DEVELOPMENT OF CHROMATE-FREE PASSIVATION PROCESSES FOR GALVANIZED STEEL

ABRASHOV Aleksey[1], ZHELUDKOVA Ekaterina[2], GRIGORYAN Nelya[3], VAGRAMYAN Tigran[4], MENSHIKOV Vladimir[5]

MUCTR - D.Mendeleev University of Chemical Technology of Russia, Moscow, Russian Federation
[1]abr-aleksey@yandex.ru, [2]ilyakhinaa@mail.ru, [3]ngrig108@mail.ru, [4]vagramyan@muctr.ru,
[5]vm_uti@muctr.ru,

Abstract

In recent years, nano-sized cerium and silicon-containing coatings have been increasingly used as alternatives to chromate layers on galvanized steel. The present work is devoted to the development of the technology for obtaining these coatings. The processes of applying cerium and silicon-containing coatings to galvanized steel have been developed. The solution for the application of cerium-containing coatings contains in its composition: 10-25 g/l $Ce(NO_3)_3•6H_2O$; 15-25 ml/l H_2O_2, 0.5-2 g/l PEG 1500.Solution for the deposition of silicon-containing coatings contains: 25-35 g/l $Na_2SiO_3•5H_2O$; 20-30 ml/l H_2O_2, 0.2-0.5 g/l oxyethylenediphosphonic acid (OEDP). It is established that the developed passivation coatings applied on galvanized steel parts for corrosion resistance and protective ability are comparable with chromate coatings. It has been revealed that cerium-containing coatings, like chromate coatings, have the ability to self-heal. It was revealed that, unlike chromate coatings, the developed cerium and silicon-containing coatings withstand the thermal shock without degrading of characteristics. It was established that the thickness of cerium-containing coatings is about 65 nm, and that of silicon-containing coatings is about 50 nm. It should be specially noted that the thickness of these coatings is noticeably less than the thickness of the chromate layers (200-1000 nm).

Keywords: Corrosion protection, conversion coatings, cerium-containing coatings, silicon-containing coatings, surface treatment, chromate-free passivation

1. INTRODUCTION

To improve the corrosion resistance of galvanic zinc protective coatings, chromate treatment processes are applied. The resulting conversion chromate films inhibit corrosion processes on the surfaces of these metals and, in addition, have the ability to self-heal at mechanical damage of the film. It is known that chromate solutions are highly toxic due to the hexavalent chromium ions. The problem of replacing the chromating processes has become critical after the adoption of the European Directive 2000/53/EC in 2000 restricting the presence of Cr (VI) compounds in conversion coatings [1], and in 2002 the amendments to the directive, which completely prohibits from July 2007 the presence of Cr (VI) in conversion coatings applied in the production of automobiles [2]. Similar directives have come into operation in China since March 1, 2007, and in South Korea since July 1, 2007. In addition, RoHS [3] and WEEE [4] prohibit the presence of Cr (VI) in metallic coatings of electrical and electronic equipment; the use of Cr (VI) limits the REACH regulation [5].

In the literature there are some technologies for the application of functional coatings that do not contain chromium in their composition, however, the composition of solutions and process parameters are not disclosed by the authors. A possible alternative to chromate treatment is the passivation processes in cerium and silicon-containing solutions. There are some scientific articles about applying these coatings, but also the composition of solutions and the parameters are not given. Russian publications or patents on these processes in the scientific and technical literature, as well as in the Internet resources are absent.

Thus, the present work is devoted to the development of the processes for the deposition of cerium and silicon-containing coatings as an alternative to the chromate treatment.

2. EXPERIMENTAL MATERIALS

The samples were of cold rolled automotive steel, galvanized right before passivation. Zinc plating of steel samples was carried out in a slightly acidic electrolyte of the composition: $ZnSO_4 \cdot 7H_2O$ 140 g/l; NH_4Cl 80 g/l; H_3BO_3 25 g/l; additive TsKN-3 40 g/l; additive TsKN-1 2 ml/l, $I = 4$ A/dm^2; $T = 20$°C. All the chemicals were of grades "pure", distilled water was used.

An express method using a solution containing $Pb(CH_3COO)_2$ 50 g/l was used to evaluate the protective ability of conversion cerium-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 thickness of the coatings was determined by an ellipsometric method using an ellipsometer Gartner on a solid-state laser LSM-S-111 with a green filter.

