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Corrosion Evaluation of Zinc Coating Prepared by Two Types of Electric Currents

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***Abstract*—**In this research, zinc coatings were fabricated by electroplating process in a sulfate solution under direct and pulse current conditions. In direct and pulse current conditions, effect of maximum current was investigated on the coating properties. Also a comparison was made between the obtained coatings under direct and pulse current. Morphology of the coatings was investigated by scanning electron microscopy (SEM). Corrosion behavior of the coatings was investigated by potentiodynamic polarization test. In pulse current conditions, the effect of pulse frequency and duty cycle was also studied. The effect of these conditions and parameters were also investigated on morphology and corrosion behavior. All of DC plated coatings are showing a distinct passivation area in -1 to -0.4 V range. Pulsed current coatings possessed a higher corrosion resistance. The results showed that current density is the most important factor regarding the fabrication process. Furthermore, a rise in duty cycle deteriorated corrosion resistance of coatings. Pulsed plated coatings performed almost 10 times better than DC plated coatings.

***Keywords*—**Corrosion, duty cycle, pulsed current, zinc.

I. Introduction

ZINC coatings created by electrodeposition method are generally used in order to protect steel and cast iron substrates. The coated zinc catholically protects the iron substrate by acting as a sacrificial cathode, thus preventing corrosion. Furthermore, the coating acts as a barrier from aggressive species in the environments, just as a normal paint would. Unfortunately, zinc electroplated coatings are susceptible to certain phenomenon, such as spotting and darkening. The general weak behavior in aggressive environments also adds to the further burden that these coatings are only practical in the limited pH range of 6 to 12 [1], [2]. Although certain methods such as chromating have been undertaken to enhance the corrosion resistance in the past, they are generally avoided due to newer environmental concerns. On the other hand, abrasion damage limits the application of soft zinc coatings, thus enhancing the mechanical properties are unavoidable. One of the few parameters that can be altered in electrodeposition is the type of applied current.

Three types of applied current have been extensively used in the literature to produce zinc electroplated coatings. Direct current (DC), pulsed current (PC) and pulsed reversed current (PRC). In the DC technique, the only variable parameter is the current density. However, in PC three additional parameters are introduced that affects the procedure: ON-time (T_{on}), OFF-time (T_{off}) and the peak current (I_P). Duty cycle (γ) is the correlation of these parameters as in (1) and (2):

$$\gamma = \frac{T_{on}}{T_{on}+T_{off}} \quad (1)$$

Also, pulse frequency can be defined as:

$$f = \frac{1}{T_{on}+T_{off}} \quad (2)$$

The main advantage of using PC is a phenomenon called the relaxation time [3]-[6]. When the process is under way, a negative charged layer is formed around the cathode which prevents ions from reaching the electrode [7]-[9]. By using the PC techniques, the induced off time will let this layer to partially discharge, thus omitting the mentioned problem [10]-[13].

The literature unanimously reports that by utilizing PC the behavior of the resulted coatings change [4], [5], [14]. The aim of this study is to compare the corrosion characteristics of two pure Zn coatings that have been created using DC and PC technique.

II. Material and Methods

A glass cell was chosen to for the electroplating process. A zinc specimen of 99.96% purity was used as anode and a St 37 steel specimen was used as a cathode. The anode was chosen to be 4 times larger than the cathode to mitigate the anodic polarization of zing during the process, especially at higher current densities. Anode was distanced 3 cm from the cathode. Steel sheets were abraded up to #200 by SiC grit papers, they were cleaned using ethanol in an ultrasonic bath for five minutes and activated in a 15% HCl solution and then washed using distilled water. Composition of the deposition bath is presented in Table I.

The surface morphology was photographed using SEM. The corrosion tests were performed in a 1M NaCl solution and the polarization tests were done with a potentiostat Autolab-PGSTAT 10.

III. Results and Discussion

A. DC Current Coatings

Fig. 1 shows the coatings that were created using DC

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currents of 0.08, 0.10 and 0.12 A.cm^{-2}. The hexagonal shapes that are normally observed in zinc coatings are also observable [2], [7], [15]. The largest grains are seen in the sample that has been fabricated using the lowest current density of 0.08 A.cm^{-2}.

