimental material and its discussion on the use of cyclic voltammetry to determine the optimal conditions for the formation of protective anticorrosive coatings on the surface of iron samples deposited from phosphating solutions containing phosphatization accelerators of various nature (hydroxylamine, nitrophenol). The concentration of phosphate accelerators was established on the basis of a change in the cathode current maximum due to the electroreduction of products during the sequential cycling of current-voltage curves on a steel electrode without updating the surface of phosphate films in a solution of 0.3 M Na_2SO_4. The optimal concentration of the phosphate accelerator was found by the absence of a current maximum on the cathode part of the cyclic current — voltage curves during sequential cycling. According to this method, the optimal concentrations of the phosphating accelerators of hydroxylamine and nitrophenol were determined. The data obtained are consistent with the protective ability of phosphate coatings, defined by the drip method of Akimov.

Keywords: phosphate coatings, corrosion resistance, voltammetry, hydroxylamine, nitrophenol.

Використання циклічної вольтамперометрії для визначення захисної здатності фосфатних покриттів. *В.Стацюк, А.Болд, М.Журинов, Л.Фогель, Л.Сассікова, Т.Ваграмян, О.Абрашов.*

Досліджено можливість використання циклічної вольтамперометрії для визначення оптимальних умов формування захисних антикорозійних покриттів на поверхні залізних зразків, осаджених з фосфатуючих розчинів, що містять прискорювачі фосфатування різної природи (гідроксиламін, нітрофенол). Концентрацію прискорювачів фосфатування встановлено на підставі зміни катодного струму максимуму, обумовленого електровідновленням продуктів у процесі послідовного циклювання вольтамперних кривих на сталевому електроді без відновлення поверхні фосфатних плівок у розчині 0,3 М Na_2SO_4. Оптимальну концентрацію прискорювача фосфатування знайдено за відсутності струму максимуму на катодній частині циклічних вольтамперних кривих у процесі послідовного циклювання. За цим методом визначено оптимальні концентрації прискорювачів фосфатування гідроксиламіну і нітрофенолу. Отримані дані узгоджуються з захисною здатністю фосфатних покриттів, що визначена за методом Акімова.

Исследована возможность использования циклической вольтамперометрии для определения оптимальных условий формирования защитных антикоррозионных покрытий на поверхности железных образцов, осажденных из фосфатирующих растворов, содержащих ускорители фосфатирования разной природы (гидроксиламин, нитрофенол). Концентрация ускорителей фосфатирования устанавлена на основании изменения катодного тока максимума, обусловленного электровосстановлением продуктов в процессе последовательного циклирования вольтамперных кривых на стальном электроде без обновления поверхности фосфатных пленок в растворе 0,3M Na_2SO_4. Оптимальная концентрация ускорителя фосфатирования найдена по отсутствию тока максимума на катодной части циклических вольтамперных кривых в процессе последовательного циклирования. По этому методу определены оптимальные концентрации ускорителей фосфатирования гидроксиламина и нитрофенола. Полученные данные согласуются с защитной способностью фосфатных покрытий, определенной по методу Акимова.

1. Introduction

Constantly increasing requirements for protective coatings with anti-corrosion properties result in the need to improve the process of their formation. This problem requires reliable, easily defined criteria for the protective properties and quality of the formed anti-corrosion coatings. Today, a large number of methods have been proposed for assessing the protective properties of anticorrosion coatings on a metal surface [1–16]. Since all corrosion processes are caused by the occurrence of electrochemical reactions, electrochemical methods [17–21] which are characterized by high expressivity and measurement accuracy can be used to evaluate and control the protective properties of anticorrosion coatings. The present study is devoted to the development of an easily defined criterion for the formation of phosphate coatings with high anticorrosive properties on an iron electrode in the presence of nitrophenol and hydroxylamine phosphate accelerators using cyclic voltammetry.

Our approach to determining the corrosion resistance of phosphate coatings is based on a comparison of cyclic current-voltage curves obtained for the updated surface of an iron electrode with similar curves obtained for a surface with a phosphate coating. Of particular interest is the use of electrochemical methods to obtain qualitative and quantitative characteristics, with which you can establish the electrochemical activity and anticorrosive ability of the resulting coatings in a wide range of potentials. The use of accelerators of a different nature made it possible to obtain phosphate coatings with high anticorrosive properties on iron samples. The protective ability of the formed coatings was evaluated by the drip method of Akimov in combination with the method of cyclic voltammetry.