XPS measurements were performed on an OMICRON ESCA+ spectrometer (FRG) with the Mg-anode (the radiation energy 1253.6 eV and power 252 W). The pass energy of the analyzer was set at 20 eV. To take into account the charge of the samples, the position of the XPS peaks was standardized by the C1s peak of the hydrocarbon impurities from the atmosphere, the binding energy Eb of which was taken equal to 285.0 eV. The base pressure in the analyzer chamber was kept no higher than $8 \cdot 10^{-10}$ mbar. The spectra were deconvoluted into components after subtraction of the background determined by the Shirley method [6]. The peak position accuracy was determined of ± 0.15 eV. The element ratios were calculated using integral intensities under the peaks, taking into account the photoionization cross sections σ of the corresponding electron shells [7]. Using the integrated intensity of the peaks and the MultiQuant program [8], the thicknesses of the layers formed on the surface were calculated with allowance for the mean free path of the electrons λ, according to the formula of Cumpson and Seah [9].

To analyze the quantitative and qualitative composition of films formed on the surface of metal samples, the spectra of C1s, O1s, N1s, Si2p, Ce3d, Zn2p3/2, ZnLMM electrons were analyzed.

To determine the self-healing ability of the applied coatings, transverse incisions were made on the surface. The area was photographed with the Metam PB-21-2 metallographic microscope. The samples were then placed in a 0.05 M NaCl solution. After a predetermined time (12 or 24 hours), the samples were removed from the chamber, dried in air, and then again photographed the same section of the sample surface.

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, adopted in the automotive industry.

3. EXPERIMENTAL WORK

Taking into account the literature information, solutions were prepared on the basis of a nitrate salt of cerium [$Ce(NO_3)_3 \cdot 6H_2O$] or sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) and hydrogen peroxide (H_2O_2) as an oxidant.

3.1. Determination of the cerium-containing coatings depositing process parameters

The experiments carried out made it possible to determine the optimum concentration range of the solution components in which cerium-containing coatings are formed. It has been established that in the concentration range 10-25 g/l of cerium nitrate and 15-25 ml/l of hydrogen peroxide in the solution, homogeneous continuous coatings with a protective capacity (ES) of 12-17 s are formed on the surface of galvanized surfaces.

Studies have shown that the permissible pH values of solutions are in the range 2.0-3.0 units.

In this pH range, the following reactions may occur [10]:

$Ce^{3+} \rightarrow Ce^{4+} + e^-$ (1)

$4Ce^{3+} + O_2 + 2H_2O + 4OH^- \rightarrow 4Ce(OH)_2^{2+}$ (2)

At the same time, according to the Purbe diagram, the zinc base dissolves and the following reactions occur:

$Zn \rightarrow Zn^{2+} + 2e^-$ (3)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (4)

Formed zinc ions, as well as not oxidized by hydrogen peroxide, Ce^{3+} ions form zinc and cerium hydroxides:

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$ (5)

$Ce^{3+} + 3OH^- \rightarrow Ce(OH)_3$ (6)

It should be noted that the complex ion $Ce(OH)_2^{2+}$ can be reduced to $Ce(OH)_3$ by the reaction:

$Ce(OH)_2^{2+} + OH^- + e- \rightarrow Ce(OH)_3$ (7)

During subsequent drying, the resulting coatings are dewatered according to the reactions:

$2Ce(OH)_3 \rightarrow Ce_2O_3 + 3H_2O$ (8)

$2Ce_2O_3 + O_2 \rightarrow 4CeO_2$ (9)

$Zn(OH)_2 \rightarrow ZnO + H_2O$ (10)

Reactions 1-10 describe the mechanism of a cerium-containing coating formation, which, apparently, consists of oxides Ce_2O_3, CeO_2 and ZnO. This is confirmed by the results of a study of the chemical composition of the coatings. Observing XPS spectra of coatings indicate the presence of oxygen, cerium, zinc and carbon on the surface. It was found that cerium presents in the coating in the trivalent and tetravalent state, which corresponds with the above described mechanism of literary data.

Experiments revealed that at a solution temperature of less than 40°C, unsatisfactory coatings with low protective ability are formed, and when the solution is heated above 60°C, the coatings become not uniform, their appearance deteriorates, and the protective ability decreases. Taking into account these results, a range of solution temperatures of 40-60°C was chosen. It was found that coating formation at a temperature of 50°C and a pH of 2.5 is completed within 45 seconds, protective ability of coatings during this time reaches a maximum and then almost does not change.

It is established that addition of PEG 1500 in the amount of 0.5-2 g/l promotes an increase inprotective ability up to 35 seconds.