TABLE I
CHEMICAL COMPOSITION OF THE BATH AND THE PARAMETERS OF THE ELECTRODEPOSITION

Variable	Range
$ZnSO_4$	200 g/L
$H3BO_3$	50 g/L
SDS	0.3 g/L
Temperature	25 °C
Peak current density	0.8, 0.10, 0.12 A/dm^2
Pulse frequency	0, 10, 50, 100 Hz
Duty cycle	10, 25, 50, 75 %
pH	4.5
Stirring rate	250 rpm

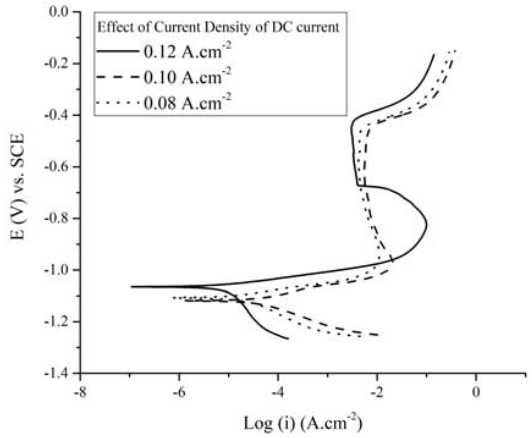

Fig. 1 Polarization behavior of DC plated coating under three current densities

TABLE II
CORROSION CHARACTERISTICS OF COATINGS OBTAINED USING DC CURRENT

i (A.cm^{-2})	E_{corr} (mV vs. SCE)	I_{corr} (μA.cm^{-2})	Corrosion Rate (mm.year^{-1})
0.08	-1.11	9.6	0.11
0.10	-1.12	15.6	0.18
0.12	-1.06	9.7	0.11

The potentiodynamic polarization curves of the aforementioned samples are also presented in Fig. 2 and the corrosion characteristics in 1M NaCl solution are presented in Table II. It is widely accepted that the main cathodic reaction of the related environments is the oxygen reduction (O_2 + $2H_2O$ + 4e ↔ 4OH$^-$). After the layer is formed on the cathode, during the transportation process an air formed layer forms on the zinc. Then when the zinc is immersed into the NaCl solution these films dissolute and then the dissolution of zinc itself creates colloids on the surface. Given time, these colloids turn into zinc compounds [15]. The main compounds are as follows: ZnO, $Zn_5(OH)_8Cl_2.H_2O$ and $Zn(OH)_2$ [15]. Focusing on the polarization curves, it can be observed that all of them are showing a distinct passivation area in -1 to -0.4 V range. This is accepted to be the result of formation of protective passive layers.

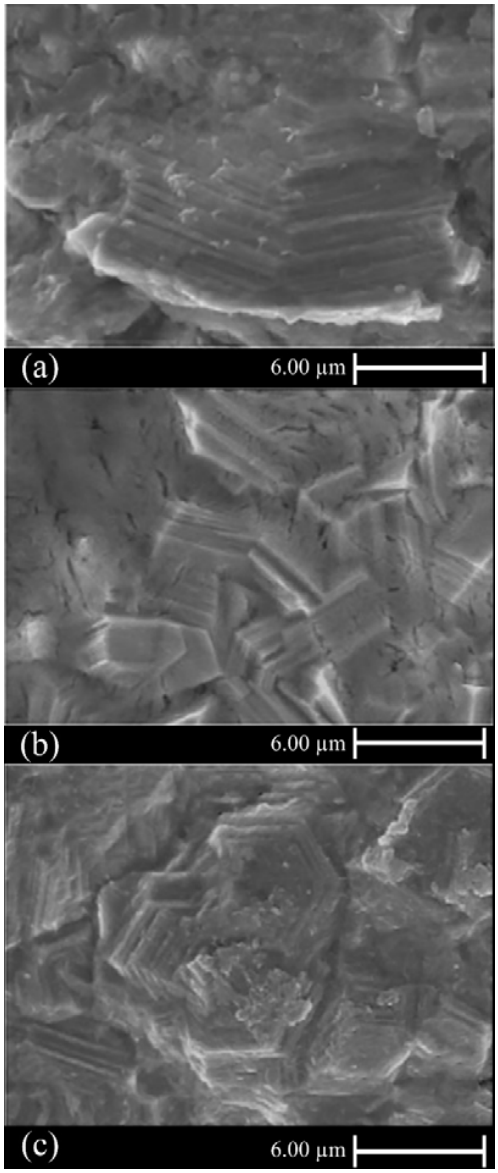

Fig. 2 Morphology of coatings obtained using DC current: (a) 0.08 A.cm^{-2} (b) 0.10 A.cm^{-2} and (c) 0.12 A.cm^{-2}

