

An Environmentally Friendly Passivation Technology for the Water-cooling Process of Batch Hot-dip Galvanization

Yongfeng Long^{1,*}, Changsheng Liu¹ and Hongxin Wen²

¹College of Materials Science and Engineering, Northeastern University, Shenyang 113024, China

²ZhengYuan Steel Pipe Co, TANGSHAN, Tangshan 063000, China

*Corresponding author

Abstract—In batch hot-dip galvanizing, 0.2-0.3 wt% chromic anhydride solution is traditionally used as a water-cooling medium to prevent white rust. It generates a lot of chromium acid mist and wastewater, both of which are very harmful to humans and the environment. In our study, an environmental-friendly passivation technology as a water-cooling medium was developed for the first time. It consisted of several inorganic inhibitors to prevent zinc corrosion such as molybdate, tungstate, vanadate and phosphate. The corrosion resistance, surface morphology, chemical composition and electrochemical behavior of the samples prepared with tap water, 0.2 wt% chromic anhydride solution and new green passivation solution were compared. The new environmentally friendly passivation technology had a similar effect to that of chromic anhydride solution, thus, it had a strong industrial application potential.

Keywords—batch hot-dip galvanizing; water-cooling medium; chromic anhydride passivation; environment-friendly passivation

I. INTRODUCTION

The batch hot-dip galvanizing (also called hot dip galvanizing by fluxes [1]) is a technology, in which the work piece is firstly soaked to remove oxide, then dipped in fluxes and finally put into the zinc pot to achieve hot-dip galvanizing. This technology is suitable for the galvanizing of structural steel, steels wire and pipes. Its products are widely used in transportation, infrastructure construction, electric power, communication and tower masts, metal ware, etc. The batch hot-dip galvanizing has developed rapidly in China and its annual capacity has exceeded 1 million tons by the end of 2014.

The post-treatment of batch hot-dip galvanizing includes water-cooling and final passivation. Currently, 0.2-0.3% of chromic anhydride solution is used as both the water-cooling medium and anti-corrosion additive. As a result, there are massive discharges of chromate wastewater because of this process. Additionally, because of the high temperature of water-cooling solution (>80°C), lots of chromate acid mist is produced and it seriously endangers the safety and health of workers. Furthermore, the final passivation solution is also chromate. Thus, the hexavalent chromium pollution is a serious problem that restricts the development of the whole industry.

Engineers have carried out extensive research [2-19] of environment-friendly passivation technology in the recently ten years, yet, almost all feasible solutions are related to the

continuous hot-dip galvanizing process or to applications of the hot-dip galvanized strip production.

However, because of the characteristics of the process and equipment for batch hot-dip galvanizing, the application of the green passivation technology is very harsh. For instance, the water-cooling solution should be stable and without obvious corrosion on the surface of the work piece under the high temperature (above 80°C). So the investigations of chromium-free passivation technologies used at the batch hot-dip galvanizing are rare. But with the improvement of the awareness of environmental protection and the governmental policies on the waste discharges, the development of environmentally friendly technology for this industry is urgent and imperative.

In this paper we report environmentally friendly passivation technology for the water-cooling process of batch hot-dip galvanizing. This new technology could replace current passivation solution containing chromic anhydride, a harmful chemical, and promote the green and healthy development of the industry.

II. EXPERIMENTAL

A. Sample Preparation

Q235 hot rolled plate with the size 80 mm × 50 mm × 2 mm was used as a substrate. All samples underwent the following procedure in the following order: soaking → rinsing → dipping in fluxes → drying → hot-dip galvanizing → water-cooling. Three different solutions were used as water-cooling media: tap water (the corresponding galvanized work piece as sample 1), 0.2% chromic anhydride solution (sample 2), 0.5% chromium-free passivation solution (sample 3). The basic formula of chromium-free passivation solution was comprised of 2-5 wt% (NH₄)₂MoO₄, 3-6 wt% NH₄VO₃, 8-10 wt% KH₂PO₄, 0.5-0.8 wt% CoSO₄.

The soaking solution 20% hydrochloric acid. The rinsing solution was tap water. The fluxes were a mixed solution of 22% zinc chloride and 18% ammonium chloride. The temperature of fluxes was ~ 40°C. The dipping times were 60 seconds. The drying temperature was ~ 80°C. The drying time was 3 minutes. The temperature of hot-dip galvanizing was ~ 460°C and the time was 1 minute. The parameters of water-cooling were: 85°C, pH = 6 and 120 s operating time.

