Corrosion investigation of zinc coatings treated with silicon organic compounds

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Zinc coatings treated with organo-silicon compounds were investigated by an electrochemical method. The coatings were modified in tetraethoxisilane, methyltriacetoxisilane and triacetoximoxivinylsilane solutions. The silicon-organic compounds studies caused an increse of zinc polarization resistance. The corrosion behaviour of these coatings depended on the nature of silicon organic compounds, as well on its concentration and the time of application.

Keywords: zinc coatings, organo-silicon compounds, corrosion, tetraethoxisilane, methyltriacetoxisilane, triacetoximoxivinylsilane

INTRODUCTION

Zinc coatings are widely used for prevention of steel corrosion. As a rule, deposited zinc coatings undergo passivation. The best known passivation method is chromatizing. The surface layer created by chromatizing provides good protection, but it is toxic due to the chromium compounds involved. In addition, there are some problems dealing with hydrogen removal from the coated products as chromatized layers are not resistant at elevated temperatures.

The treatment of steel [1], aluminum, and magnesium Mg-1 [2] by alkoxi- and chlorosilanes has been suggested as an alternative method of metal passivation. The increase in metal resistance to corrosion may be caused by adhesive links between the metal surface and the silane layer. Adhesive links of this kind were employed at first, to enhance the bonding strengths between polymers and various surfaces [3, 4]. It is supposed that the silanes create adhesive sites on the surface and so enhance the adhesion of polymeric coatings. Alkoxi- and chlorosilanes, having Si-OR and Si-Cl groups, can easily hydrolyze and react with a hydroxilated surface (S), (*e.g.* glass) as follows (1, 2) [5]:

$$S|\text{-}(OH)_n + nR_3^1Si\text{-}OR \rightarrow S\text{-}(O\text{-}SiR_3^1)_n + nROH, \quad (1)$$

or

$$S|\text{-}(OH)_n + nR_3SiCl \rightarrow S\text{-}(O\text{-}SiR_3)_n + nHCl. \quad (2)$$

Thus, it can be considered that organo-silicon compounds are carriers of the links between a hydroxilated surface and polymeric coatings. The energy of these links is of an order 50–100 kkal/mol [6].

Silanols (R_3SiOH) and silanolates (R_3SiONa) form compounds with metal hydroxides in water. For example, they form ferrosilanes with iron hydroxides (3) [7]:

$$R_3SiONa + Fe(OH)_n \rightarrow R_3(SiO)_3Fe + NaOH. \quad (3)$$

These compounds are thermoresistant up to 300–400 °C due to covalent bond between Fe-O-Si. This type of bond was found by infrared spectroscopy method on an oxidized iron surface [8].

Since the surface of zinc is always hydroxilated, one can expect the occurrence of Zn-O-Si link on it, which further can react with silicon organic compounds. Electrochemical corrosion investigations of zinc coatings treated with silicon organic compounds would explain their interaction.

Therefore, the aim of this work was to investigate the corrosion behavior of zinc coatings modified by organo-silicon compounds.

EXPERIMENTAL

Electrochemical experiments were done in a standard three-electrode cell with the use of a PI-50-1 potentiostat.

The polarization resistance (R_p) values were obtained from potentiodynamic current-voltage measurements near the corrosion potential (±20 mV). The potential sweep rate was set 0.2 mV/s. This rate was sufficiently low to take measurements under steady-state conditions.

The reference electrode was zinc foil placed in a separate vessel and connected with the cell solution by means of a Luggin capillary. Its potential was monitored using a silver chloride electrode. The stable value for Zn electrode was achieved within 20–30 min after immersion.

Electrochemical measurements were carried out in 5% NaCl solution. Analytical grade salt and distilled water were used to prepare the solution.

An AgCl reference electrode was used for the measurement of cyclic voltammograms. Potencial sweep rate was 0.5 mV/sec.

A 99.99% pure zinc electrode was used for electrochemical experiments. It was pressed into a teflon body, its surface area amounted to 1 cm^2. Prior to each experiment, the zinc surface was abraded with fine-size emery paper, cleaned with filter paper, treated with a mixture of MgO and CaO (weight proportion 1:1) and washed with distilled water. Zinc coating 9 μk thick was deposited on the electrode from a Likonda ZnSR low acidity electrolyte at a cathodic curent density of 3 A/dm^2, washed successively with water, isopropyl alcohol and dried.