2. Experimental

The formation of protective anti-corrosion coatings on iron samples and electrodes (St. 3) was carried out using a phosphate solution FR-2, having the following composition: ZnO — 1.16 g/l; $NiNO_3 \cdot 6H_2O$ — 0.5208 g/l; HNO_3 — 0.614 ml; H_3PO_4 — 1.472 ml; $NaOH$ — 0.252 g/l. The deposition of phosphate coatings was carried out under optimal conditions in this solution: a temperature of 40°C, a deposition time of 10 min, and stirring speeds of 500 rpm. Hydroxylamine and nitrophenol were used as phosphate accelerators. After deposition of the coating, iron samples and electrodes were washed with distilled water and dried in a drying chamber at a temperature of 120°C for 10 min.

The reagents used in the work: sodium sulfate Na_2SO_4, zinc oxide ZnO, nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$, nitric acid HNO_3, phosphoric acid H_3PO_4, sodium hydroxide $NaOH$, nitrophenol $C_6H_5NO_3$, and hydroxylamine NH_2OH had the mark "Chemically Pure" and "High Pure". Distilled water was used to prepare the solutions. Preliminary treatment of iron samples was carried out using abrasive materials, followed by washing with distilled water.

To establish the protective ability of the obtained phosphate coatings, Akimov's drip method was used in combination with the cyclic voltammetry method. The drip method for determining the corrosion resistance of a protective coating is based on the use of Akimov's reagent — a solution containing $CuSO_4 \cdot 5H_2O$, $NaCl$, and HCl [22]. According to this method, the protective ability of the coating (ASA) is estimated in seconds as the time of change in the color of the control area under a drop of solution from gray to red-brown.

Cyclic current-voltage curves were obtained using a Gamry 3000 potentiostat (USA) in a thermostated electrochemical cell. The working electrode was an iron (St. 3) disk with an area of 0.03 cm^2 in contact with the electrolyte. A platinum electrode was used as a counter electrode. The potentials given in the article were measured relative to a silver chloride electrode manufactured by Metrom (Switzerland) with a

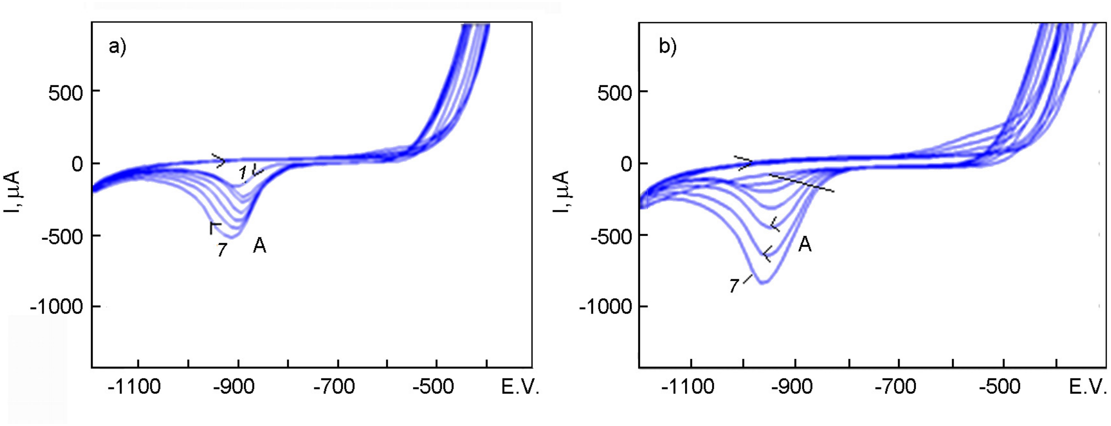

Fig. 1. Cycling current-voltage curves for an iron electrode without a phosphate film (a) and in the presence of a phosphate film (b).

potential of 196 mV relative to a hydrogen electrode. A solution of 0.3 M Na_2SO_4 was used as the electrolyte. Cyclic current-voltage curves were recorded in the potential region from −0.3 to −1.2 V with a potential sweep rate of 20 mV/s. Before obtaining cyclic current-voltage curves, the surface of the working electrode was updated with an abrasive material and washed with distilled water. Cyclic current-voltage curves for a phosphate-coated iron electrode were obtained without updating the electrode surface.

