

TI-BASED CONVERSION COATING FOR THE CORROSION PROTECTION OF ELECTROGALVANIZED STEEL

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Abstract

Process was developed for free-chromate passivation of zinc coatings. An optimal composition of the solution was developed. It was shown that titanium-based passivating coatings on the electrogalvanized steel articles compare well in corrosion resistance and protecting capacity with iridescent chromate coatings. It was revealed that, unlike chromate coatings, the developed titanium-based coatings withstand the thermal shock without degrading of characteristics.

Keywords: Corrosion protection, conversion coatings, Ti-based coatings, chromate-free passivation

1. INTRODUCTION

To improve the corrosion resistance of galvanic zinc and cadmium protective coatings, as well as aluminum surfaces, chromate processes are applied. Protective chromate films inhibit corrosion processes on the surfaces of these metals and, besides, have the ability to self-heal in case of mechanical violations of the integrity of the film [1].

Unfortunately, chromate solutions are very toxic because of the constituent ions of hexavalent chromium. The problem of replacing the chromating processes became more acute after the adoption of the European Directive 2000/53/EC in 2000 limiting the presence of Cr (VI) compounds in conversion coatings [2], and in 2002 the additions to the directive, which completely prohibits the presence of Cr (VI) in conversion coatings applied to parts of cars from July, 2007 [3]. The RoHS [4] and WEEE [5] directives also prohibit the presence of Cr (VI) in coatings of electrical and electronic equipment. In connection with this, the use of hexavalent chromium has recently been severely restricted.

Another significant disadvantage of the chromating processes is the low thermal stability of the coatings formed: when heated to temperatures of 160 ° C or more, their protective ability sharply decreases, which is unacceptable for parts working, for example, in the engine compartment or other "hot spots" of the car. In addition, as a result of thermoshock, chromate films lose the ability to self-heal [1].

A possible alternative to chromating is the chromite process - the formation of a protective film in solutions based on trivalent chromium [6,7]. The disadvantages of chromite films include the lack of the effect of "self-healing", as a result of which "white" corrosion appears much faster on zinc coatings with chromium passivation. In a number of cases, chromating processes are proposed to be replaced by passivation processes in cerium-containing [8,9], silicon-containing [10,11], or molybdate solutions [12].

According to some authors, the most promising replacement for chromate films are conversion zirconium oxide and titanium oxide coatings [13,14]. In the scientific articles some technologies for applying these conversion coatings are mentioned, however, the composition of solutions and process parameters are not disclosed by the authors. Domestic publications or patents on these processes in the scientific and technical literature, as well as in the Internet resources are absent.

The present work is devoted to the development of the process of applying protective conversion titanium-containing coatings to galvanized surfaces.

2. EXPERIMENTAL MATERIALS

The samples were of zinc-galvanized plates of cold rolled steel grade 08ps, widely used in the automotive industry. Zinc coating of steel samples was carried out in a weakly acidic electrolyte of the composition: ZnSO₄ 7H₂O 120 g/l; Na₂SO₄ 18H₂O 20 g/l; NaCl 30 g/l; CH₃COONa 25 g/l; TsKN-3 40 ml/l; TsKN-4 50 ml/l; $i=2$ A/dm²; $t=20^{\circ}\text{C}$.

For the preparation of solutions in this study the chemical reagents of pro analysis, pure grades, and distilled water were used.

An express method (drop method) using a solution containing Pb(CH₃COO)₂ 50 g/l was used to accelerate the evaluation of the protective ability of the conversion titanium-containing coatings. According to this method, the protective ability of the coating was estimated in seconds, like the time before the color change of the control section from the transparent to black under a drop of a solution on a zinc base.

The morphology of the surface was studied using an INTEGRA Prima atomic force microscope (NT-MDT, Russia). Scanning mode - semi-contact, cantilever - HA_NC Etalon (NT-MDT, Russia).

The thickness of the coatings was determined by an ellipsometric method using an ellipsometer Gartner equipped with a solid-state laser LSM-S-111 with a green filter.