B. PC Plated Coatings

1) Effect of Duty Cycle

Fig. 3 depicts the polarization curves that have been obtained in order to find the effect of duty cycle on the corrosion behavior of the zinc coatings. It is apparent that the most positive potential is for the duty cycle of 10% and the most negative potential is the sample that has been produced in 25%. However, after tafel extrapolation it became obvious that the 25% sample possesses the highest i_{corr}, as a result, this sample has the lowest corrosion rate of all. It is also noticeable that the passive area of this sample is somewhat more limited

than other samples. While other specimens are passive between -1.0 to -0.4, this sample is passive in -0.8 and -0.4 range. Table III contains the corrosion characteristics of this part. It is also noteworthy to mention that the worst behavior is seen from the sample with the highest duty cycle.

TABLE III
CORROSION CHARACTERISTICS OF COATINGS OBTAINED USING PC CURRENT: EFFECT OF DUTY CYCLE

Coating	i (A.cm^{-2})	γ (%)	*f* (Hz)	E_{corr} (mV)	i_{corr}	R_{corr}
Zn-1	0.12	10	10	-1.10	3.81	.0443
Zn-2	0.12	25	10	-1.13	1.99	0.023
Zn-4	0.12	50	10	-1.12	3.57	0.041
Zn-3	0.12	75	10	-1.09	68.8	0.799

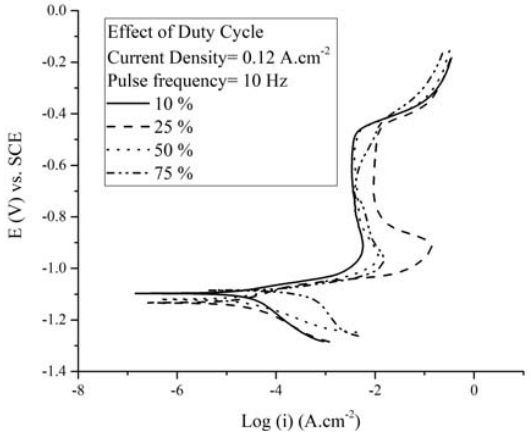

Fig. 3 Polarization behavior of PC plated coating under different duty cycles

2) Effect of Pulse Frequency

Fig. 4 and Table IV represent the corrosion characteristics of the coatings tested in order to find the effect of pulse frequency. It can be observed that by increasing the frequency, the graphs have shifted to more negative potentials. However, they have also shifted to more positive currents. Hence the pulse frequency has a negligible effect on corrosion rate.

TABLE IV
CORROSION CHARACTERISTICS OF COATINGS OBTAINED USING PC CURRENT: EFFECT OF PULSE FREQUENCY

Coating	i (A.cm^{-2})	γ (%)	*f* (Hz)	E_{corr} (mV)	i_{corr}	R_{corr}
Zn-4	0.12	50	10	-1.12	3.57	0.041
Zn-5	0.12	50	50	-1.10	16.0	0.019
Zn-6	0.12	50	100	-1.09	20.2	0.234

3) Effect of Current Density

It seems that among all parameters, the current density has the most applicable effect on the corrosion behavior of pure zinc coatings fabricated by pulse electrodeposition. It can be inferred from Fig. 5 and Table V that by increasing the maximum current density the graph has shifted downward and to left, indicating that the corrosion potential and current have become more negative, hence a notable rise in corrosion rate.

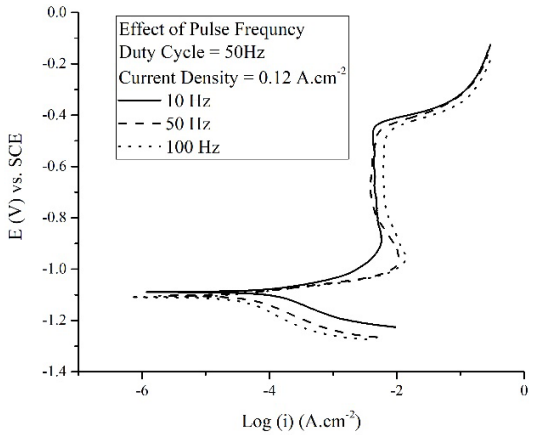

Fig. 4 Polarization behavior of PC plated coating under different pulse frequency