3. Results and discussion

Figure 1 shows cyclic current-voltage curves (with a number of cycles of 7) obtained for an iron electrode in the absence of a phosphate coating (Fig. 1a) and with a phosphate coating deposited from a phosphating solution FR-2 (Fig. 1b) in 0.3 M Na_2SO_4. According to Fig. 1, on the cyclic current-voltage curves of the iron electrode obtained from a solution of 0.3 M Na_2SO_4 in the cathode region, the current maximum (A) is observed in the potential region ($E \approx -0.9 \div 0.1$ V) due to the electroreduction of iron hydroxide compounds formed on the surface of the electrode during anodic polarization.

The current maximum (A) was used to judge the corrosion resistance of the formed phosphate coatings. With an increase in the number of cycles (1−7), a systematic increase in the cathode maximum (A) is observed. The cyclic current-voltage curves obtained for an iron electrode with a phosphate coating (Fig. 1b) are in many respects similar to the curves obtained for an iron electrode without a coating (Fig. 1a). However, for cycles (1−3), the maximum current (A) (Fig. 1b) is noticeably less than the maximum current (A) in Fig. 1a. With an increase in the number of cycles (5−7), the maximum current (A) on the cyclic current-voltage curves for an iron electrode with a phosphate coating (Fig. 1b) is noticeably larger than the corresponding maximum on the current-voltage curves of an uncoated iron electrode (Fig. 1a).

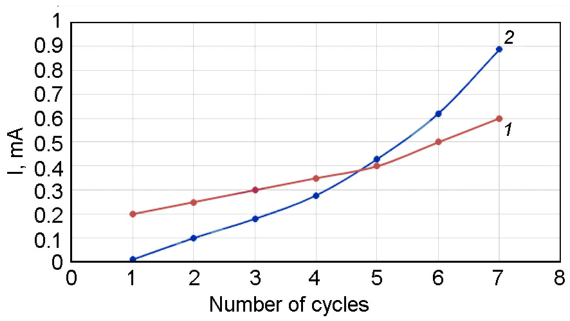

Fig. 2. Dependences of the maximum current (A) on the iron electrode in 0.3 M Na_2SO_4 on the number of cycles of the current-voltage curves without coating (curve *1*) and with a phosphate coating (curve *2*).

The effect of the number of cycles on the current value of the cathode maxima (A) can be more clearly seen in Fig. 2, which shows the dependence of the change in the current value of the cathode maxima (A) (curves *1*,*2*) on the number of cycles for the studied electrodes.

The observed change in the value of the cathode current maximum (A) during cycling allows us to conclude that the presence of a phosphate coating on the iron electrode leads to a noticeable decrease in the current maximum (A) only in the first cycles (1−3). With an increase in the number of cycles, the increase in the current maximum (A) for the iron electrode with a phosphate coating (curve *2*) noticeably exceeds the similar current maximum for an un-

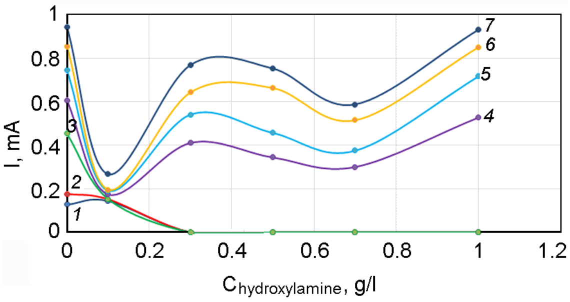

Fig. 3. Effect of hydroxylamine in a phosphating solution on cyclic current-voltage curves of a phosphate-coated iron electrode during cycling. Designations of cycles: *1* — 1, *2* — 2, *3* — 3, *4* — 4, *5* — 5, *6* — 6, *7* — 7.