The wetting angle at the surfaces of metal plates was measured on the Goniometer

LK-1. The photos of drops were taken with the camera "Levenhuk C310 NG", and then the wetting angle was calculated using the DropShape software.

XPS-spectra were obtained by means of a special chamber CLAM100, mounted on the Auger microscope HB100 (Vacuum Generators, GB).

Corrosion tests of cerium and silicon-containing coatings were carried out in a salt fog chamber Ascott S120iP in accordance with the international standard ASTM B117.

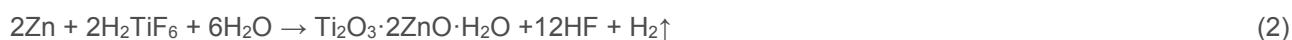
3. EXPERIMENTAL WORK

According to the recommendations from other studies, solutions for the formation of titanium-containing coatings should contain hexafluorotitanic acid as the main component, as well as heavy metal ions, that plate contactly or in form of compounds on the surface of the metal substrate, initiating the subsequent formation of protective coatings [15,16]. Taking this into account, Ni²⁺ nickel ions were introduced into solutions based on H₂TiF₆ in the form of a nitrate salt: Ni(NO₃)₂·6H₂O.

3.1. Determination of the parameters of the process of titanium-containing coatings deposition

The experiments carried out revealed the concentration range of the solution components in which it is possible to obtain homogeneous uniform coatings: 0.5-2.5 g/l H₂TiF₆ and 20-160 mg/l Ni²⁺. The protective ability of the coatings formed in this range determined by the drop method is about 7 seconds.

Studies have shown that the reasonable pH values of the solutions are in the interval of 4.0-5.5 units. Up to pH 4.0, no coatings are formed, and at a pH greater than 5.5, the coatings become non-uniform and discontinuous. Thus, the pH range 4.0-5.5 is optimal, which is consistent with the coating formation mechanism described in the literature. It is known that in this region of the pH hexafluorotitanic acid reacts with the zinc-galvanized surface forming titanium and zinc oxides that deposit and adsorb initially on the surface of the contactly deposited nickel. Over time this coating expands to form a continuous film.



In this study, the protective ability of coatings was investigated depending on the duration of the process. It was revealed that the protective capacity of the coating increases during the first minute of the process and then stabilizes at the values of protective ability. The immersion of coated sample in the solution for more than 4 minutes is undesirable, since this leads to a deterioration in the appearance of the coatings and a decrease in the protective ability. Taking into account the obtained results, the optimal process duration was assumed to be 1 min.

It was found that heating of solution to 40°C does not lead to significant changes in the appearance and protective ability of the coatings, but at higher solution temperatures, the protective ability decreases. Therefore, the range of 18-25°C was chosen for the operating range and it was noted that heating of the solution to 40°C, for example in the summertime, is allowed.

It was found that the protective ability of the coatings is affected by the drying temperature of the coatings, and the dependence is of an extreme nature: coatings dried at a temperature of 80-120°C have the greatest protective capacity (20 sec), and outside the interval, the protective ability of the coatings decreases.

The survey spectra of coatings obtained by the XPS revealed the presence of titanium, zinc, oxygen and fluorine compounds on the surface. Individual spectra of the elements made it possible to establish that zinc is included in the coating in the form of ZnO, and titanium in the form of TiO₂-Ti₂O₃, which agrees with the above-described mechanism of coating formation.

Investigating the morphology of coatings using atomic-force microscopy allowed us to determine the grain size of the coating: it does not exceed 50 nm.

The effect of hydroxycarboxylic acids such as citric, malic, tartaric, lactic and oxalic acids has been studied. It was found that the introduction of tartaric acid in the amount of at least 0.4 g/l increases the protective ability of the coatings obtained from 17 to 36 s.

3.2. Formation of top-coat at titanium-containing coatings

In order to increase the protective ability of chromite passivation coatings on zinc, practically the additional protection or "sealer" are used, which are thin organic or inorganic films that are applied as a finishing coat.