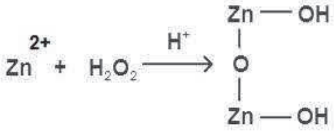
3.2. Determination of the silicon-containing coatings deposition process parameters

It has been established that in the concentration range 25-35 g/l of five-water sodium metasilicate and 20-30 ml/l of hydrogen peroxide in the solution on the surface of galvanized samples, homogeneous, colorless and iridescent coatings with low protective ability of 5-8 seconds are formed. Studies have shown that the permissible pH values of solutions are in the range of 2.0-2.5. In this pH range, the zinc substrate dissolves according to the following reactions:

$Zn \rightarrow Zn^{2+} + 2e^-$ (11)

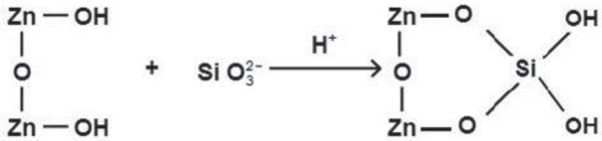
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (12)

The resulting zinc ions react with hydrogen peroxide to form zinc oxyhydrate:

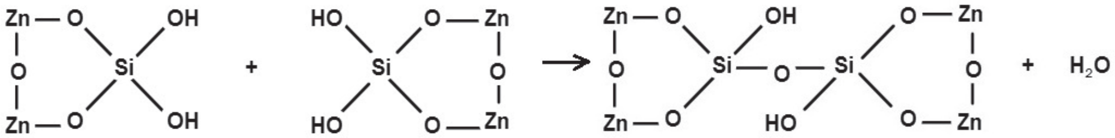


(14)

The zinc hydroxide formed by reaction 14 reacts with sodium silicate, resulting in reactions 15 and 16 forming a silicate polymer on the zinc surface [11]:



(15)



(16)

It was experimentally established that the formation of silicon-containing coating at a temperature of 20°C and pH = 1.5-3 is completed within 1.5-3 minutes, while the protective ability of coatings reaches maximum (10 s).The XPS spectra of the developed silicon-containing coating revealed the presence of silicon, zinc, oxygen, and hydrogen in the coating, which is consistent with the known mechanism for the formation of a PCB. It has been found that the introduction of oxyethylenediphosphonic acid (OEDP) in the amount of 0.2-0.5 g/l leads to a sharp increase in the protective capacity of up to 25 seconds.

3.3. The thickness and mass of the coatings produced

The thickness of cerium and silicon-containing coatings was determined by an ellipsometric method in comparison with chromatic coatings (**Table 1**).

It is established that the thickness of cerium-containing coatings is about 65 nm, and that of silicon-containing coatings is about 50 nm. It should be specially noted that the thickness of these coatings is noticeably less than the thickness of the chromate layers (200-1000 nm).

Table 1 Thickness and mass of coatings produced

Type of coating	Thickness, nm	Coating weight, g/m^2
Chromate	200	1.3
Cerium-containing	65	0.85
Silicon-containing	50	0.83

It was found that the greatest amount of zinc from galvanized steel is discharged in a silicon-containing solution

(2.65 g/m^2), which is apparently explained by a more acidic pH.

3.4. Tests of the coatings

It was found that the protective ability and appearance of conversion cerium- and silicon-containing coatings does not depend on the nature of the zinc substrate. Coatings formed on zinc precipitated from acidic, weakly acidic or alkaline electrolytes have approximately the same protective capacity.In order to identify the possibility of operating coatings under high-temperature conditions (thermal shock), the samples were heated for 1 hour at a temperature of 150°C (**Figure 1**). It was found that the protective ability of cerium-containing coatings after thermal shock did not change, and silicon-containing coatings even increased from 35 to 40 seconds, while the protective ability of chromate coatings, as expected, decreased to 12 seconds.

It has been found that cerium-containing coatings are capable of self-healing: scratches on galvanized steel samples with a protective cerium-containing film completely overgrow the newly formed coating in the presence of moisture in 24 hours. It should be noted that the silicon-containing coating does not possess this ability.Corrosion tests (ASTM B117) of the resulting cerium and silicon-containing coatings in a salt fog chamber were carried out (**Figure 2**).