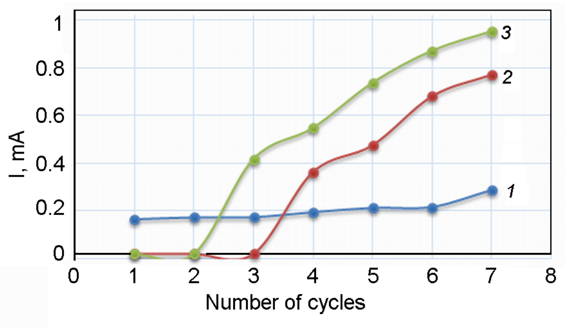

Fig. 4. Influence of the number of cycles of current-voltage curves on the maximum current (A) at different concentrations of hydroxylamine in the phosphating solution (g/l): *1* — 0.1, *2* — 0.5, *3* — 1.

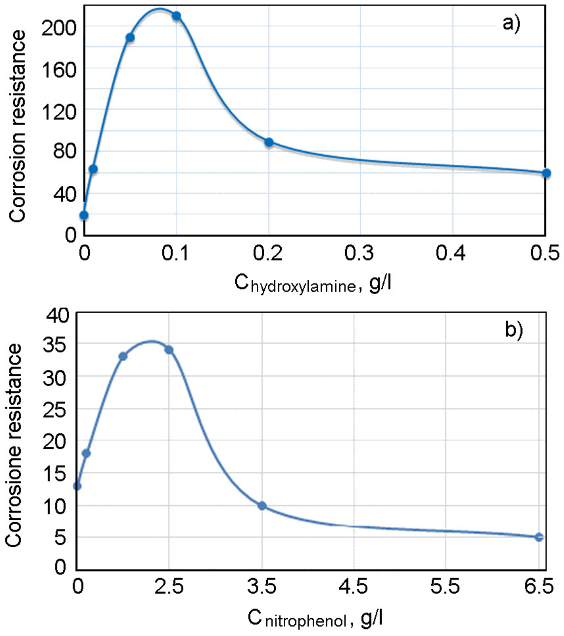

Fig. 5. Dependences of the corrosion resistance on the concentration of hydroxylamine (a) and nitrophenol (b) for phosphating coatings deposited on the surface of iron samples from a FR-2 solution.

coated iron electrode (curve *1*). It follows that a systematic change in the course of the cathodic and anodic processes when obtaining cyclic current-voltage curves in the studied potential region does not lead to an increase in the corrosion resistance of the phosphate coatings used, but, on the contrary, contributes to the course of corrosion processes.

In connection with the foregoing, it was of interest to use the cyclic voltammetry method for evaluation of the effect of phosphate accelerators (using hydroxylamine and nitrophenol as an example) on the change in the corrosion resistance of phosphate coatings on iron electrodes. Figure 3 shows the dependence of the change in the cathode maximum current (A) on the concentration of hydroxylamine in the FR-2 phosphating solution at a different number of cycles (1–7) on the cyclic current-voltage curves an iron electrode with a phosphate coating.

According to Fig. 3, with a small concentration of hydroxylamine in the phosphate solution, the maximum cathode current (A) is practically not observed on the cyclic current-voltage curves of the iron electrode (Fig. 3, curves *1*, *2*). However, when the concentration of hydroxylamine in the phosphating solution is close to 0.1 g/l, the maximum cathode current (A) does not change with the number of cycles (1–7) within the experimental error. This is most clearly seen in Fig. 4, which shows the dependences of the maximum current (A) on the number of cycles for different concentrations of hydroxylamine in the phosphate solution.

According to Fig. 4, at a hydroxylamine concentration of 0.1 g/l in the phosphate solution (curve *1*), the maximum cathode current (A) remains almost unchanged during the cycling process, while at higher concentrations, an increase in the maximum cathode current (A) is observed (curves *2*, *3*). Thus, when the concentration of hydroxylamine in the deposition solution FR-2 equals to 0.1 g/l, phosphate coatings having the highest corrosion resistance are formed.

It should be noted that the determination of the optimal concentration of the hydroxylamine phosphate accelerator based on the change in the maximum current (A) on the cyclic current-voltage curves is in agreement with experimental data obtained from the dependence of the protective ability of the phosphate coatings on the concentration of hydroxylamine determined by Akimov's method on iron samples.