B. Performance Tests

1) Corrosion resistance evaluation:

•Procedure for the accelerated corrosion test #1 was performed as follows:

1 ml of 5 wt% lead acetate solution was dropped on the sample surface. The surface was observed and the blackening time of three samples was record.

•Procedure for the accelerated corrosion test #2 was performed as follows:

According to the standard of GB/T2423.17, neutral salt spray test was performed for three samples. Time during, which white rust appeared, was recorded. The neutral salt spray test box was SYW-60 (XIANGFENG Laboratory Apparatus Co., Shanghai, China).

•Electrochemical tests:

The tests were carried out by an electrochemical workstation (Wuhan Corrtest Instruments Co., China) with the classic three-electrode cell comprised of a saturated calomel electrode (as a reference electrode), a platinum electrode (used as a counter electrode), the plating samples (used as working electrodes), and the 3.5 wt% NaCl solution (used as electrolyte). In the potentiodynamic polarization measurements, the sweeping potentials ranged from -1500 to -500 mV with the 1 mV/s rate. During the electrochemical impedance spectroscopy (EIS), the frequency range was between 10 mHz to 100 KHz with an amplitude of 10 mV.

2) Microstructure and composition analysis

•Scanning electron microscope (SEM, ZEISS EVO18, Germany) coupled with the energy dispersive spectrometer (EDS) was used to observe the microstructure and surface composition.

III. RESULTS AND DISCUSSION

A. Accelerated Corrosion Tests

A layer of passivation film formed on the samples have a certain corrosion resistance. In the tests of accelerated corrosion tests, the longer the time of black or white rust appearance, the better the film protective performance [20] is.

Results of accelerated corrosion tests indicated the sample 2 and 3 have obvious anti-corrosion ability, and this ability is better for sample 3 (see Table I).

TABLE I . RESULTS OF ACCELERATED CORROSION TESTS FOR DIFFERENT SAMPLES

	SAMPLE 1	SAMPLE 2	SAMPLE 3
TEST 1 (SECOND)	AVERAGE 0.36	AVERAGE 6.21	AVERAGE 7.45
TEST 2 (HOURS)	0.5	8.0	10.5

B. Electrochemical Tests

Figure I shows the potentiodynamic polarization curves of three samples prepared with different water-cooling solutions. Cathodic branches of all the samples are similar, but the anodic branches are different. The curves of samples 2 and 3 have very similar shapes and are shifted to the bottom right relative to the

curve of sample 1. It indicates, that samples 2 and 3 have good corrosion resistance and that the corrosion process was under the control of anodic reactions [21-23].

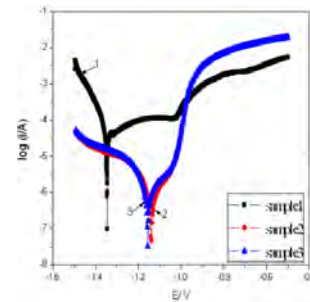


FIGURE I. POTENTIODYNAMIC POLARIZATION CURVES OF SAMPLES PREPARED WITH DIFFERENT WATER-COOLING MEDIA.

The related electrochemical parameters of corrosion potential (E_{corr}), corrosion current density (I_{corr}) and polarization resistance (R_p) were calculated from the potentiodynamic polarization curves using the software on th workstation (see Table II). The results showed that the corrosion potentials of samples 2 and 3 were higher comparing to that of sample 1. Corrosion current densities of samples 2 and 3 decreased comparing with that of sample 1, and samples 2 and 3 have significantly larger polarization resistance than sample 1. Sample 3 has a slightly higher corrosion potential. However, sample 3 has smaller corrosion current and significantly larger polarization resistance than those of sample 2 [24-25].

TABLE II. TAFEL POLARIZATION PARAMETERS FOR SAMPLES PREPARED WITH DIFFERENT WATER-COOLING MEDIA

SAMPLE NUMBER	$E_{CORR}(V)$	$I_{CORR}(MA/CM^2)$	$R_p(\Omega)$
SAMPLE 1	-1.35	80.84	1226
SAMPLE 2	-1.16	9.77	2251
SAMPLE 3	-1.12	2.39	2666

Figure II shows Nyquist plots of samples prepared with different water-cooling media. The shapes of all curves are single capacitive semicircles. There are obvious differences in the radii between samples, however, the radii of samples 2 and 3 are significantly larger than that of sample 1. It indicates the corrosion resistance of samples 2 and 3 are obviously better than that of sample 1 [26-27].