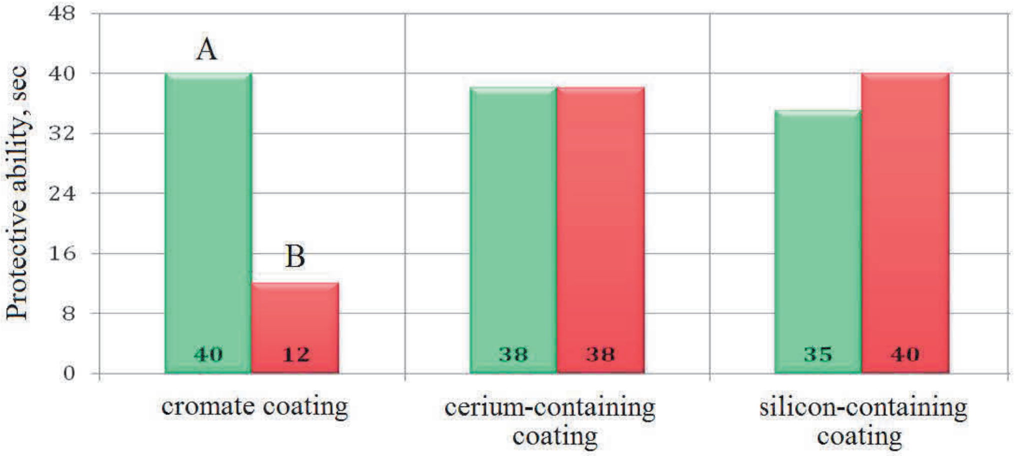


Figure 1 The protective ability of coatings before and after exposure to high temperatures
A - without thermal shock; B - after thermal shock

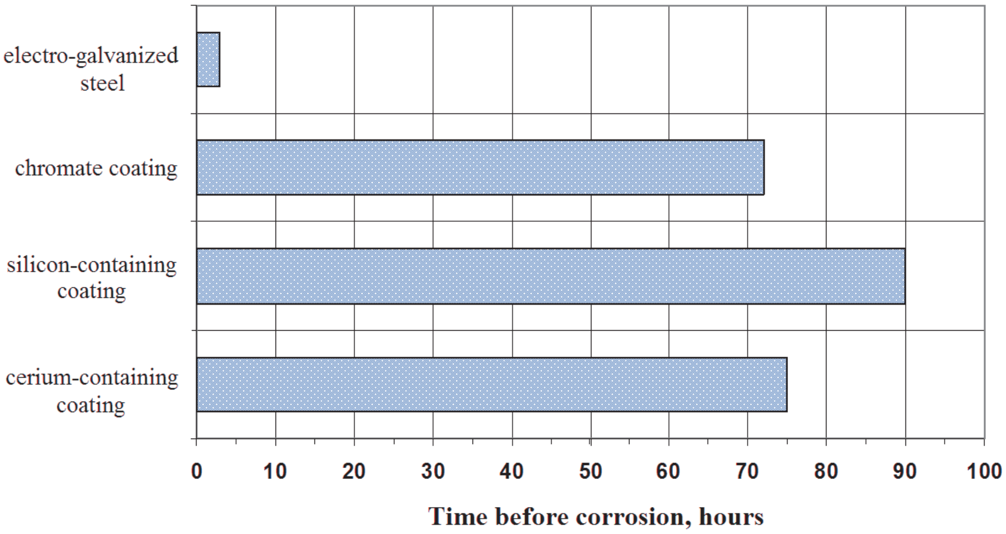


Figure 2 Results of corrosion tests of coatings in a salt fog chamber

It is established that the time before the appearance of the first white corrosion centers on cerium-containing coatings is 75 hours, and the silicon-containing is 90 hours, which correlates with the 72 hours regulated by the ISO 9227 standard for iridescent chromate coatings.

4. CONCLUSION

As a result of this study, it was shown that the developed cerium and silicon-containing passivation coatings on electro-galvanized steel parts for corrosion resistance and protective ability are comparable to iridescent chromate coatings.

ACKNOWLEDGEMENTS

The reported study was funded by RFBR according to the research project № 17-03-00523\17.

REFERENCES

[1] 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.

[2] Replacement hexavalent chromium in automotive industry for ELV Directive. // Harris A. Bhatt, technical paper, Sur/Fin. 6/2002.

[3] 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.

[4] Directive 2002/96 / EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment.

[5] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the registration, assessment, authorization and limitation of chemicals (REACH), the establishment of the European Chemicals Agency.

[6] D.A. Shirley, High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold, Phys. Rev. B. 1972. Vol 5. no 12. pp 4709-4713.

[7] H. Scofield, Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV, J. Electron Spectrosc. Relat. Phenom. 1976. no 8. pp 129 -137.

[8] M. Mohai, XPS MultiQuant: Multimodel XPS Quantification Software. Surf. Interface Anal. 2004. no 36. pp 828-832.

[9] P.J. Cumpson, M.P. Seah, Elastic Scattering Corrections in AES and XPS. II. Estimating Attenuation Lengths and Conditions Required for their Valid Use in Overlayer/Substrate Experiments,Surf. Interface Anal. 1997. no 25. pp 430-446.

[10] Abrashov AA, Grigoryan NS, Vagramyan TA, Zheludkova EA Passivation of zinc coatings in cerium-containing solutions. Russian Journal of Applied Chemistry. 2015. Vol. 88. no. 10. pp. 1409-1413.

[11] Yunying Fan, Yehua Jiang, Rong Zhou New Passivating Method to Galvanized Zn Coatings on Steel Substrate. Advanced Materials Research. 2011. Vol. 163-167. pp. 4555-4558.