In this work, a nontoxic composition based on gallic acid esters was developed to form the final "top-coat" on titanium-containing coatings.

It was determined that the protective ability of titanium-containing coatings impregnated for 2 minutes in an aqueous solution containing 2.5 g/l of this composition at pH 4 and temperature of 18-30°C increases more than 8 times and reaches a value of 300 s.

It should be noted that the color and appearance of titanium-containing coatings almost has no difference with colorless chromate coatings on zinc, and impregnation of oxide-titanium coatings with the final composition changes the color of the coating from colorless to iridescent.

It is ellipsometrically established that the thickness of the titanium-containing layers is 60 nm, and after coating, the top-coat increases to 70 -80 nm, which is much less than the thickness of chromate coatings on zinc (200-1000 nm).

The increase of the thickness of the titanium-containing layers after finishing is apparently due to the formation of complex zinc and iron compounds with gallic acid in the pores and on the surface of titanium-containing coating.

3.3. Examination of coatings

It is known that the contact angle of the surface wetting, indicating the degree of hydrophilicity of the surface, can be a criterion of its corrosion-protective characteristics. Our investigations showed that the surface of galvanized steel is hydrophilic, the contact angle is 41° (**Figure 1a**). The surface of galvanized steel with a titanium-containing coating becomes hydrophobic: the contact angle is 92° (**Figure 1b**). For comparison: this parameter for a chromate coating is 85° (**Figure 1c**). The largest wetting angle (99°) and therefore the best protective characteristics has a surface of a titanium-containing coating with a "top-coat" (**Figure 1d**).

In order to identify the possibility of operating coatings under high-temperature conditions, the samples were exposed to heat shock: they were heated for 1 hour at a temperature of 160°C. It was found that the protective ability of titanium-containing coatings does not decrease after heating, while the protective ability of chromate coatings, as expected, decreased from 60 to 12 seconds.

To evaluate the passivating effect of titanium-containing coatings, the corrosion rate of galvanized samples passivated in a chromate and titanium-containing solution was determined, for which corrosion diagrams were obtained in a 5% NaCl solution. Comparison of the values of corrosion rates found from the diagrams shows that the corrosion resistance of zinc, passivated in a titanium-containing solution with subsequent finishing, is higher than that of chromated zinc: corrosion rates are $1.0 \cdot 10^{-4}$ and $3.6 \cdot 10^{-4}$ A/cm², respectively.

These results correlate the results of the cyclic corrosion test (ASTM B117) in a salt fog chamber (**Figure 2**).