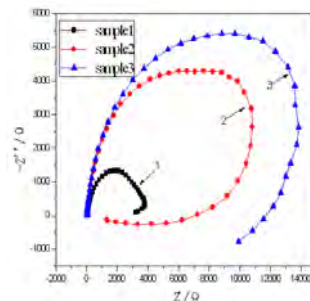


FIGURE II. NYQUIST PLOTS OF SAMPLES PREPARED WITH DIFFERENT WATER-COOLING MEDIA.

C. Surface Morphology and Chemical Composition

1) SEM results:

Figure III are the SEM results of micro-topography for three samples. The surface of sample 1 is not smooth with sporadic defects from zinc-slag and zinc-gray. Fewer zinc-slags and zinc-grays are observed on the surface of sample 2, however, reaction etchings are seen. Thus, we believe that there is a dissolution reaction between the surface of the sample 2 and water-cooling solution at high temperature. The surface of sample 3 is smooth and no obvious reactive etchings are observed. However, some micro-cracks are seen, all of which makes us believe that the reaction between the surface of the sample 3 and the solution at high temperature is moderate.

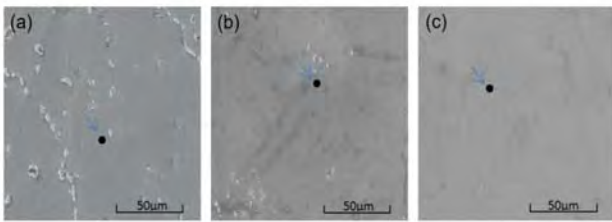


FIGURE III. SEM IMAGES OF DIFFERENT SAMPLES. A) SAMPLE 1, B) SAMPLE 2, C) SAMPLE 3

2) EDS results:

Figure VI and Table III show the graphical and qualitative EDS analysis, respectively. Surface of sample 1 mainly contains elements such as zinc, oxygen, aluminum, magnesium and silicon, thus, most of the components are very likely oxides. Based on these results, we believe that there were no obvious interface reactions between the surface of samples and water-cooling solution. The surface of the sample 2 mainly contains zinc, oxygen, chromium, aluminum and other minor elements. By calculating the atomic ratio of each element, the passivation film is very likely composed of $ZnCrO_4$ and $ZnCr_2O_4$. The

surface of the sample 3 mainly contains zinc, oxygen, molybdenum, phosphorus, aluminum and other minor elements, thus, the film formed on the surface is very likely composed of $ZnMo_5P_2O_3$.

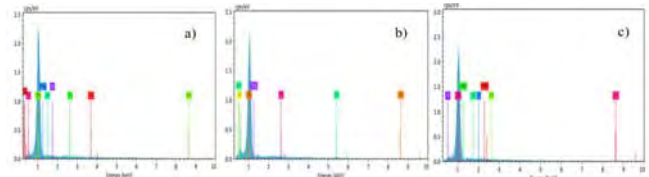


FIGURE IV. EDS SPECTRUMS OF DIFFERENT SAMPLES. A) SAMPLE 1, B) SAMPLE 2, C) SAMPLE 3

IV. CONCLUSION

In our research we reached the following conclusions:

- (1) The sample with 0.2 wt% chromic anhydride and environmentally friendly passivation solution as water-cooling media have a certain anti-corrosion abilities at certain corrosive atmosphere (i.g. coastal salinity and high humidity). Moreover, the anti-corrosion performance of the sample with environmentally friendly passivation solution was slightly better.
- (2) Based on the electrochemical behavior, the corrosion resistance of the sample prepared by the environmentally friendly passivation solution as water-cooling media is also superior to that of sample prepared by the 0.2 wt% chromic anhydride solution.
- (3) The galvanized work pieces prepared by the environmentally friendly passivation solution as water-cooling media has good appearance and no harmful ingredients.

Thus, our proposed green technology for batch hot-dip galvanizing has a high potential for industrial nature-friendly applications.