Protective layers were formed in the following organo-silicon compound solutions in isopropyl alcohol:

a) Tetraethoxisilane $Si\text{-}(O\text{-}C_2H_5)_4$ (silane a)

b) Methyltriacethoxisilane $CH_3\text{-}Si\text{-}(O\text{-}CO\text{-}CH_3)_3$ (silane b)

c) Triacethoximoxivinylsilane $CH_2 = CH\text{-}Si\text{-}(O\text{-}N = = C(CH_3)_2)_3$ (silane c).

The concentration of the above silanes in isopropyl alcohol was 1, 3, 5 and 10 g/l, respectively. The duration of zinc treatment in these solutions was 10, 20, 30, and 50 min. After treatment the samples were washed in isopropyl alcohol and underwent electrochemical investigation.

RESULTS AND DISCUSSION

In order to compare the corrosion resistance of various Zn coatings treated with organo-silicon compounds in aerated 5% NaCl, the polarization resistance method has been used. Similarly it was done in the paper [9].

A comparison of polarization resistance values of zinc in neutral NaCl solution (Fig. 1a) with that ones of samples treated with organo-silicon compounds enables to evaluate the interaction of these compounds with zinc. The R_p values of untreated Zn (curve 1) do not depend on the immersion time and are close to 0.5 $k\Omega \cdot cm^2$ while the presence of organo-silicon compounds (curves 2–5) on the surface of the electrodes increases the R_p values from 0.7 to ~ 3.0 $k\Omega \cdot cm^2$. The exact R_p value depends on

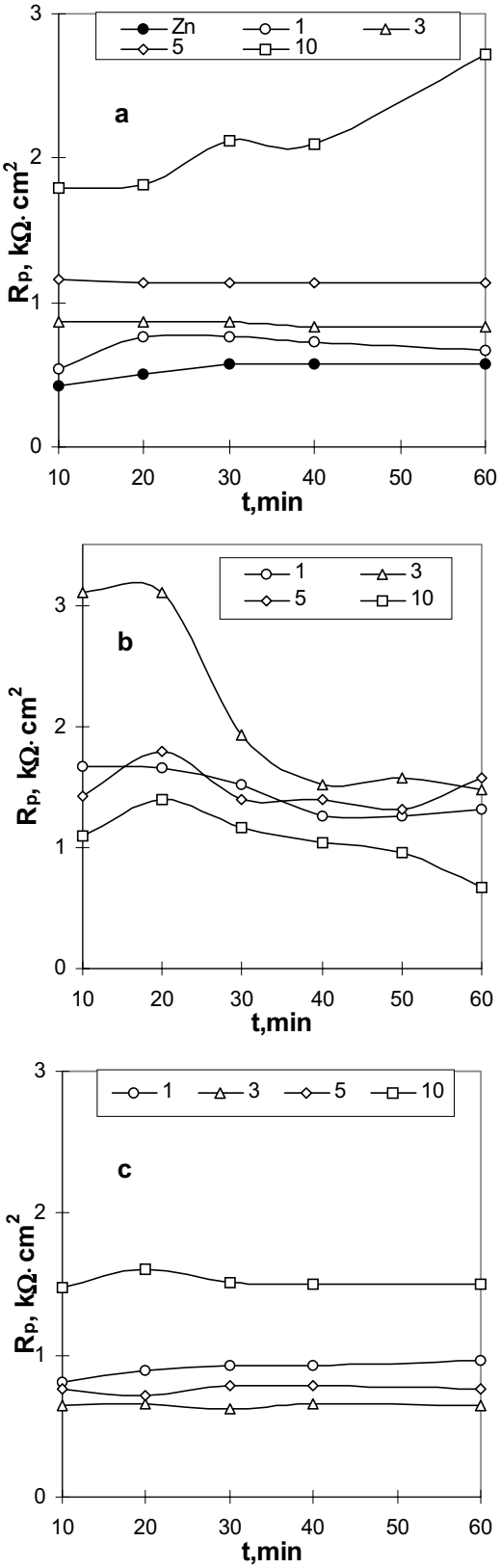

Fig. 1. Dependence of polarization resistance of non-treated zinc (*a*, curve 1) and for zinc treated with organo-silicon compounds (*a, b, c*) on the immersion time in 5% NaCl solution. Zinc was treated for 10 min in solution of tetraethoxisilane (*a*), methyltriacetoxisilane (*b*) and triacetoximoxivinylsilane (*c*). The concentration of silanes (in g/l) are indicated in the figures

the nature, concentration and application time of organo-silicon compounds.