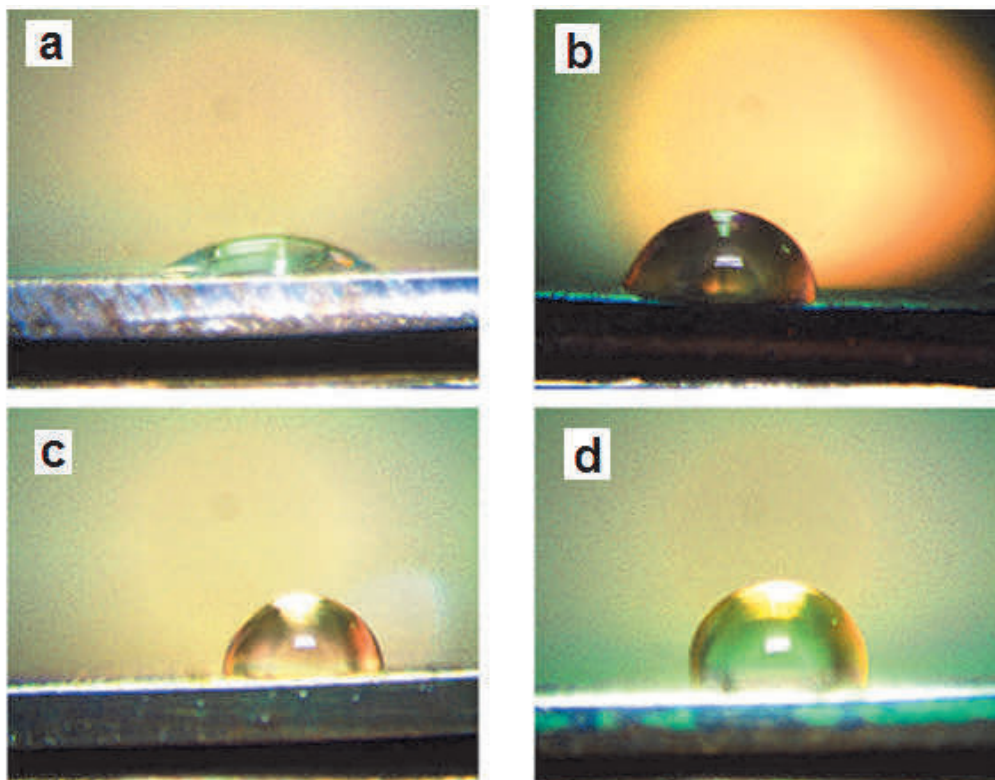


Figure 1 Wetting angle of:

a - electrogalvanized steel; b - chromated; c - titanium-oxide; d - titanium-oxide + top-coat

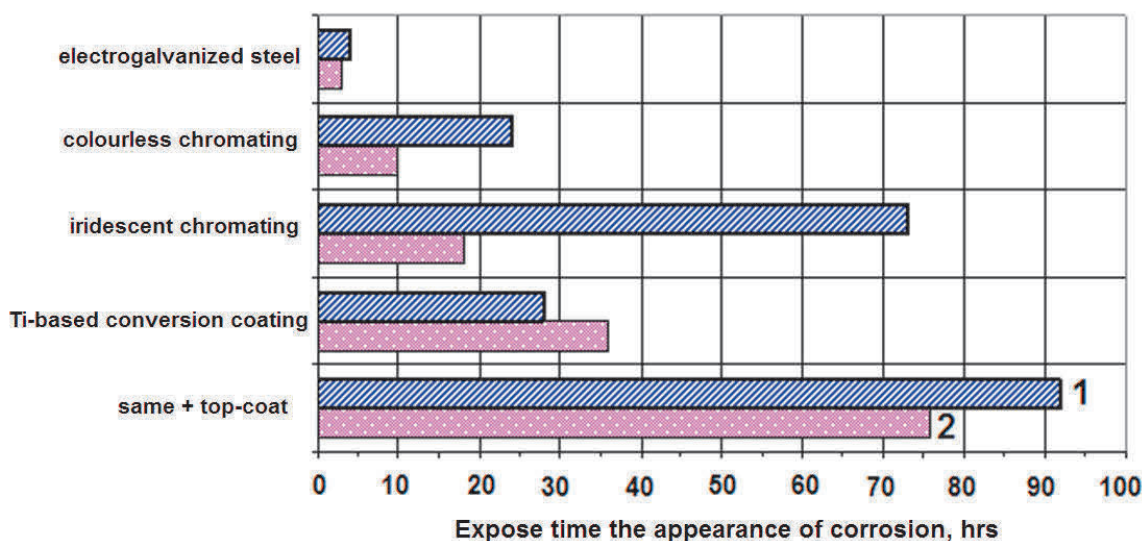


Figure 2 Expose time for the appearance of corrosion
1 - without thermal shock; 2 - after thermal shock

The time until the first white corrosion centers appear on titanium-containing coatings is 36 h, which exceeds the time prescribed for colorless chromate coatings on zinc (24 h). The time until the appearance of white corrosion for titanium-containing coatings with top-coat is 92 hours without a thermoshock, which exceeds the time (72 hours), standardized by ISO 9227:2012 for iridescent chromate coatings, and 70 hours after thermoshock (for chromate coatings is not regulated by ISO).

4. CONCLUSION

As a result of this research, it has been shown that the developed titanium-containing passivation coatings on galvanized steel parts for corrosion resistance and protective ability are comparable to iridescent chromate coatings, and in contrast to the latter, they can withstand a thermoshock without deteriorating of protective characteristics.