TABLE III. EDS ELEMENTAL COMPOSITION OF THE THREE SAMPLES PREPARED BY DIFFERENT WATER-COOLING MEDIA

		Zn	O	Cr	Mo	P	Al	Mg	Si
Sample 1	Atomic/%	48.70	44.58	-	-	-	1.56	3.93	1.23
	Mass/%	70.42	15.87	-	-	-	3.02	8.42	2.28
Sample 2	Atomic/%	40.57	42.34	16.92	-	-	0.17	-	-
	Mass/%	52.42	15.42	28.87	-	-	0.30	-	-
Sample 3	Atomic/%	28.41	44.87	-	13.93	11.23	1.56	-	-
	Mass/%	38.42	15.87	-	30.42	12.27	3.02	-	-

REFERENCES

- [1] Shengmin Wang, Xiaojun Zhao, Jianwei Dang, Mingyi He, "Research Status of the Process Mechanism of Batch Hot-dip Galvanizing," Surf. Technol., vol. 45, pp. 19–25, May 2016.
- [2] Hsiang-Yu Su, Pei-Li Chen, Chao-Sung Lin., "Sol-gel coatings doped with organosilane and cerium to improve the properties of hot-dipgalvanized steel," Corros. Sci., vol. 102, pp. 63–71, January 2016.
- [3] Cheng-Yang Tsai, Jen-Shou Liu, Pei-Li Chen, Chao-Sung Lin, "A two-step roll coating phosphate/molybdate passivation treatment for hot-dip galvanized steel sheet," Corros. Sci., vol. 52, pp. 3385–3393, October 2016.
- [4] A.M.P. Simões, R.O. Carbonari, A.R. Di Sarli, B.del Amo, R.Romagnoli, "An environmentally acceptable primer for galvanized steel: Formulation and evaluation by SVET," Corros. Sci., vol. 53, pp. 464–472, January 2011.
- [5] Y. Hamlaoui, L. Tifouti, F. Pedraza, "Corrosion behaviour of molybdate-phosphate-silicate coatings on galvanized steel," Corros. Sci., vol. 51, pp. 2455–2462, October 2009.
- [6] Cheng-Yang Tsai, Jen-Shou Liu, Pei-Li Chen, Chao-Sung Lin, "A roll coating tungstate passivation treatment for hot-dip galvanized sheet steel," Surf. Coat. Technol., vol. 205, pp. 5124–5129, August 2011.
- [7] Mei-rong Yuan, Jin-tang Lu, Gang Kong, Chun-shan Che, "Effect of silicate anion distribution in sodium silicate solution on silicate conversion coatings of hot-dip galvanized steels," Surf. Coat. Technol., vol. 205, pp. 4466–4470, June 2011.
- [8] M. Poelman, M.Fedel, C.Motte, D.Lahem, et al. "Influence of formulation and application parameters on the performance of a sol-gel/clay