Figure 1a depicts the influence of tetraetoxisilane concentration in isopropyl alcohol solution on the electrode R_p values. It can be observed that even the lowest concentration of tetraethoxisilane applied increases the R_p values of the Zn electrode. When its concentration is 1 g/l, $R_p \approx 0.73$ kΩ·cm^2. However, a significant effect is achieved when the silane concentration is 10 g/l, as R_p values are close to 2 kΩ·cm^2. The influence of sample immersion time in Cl^- solution is more evident for the highest tetraethoxisilane concentration, as R_p values after 60 min attain the value of 2.7 kΩ·cm^2.

The influence of the surface modification with tetraethoxisilane on the electrode corrosion behaviour can be observed from the data presented in Fig. 2a. It can be mentioned that the Zn treatment duration is not very important for the obtained R_p values, as after 10 min of Zn surface modification R_p does not change significantly.

The treatment of zinc with methyltriacetoxisilane causes a higher polarization resistance as well (Fig. 1b) compared to that of a zinc sample not treated with organo-silicon compounds (Fig. 1a, curve1). The highest R_p values in this system were observed when the silane b concentration was 3 g/l (Fig. 1b, curve 3). However, they decreased if the immersion time in NaCl solution was higher than 20 min. The influence of Zn surface treatment duration in silane b solution on it R_p values (Fig. 2b) is rather complex, however, it is evident from the initial moments of the sample immersion in NaCl solution that 20 minutes of surface modification is the optimal electrode treatment duration.

This phenomenona could be explained as follows. By the interaction of hydroxilated zinc with the methyltriacetoxisilane the decomposition of the latter occurs and acetic acid is formed. A scheme of this reaction could be as follows (4):

$$ZnOH + CH_3\text{-}Si(\text{-}O\text{-}CO\text{-}CH_3)_3 \rightarrow Zn\text{-}O\text{-}SiCH_3\text{-}(O\text{-}CO\text{-}CH_3)_{3\text{-}n} + nCH_3COOH. \quad (4)$$

Acetic acid could be formed not only by the creation of a film in isopropyl alcohol solution, but also by the further hydrolysis of this film in NaCl solution. Acetic acid occurring on the surface can change the character of zinc corrosion.

Cyclic potentiodynamic voltammograms in 5% NaCl solution showed that in the case of methyltriacetoxisilane a significant cathodic limiting current occurred (0.4 mA/cm^2) (Fig. 3, curve1), which could not be an oxygen reduction current. The initial corrosion potential of such an electrode moved towards a more negative values to about 50 mV, as compared to that