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REFERENCES

- [1] GARDNER A., SCHARF J. High Performance Alternative to Hexavalent Chromium Passivation of Plated Zinc and Zinc Alloys. *Electroplating & Surface Treatment*. 2002. V. X, №3, pp. 39.
- [2] Directive 2000/53/EC of the Parliament and the Council of Europe on September 18, 2000 "End-of-live-vehicles", *Official Journal of the European Communities* L269. pp. 34-43.
- [3] Replacement hexavalent chromium in automotive industry for ELV Directive. // Harris A. Bhatt, technical paper, *Sur/Fin*. 6/2002.
- [4] Directive 2011/65 / EC (RoHS II) of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment.
- [5] Directive 2002/96 / EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment.

- [6] H.H. SHEU, H.B. LEE, S.Y. JIAN, C.Y. HSU, C.Y. LEE Investigation on the corrosion resistance of trivalent chromium conversion passivate on electroplated Zn-Ni alloy. *Surface & Coatings Technology*. 2016, no 305, pp 241-248.
- [7] KEUNWOO CHO, V. SHANKAR RAO, HYUKSANG KWON Microstructure and electrochemical characterization of trivalent chromium based conversion coating on zinc. *Electrochimica Acta*. 2007, vol. 52, no. 13, pp. 4449-4456.
- [8] ZHELUDKOVA E.A., ABRASHOV A.A., GRIGORYAN N.S., VAGRAMYAN T.A. Passivation of Zinc Coatings in Cerium-containing Solutions. *Advances in Chemistry and Chemical Technology*. 2015, vol. 29, no 2 (161), pp. 83-85.
- [9] LIU GUANGMINGA, YU FEIB, YANG LIUA, et. al. Cerium-tannic acid passivation treatment on galvanized steel. *Rare metals*. 2009, vol. 28. no. 3, pp. 284.
- [10] MESHALKIN, V.P., ABRASHOV, A.A., VAGRAMYAN, T.A., GRIGORYAN, N.S. et. al. Development of composition and study of properties of a new high-efficiency silicon-containing protective conversion coating on zinc-plated surfaces. *Doklady Chemistry*. 2017, vol. 475, no 2, pp. 196-199.
- [11] XIAOKE YANG, YUNYING FAN, YEHUA JIANG, ZULAI LI Study on Chromium-free Colour Passivation for Zinc Coating Treated with Silicate. *Advanced Materials Research*. 2011, vol. 154-155, pp 1301-1304.
- [12] G.M. LIU, L. YANG, N. DU Study of molybdate-phytic acid passivation on galvanized steel. *Corrosion Engineering, Science and Technology*. 2011, vol. 46, no 4, pp. 542-546.
- [13] YU-TE TSAI, KUNG-HSU HOU, CHING-YUAN BAI, JEOU-LONG LEE et. al. The influence on immersion time of titanium conversion coatings on electrogalvanized steel. // *Thin Solid Films*. 2010. № 518. P. 7541-7544.
- [14] JOSIANE SOARES COSTA, RAQUEL DEI AGNOLI, JANE ZOPPAS FERREIRA Corrosion behavior of a conversion coating based on zirconium and colorants on galvanized steel by electrodeposition. // *Tecnol. Metal. Mater. Miner*. 2015. Vol. 12. №. 2. P.167-175.
- [15] ABRASHOV A.A., GRIGORYAN N.S., VAGRAMYAN T.A., KOLESNIKOV A.V. et. al. Protective Ceramic Titanium-Oxide Nanocoatings. *Glass and Ceramics*. 2015, vol. 71, no. 11-12, pp. 392-395.
- [16] ABRASHOV A.A., GRIGORYAN N.S., VAGRAMYAN T.A. ZHILENKO D.YU. Titaniferous protective coatings on aluminum alloys. *Non-ferrous Metals*, 2016, no 1, pp. 33-37.