- nanocomposite on the corrosion resistance of hot-dip galvanized steel. Part I. study of the sol preparation parameters," *Surf. Coat. Technol.*, vol. 274, pp. 1–8, July 2015.
- [9] L. Jiang, M. Wolpers, P. Volovitch, K. Ogle, "An atomic emission spectroelectrochemical study of passive film formation and dissolution on galvanized steel treated with silicate conversion coatings," *Surf. Coat. Technol.*, vol. 206, pp. 3151–3157, February 2012.
- [10] Rita Ghosh, D.D.N. Singh, "Kinetics, mechanism and characterisation of passive film formed on hot dip galvanized coating exposed in simulated concrete pore solution," *Surf. Coat. Technol.*, vol. 201, pp. 7346–7359, May 2007.
- [11] F. Deflorian, M. Fedel, S. Rossi, P. Kamarchik, "Evaluation of mechanically treated cerium (IV) oxides as corrosion inhibitors for galvanized steel," *Electrochim. Acta*, vol. 56, pp. 7833–7844, September 2011.
- [12] I.A. Kartsonakis, A.C. Balaskas, E.P. Koumoulos, C.A. Charitidis, G.C. Kordas, "Incorporation of ceramic nanocontainers into epoxy coatings for the corrosion protection of hot dip galvanized steel," *Corros. Sci.*, vol. 57, pp. 30–41, April 2012.
- [13] Gang Kong, Liu Lingyan, Jintang Lu, Chunshan Che, Zheng Zhong, "Corrosion behavior of lanthanum-based conversion coating modified with citric acid on hot dip galvanized steel in aerated 1M NaCl solution," *Corros. Sci.*, vol. 53, pp. 1621–1626, April 2011.
- [14] M. Olivier, A. Lanzutti, C. Motte, L. Fedrizzi, "Influence of oxidizing ability of the medium on the growth of lanthanide layers on galvanized steel," *Corros. Sci.*, vol. 52, pp. 1428–1439, April 2010.
- [15] M. Taryba, S.V. Lamaka, D. Snihirova, et al. "The combined use of scanning vibrating electrode technique and micro-potentiometry to assess the self-repair processes in defects on smart coatings applied to galvanized steel," *Electrochim. Acta*, vol. 56, pp. 4475–4488, April 2011.
- [16] Ulf Bexell, T. Mikael Grehk, "A corrosion study of hot-dip galvanized steel sheet pre-treated with γ -mercaptopropyltrimethoxysilane," *Surf. Coat. Technol.*, vol. 201, pp. 44734–4742, January 2007.
- [17] B. Ramezanzadeh, M.M. Attar, M. Farzam, "Corrosion performance of a hot-dip galvanized steel treated by different kinds of conversion coatings," *Surf. Coat. Technol.*, vol. 205, pp. 874–884, October 2010.
- [18] B.Ramezanzadeh, M.M. Attar, "An evaluation of the corrosion resistance and adhesion properties of an epoxy-nanocomposite on a hot-dip galvanized steel (HDG) treated by different kinds of conversion coatings," *Surf. Coat. Technol.*, vol. 205, pp. 4649–4657, June 2011.
- [19] Soha A. Abdel-Gawad, Mervat A. Sadik, Madiha A. Shoeib, "Enhancing corrosion resistance of galvanized steel by phosphating and silicate post-sealing," *Int. J. Electrochem. Sci.*, vol. 13, pp. 2688–2704, March 2018.
- [20] Rosa Vera, Estefania Cruz, Margarita Bagnara, Raquel Araya, Rodrigo Henriquez, Andres Diaz-Gomez, "Evaluation of anticorrosive coatings on carbon steel in marine environments: accelerated corrosion test and field exposure," *Int. J. Electrochem. Sci.*, vol. 13, pp. 898–914, January 2018.
- [21] Xuan Chen, Qing yun Xiong, Feng Zhu, Hui Li, Dong Liu, Jin ping Xiong, "The effects of chloride anions on corrosion and passivation behavior of 254 SMO stainless steel in water absorbed of blast furnace gas (BFG)," *Int. J. Electrochem. Sci.*, vol. 13, pp. 1656–1665, February 2018.
- [22] Zhu Wang, Mingliang Liu, Minxu Lu, Lei Zhang, Junyan Sun, Ziru Zhang, "The Effect of Temperature on the Hydrogen Permeation of Pipeline Steel in Wet Hydrogen Sulfide Environments," *Int. J. Electrochem. Sci.*, vol. 13, pp. 915–924, January 2018.
- [23] Liuyan Zhang, Shuimei Yang, Huishu Wu, Xiaohua Jie, Xiaoye Huang, Xiujin Wang, "Effect of surface nanocrystallization on corrosion behaviour of coated steel in chloride solution," *Int. J. Electrochem. Sci.*, vol. 13, pp. 3799–3811, April 2018.
- [24] Shifang Wang, Yu Zuo, Yuming Tang, Xuhui Zhao, "Corrosion inhibition effect of antimony potassium tartrate for Q235 carbon steel in NaCl solutions," *Int. J. Electrochem. Sci.*, vol. 13, pp. 842–851, January 2018.
- [25] Y.R Galindo-Luna, A. Torres-Islas, R.J.Romero, M.Montiel-Gonzalez and S.Serna, "Corrosion behavior of AISI 316L stainless steel in a NaOH-H₂O mixture," *Int. J. Electrochem. Sci.*, vol. 13, pp. 631–641, January 2018.
- [26] H.Lgaz, R.Salghi, Ismat H. Ali, "Corrosion inhibition behavior of 9-hydroxyrisperidone as a green corrosion inhibitor for mild steel in hydrochloric acid: electrochemical, DFT and MD simulations studies," *Int. J. Electrochem. Sci.*, vol. 13, pp. 250–264, January 2018.
- [27] Xingguo Feng, Ruilong Shi, Leyuan Zhang, et al. "Degradation of passive film on low-nickel stainless steel in groundwater with different concentration of chloride ions," *Int. J. Electrochem. Sci.*, vol. 13, pp. 2745–2757, March 2018.