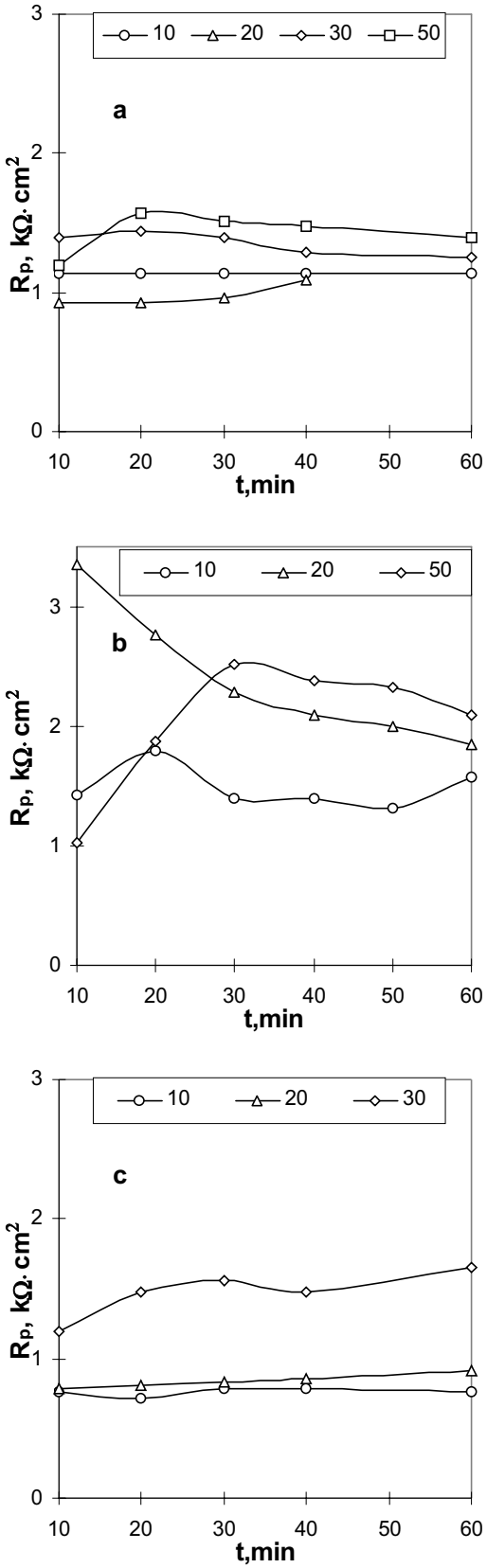

Fig. 2. Dependence of polarization resistance of zinc on the electrode immersion time in 5% NaCl solution. Zinc was treated with solutions of 5 g/l tetraethoxisilane (*a*), methylacetoxisilane (*b*) and triacetoximoxivinylsilane (*c*). Electrode exposure time (in minutes) in silane solutions is indicated in the figures

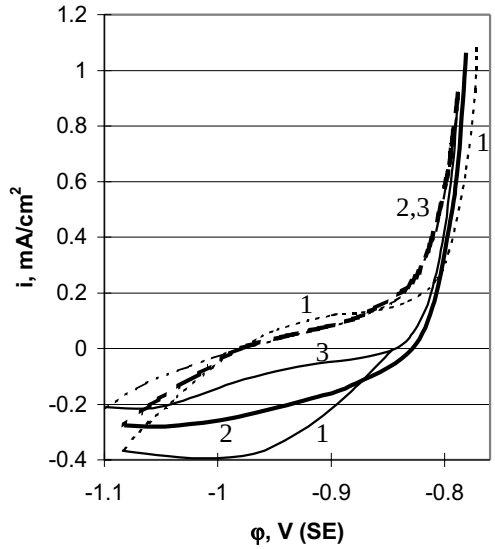

Fig. 3. Potentiodynamic voltammetric curves of zinc electrode treated for 10 min with 10 g/l methyltriacetoxisilane solution. Time of electrode immersion in 5% NaCl solution (in minutes): 1–0, 2–1, 3–5

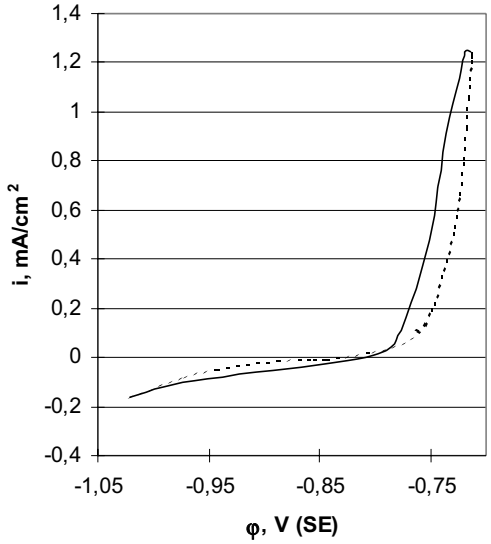

Fig. 4. Potentiodynamic polarization curve of Zn electrode not treated in 5% NaCl solution

of non-treated zinc (Fig. 4). During the following cycles, the cathodic current decreased and moved toward the negative potentials. After 5 min (Fig. 3, curve 3) in the third cycle the magnitude of the limiting current was equal to that of oxygen reduction, and the limiting current density (0.04 mA/cm^2) was observed at the potentials less negative than –1.03 V (SE).

To make sure that this limiting current was related to the reaction products described earlier, which formed in the film (created by treatment with silanes), the following test has been done. A zinc electrode prepared in the silane b solution under the same conditions as in Fig. 3, (*i.e*. treated for 10 min in 10 g/l silane (b) isopropyl alcohol solution), was immersed in water at 70 °C for 10 min to remove the soluble products from the film created by interaction of methyltriaceoxilane with zinc. The cyclic potentiodinamic voltammogram of zinc, prepared in such a manner is shown in Fig. 5. After washing away the soluble products, a significantly smaller limiting cathodic current was observed and at the same time the corrosion potential moved towards the positive potentials by 20 mV (Fig. 5, curve 1 and Fig. 3, curve 1). In this case the run of polarization curve is similar to that of zinc, treated with tetraethoxisilane (Fig. 6). Probably, after zinc interaction with methyltriacetoxisilane in NaCl solution, a mixed hydrogen and oxygen corrosion occurred. Oxygen corrosion takes place only after removal of acidic hydrolysis products (acetic acid or its derivative) from the silane film.