Fig. 5 shows the dependence of changes in the protective ability of phosphate coatings on the concentration of hydroxylamine in a phosphate solution according to Akimov's method. According to Fig. 5, phosphate coatings obtained from a phosphating solution of FR-2 in the presence of 0.1 g/l hydroxylamine possess the greatest anticorrosive protective ability. At higher concentrations of hydroxylamine, the protective ability of the phosphate coating decreases. The data obtained are highly correlated with the results of electrochemical studies on the concentration of hydroxylamine (Fig. 5a) and nitrophenol (Fig. 5b) in the phosphate solution.

Of particular interest is to study the effect of the phosphate accelerator nature on the corrosion resistance of the formed phosphate coating. The effect of the nitrophenol concentration in the FR-2 phosphating solution on the corrosion resistance of phosphate coatings was studied by cyclic voltammetry. Fig. 6 shows the dependences of the maximum current (A) on the concentration of nitrophenol in the FR-2 phosphating solution for an iron electrode with a phosphate coating (Fig. 6a) and the dependences of the maximum current (A) on the number of cycles on the voltammetric curves (Fig. 6b).

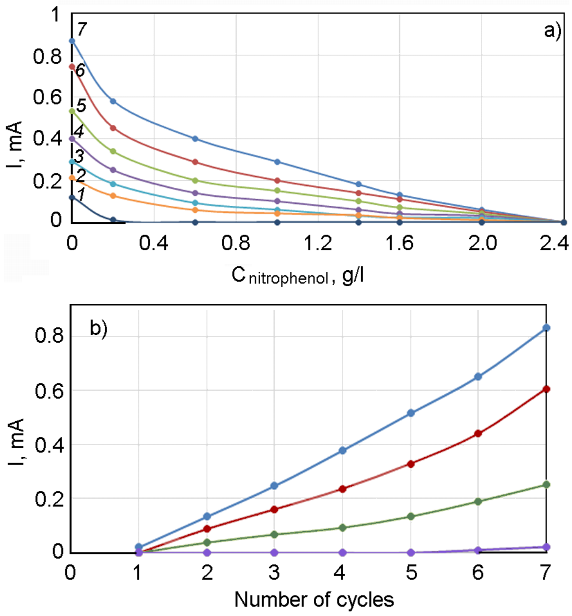

Fig. 6. Dependences of the current value of the cathode maximum (A) on the cyclic current-voltage curves of the iron electrode on the concentration of nitrophenol in the phosphating solution (numbering cycles: *1* — 1, *2* — 2, *3* — 3, *4* — 4, *5* — 5, *6* — 6, *7* — 7) (a) and the number of cycles at different concentrations of nitrophenol (g/l): *1* — 0.078, *2* — 0.25, *3* —1.3, *4* — 2.5 (b) .

According to Fig. 6a, for the first cycle, there is practically no maximum current (A) on the cyclic current-voltage curves in the studied range of nitrophenol concentrations in the phosphating solution. With an increase in the number of cycles, the maximum current (A) noticeably increases. Moreover, the greatest increase in the maximum current (A) is observed when using precipitation solutions containing low concentrations of nitrophenol. (curves 1–5). This is most clearly observed in Fig. 6b showing the dependence of the change in the maximum current (A) on the number of cycles for different concentrations of nitrophenol in the phosphating solution. According to Fig. 6b, with an increase in the concentration of nitrophenol, a decrease in the maximum current (A) is observed. At a nitrophenol concentration greater than 2 g/l, the maximum current (A) reaches a minimum value for the studied nitrophenol concentrations in the phosphating solution and does not depend on the number of cycles of sequential cycling of current-voltage curves. Therefore, the optimal concentration of nitrophenol, at which the maximum corrosion resistance of the formed phosphate coatings in the FR-2 solution is observed, is the concentration of 2–2.5 g/l.

4. Conclusions

Thus, the use of the electrochemical method of cyclic voltammetry made it possible to establish the optimal concentration of phosphatization accelerators of various nature, which provides complete corrosion protection of phosphate films on the surface of iron samples. The experimental data obtained are consistent with the independent method for determining the protective ability of phosphate coatings by Akimov's drip method.

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