Polarization resistance dependence on zinc treated with triacetoximoxivinylsilane are shown in Figs. 1c and 2c. As one can observe from Fig. 1c, the R_p was higher than that of non-treated zinc (Fig. 1a) only when the concentration of silane c was 10 g/l. Besides, it was slightly dependent on the time of exposure in NaCl solution, but the duration of exposure in silane c solution exerted an influence upon polarization resistance (Fig. 2c) when the zinc electrode was exposed for 30 min. The R_p for such samples increased, and its value was within 1.5 kΩ·cm^2.

Different organo-silicon compounds employed for the modification of hydroxilated zinc would determine various runs of polarization curves. For example, the reaction of triacetoximoxivinylsilane with

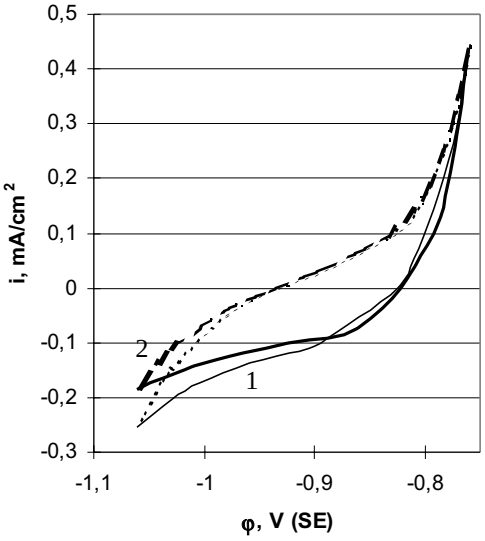

Fig. 5. Potentiodynamic voltammetric curves of zinc electrode, treated for 10 min with 10 g/l methyltriacetoxisilane solution and exposed for 10 min in 70 °C water in 5% NaCl solution. Time of electrode exposure in 5% NaCl solution (in minutes): 1–0, 2–5

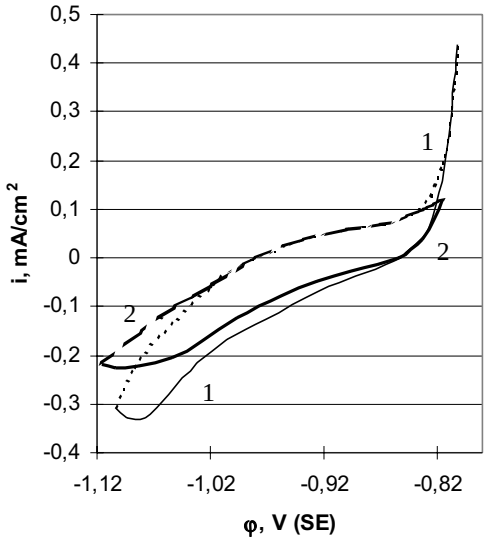

Fig. 6. Potentiodynamic voltammetric curves of zinc electrode treated for 10 min with 10 g/l tetraethoxisilane solution in 5% NaCl solution. Time of electrode exposure in 5% NaCl solution (in minutes): 1–0, 2–5

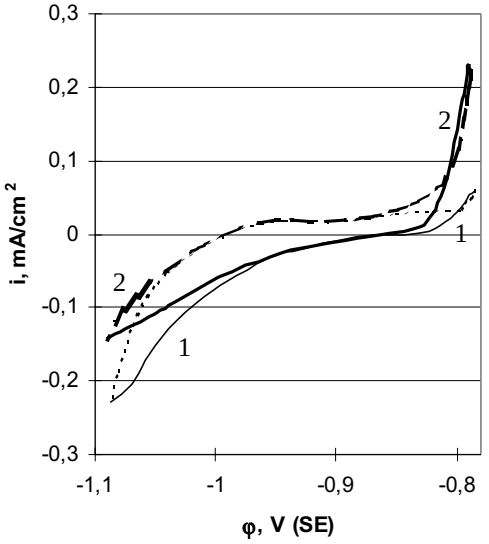

Fig. 7. Potentiodynamic voltammetric curves of zinc electrode treated for 10 min with 10 g/l triacetoximoxivinylsilane solution in 5% NaCl solution. Time of electrode exposure in 5% NaCl solution (in minutes): 1–0, 2–5

hydroxilated zinc formed a film to which the reaction product, acetoxime, could penetrate according to (5):

$$ZnOH + C_2H_3\text{-}Si(\text{-}O\text{-}N = C(CH_3)_2)_3 \rightarrow$$
$$\rightarrow Zn\text{-}O\text{-}SiC_2H_3(\text{-}O\text{-}N = C(CH_3)_2)_{3\text{-}n} +$$
$$+ n(CH_3)_2C = N\text{-}OH. \quad (5)$$

Figure 7 depicts the cyclic potentiodinamic voltammograms of zinc electrode treated with silane c compound. As one can see, the corrosion potential is shifted to the positiv side by 45 mV in comparison with a zinc coating non-treated with organosilane (Fig. 4). Meanwhile, the oxygen reduction current was negligible up to the potential –0.935 V, and when the potential was less than –0.935 V the cathodic current coincided with the polarization curves for zinc not treated with organo-silanes (Fig. 4). It is known that in this region of potentials oxygen reduction occurs [10]. By polarization of the electrode in an opposite direction, the anodic limiting current reached 0.04 mA/cm^2 when the potential was by 100 mV more negative than that of a non-modified zinc electrode, at which the anodic process begins. It is worth mentioning that by polarization of the electrode to a positive direction, when the corrosion potential exceeded 60 mV, the anodic current in the first cycle remained constant and began slightly to increase only later. After 5 min in the second cycle the anodic current was bigger than that of the first cycle at the same potential. Probably it was due to the reduction and oxidation of the hydrolysis products of a silicon organic compound in the film formed on the zinc surface.

CONCLUSIONS

Zinc coatings were modified in tetraethoxisilane($Si(O\text{-}C_2H_5)_4$), methyltriacetoxisilane ($CH_3\text{-}Si(O\text{-}CO\text{-}CH_3)_3$) and triacetoximoxivinylsilane ($CH_2 = CH\text{-}Si(O\text{-}N = C(CH_3)_2)_3$) solutions. Investigated silicon-organic compounds caused an increase of zinc polarization resistance. The highest R_p values were observed when the methyltriacetoxisilane concentration was 3 g/l. It was evident from the initial moments of the coatings immersion in NaCl solution that 20 minutes of surface modification was the optimal electrode treatment duration.

The influence of immersion time in silicon-organic compounds for investigated Zn coatings varies. For Zn coatings treated with tetraethoxisilane and triacetoximoxivinylsilane it increases, while for methyltriacetoxisilane 20 minutes is the optimal electrode treatment duration.

Received 2 July 1998
Revised version received 24 January 2000
Accepted 22 June 2000

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CINKO DANGŲ, MODIFIKUOTŲ SILICIO ORGANINIAIS JUNGINIAIS, KOROZINIAI TYRIMAI

S a n t r a u k a

Cinko dangos, modifikuotos silicio organiniais junginiais, tirtos elektrocheminiu metodu laisvai aeruojamame 5% NaCl tirpale. Dangos modifikuotos tetraetoksisilano, metiltriacetoksisilano ir triacetoksimoksivinilsilano tirpaluose.

Nustatyta, kad ištirti organiniai silicio junginiai padidina cinko dangų poliarizacinę varžą. Zinko dangų, paveiktų silicio organiniais junginiais, korozinis atsparumas priklauso nuo silicio organinio junginio prigimties, jo koncentracijos ir išlaikymo jame laiko.

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КОРРОЗИОННЫЕ ИССЛЕДОВАНИЯ ЦИНКОВЫХ ПОКРЫТИЙ, МОДИФИЦИРОВАННЫХ ОРГАНИЧЕСКИМИ СОЕДИНЕНИЯМИ КРЕМНИЯ

Р е з ю м е

Цинковые покрытия, модифицированные органическими соединениями кремния, исследованы электрохимическим методом в свободно аэрированном растворе NaCl. Для модифицирования покрытий использовались растворы тетраэтоксисилана, метилтриацетоксисилана и триацетоксимоксивинилсилана. Установлено, что исследованные органические соединения кремния повышают поляризационное сопротивление Zn покрытий. Коррозионная устойчивость этих покрытий зависит от типа органического соединения кремния, его концентрации и времени выдержки в нём.