TABLE V
CORROSION CHARACTERISTICS OF COATINGS OBTAINED USING PC CURRENT: EFFECT OF CURRENT DENSITY

Coating	i (A.cm^{-2})	γ (%)	*f* (Hz)	E_{corr} (mV)	i_{corr}	R_{corr}
Zn-4	0.12	50	10	-1.12	3.57	0.041
Zn-7	0.10	50	10	-1.08	38.4	0.447
Zn-8	0.08	50	10	-1.03	216	2.510

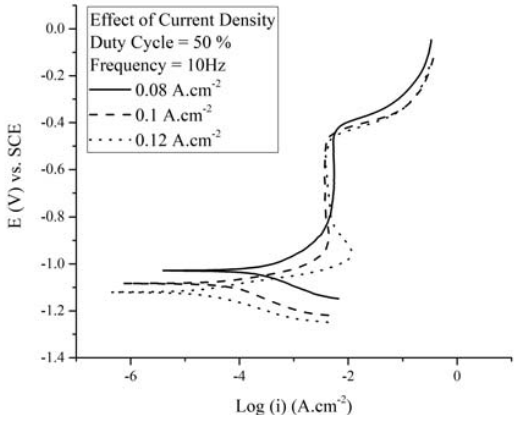

Fig. 5 Polarization behavior of PC plated coating under different current densities

4) Comparison of DC and PC coatings

Fig. 6 and Table VI show the best behavior that has been obtained in this paper for both types of currents. It is easily observed in the graph that the difference is very apparent. The graph has shifted and the passive region in the PC plated coating is much more prominent. The numbers also indicate the same with the corrosion rate of the PC coating to be almost 10 times better that the DC counterpart.

TABLE VI
COMPARISON OF CORROSION CHARACTERISTICS OF HIGHEST RESISTANCE SAMPLES CREATED BY DC AND PC METHOD

Coating	i (A.cm^{-2})	γ (%)	*f* (Hz)	E_{corr} (mV)	i_{corr}	R_{corr}
DC	0.12	---	---	-1.06	9.7	0.11
PC; Zn-5	0.12	50	50	-1.10	16.0	0.019

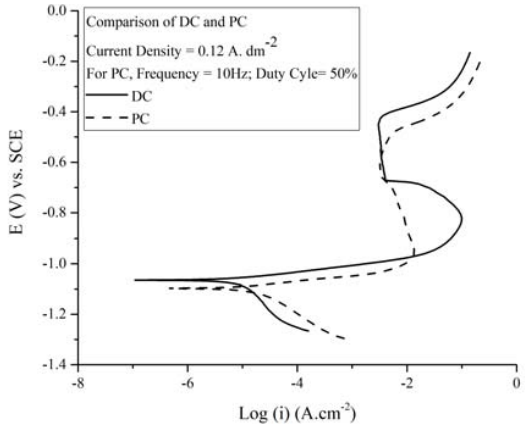

Fig. 6 Comparison of polarization curves of highest resistance samples created by DC and PC method

IV. Conclusion

Pure Zn coatings have been fabricated by the use of two different current in the electrodeposition process. Polarization tests were done in order to find out the corrosion behavior of each coating. Furthermore, the effect of different parameters of pulse current technique has also been discussed. It was found out that the current density is the most effective parameters in controlling the corrosion behavior of the PC plated coating. In comparison, PC plating proved to produce a higher corrosion resistant coating.

References

[1] T. J. Tuaweri and G. D. Wilcox, "Behaviour of Zn-SiO_2 electrodeposition in the presence of N, N-dimethyldodecylamine," *Surf. Coatings Technol.*, vol. 200, no. 20–21, pp. 5921–5930, 2006.

[2] F. C. Porter, *Corrosion resistance of zinc and zinc alloys*. CRC Press, 1994.

[3] J. Steinbach and H. Ferkel, "Nanostructured Ni-Al_2O_3 films prepared by DC and pulsed DC electroplating," *Scr. Mater.*, vol. 8, no. 44, pp. 1813–1816, 2001.

[4] M. E. Bahrololoom and R. Sani, "The influence of pulse plating parameters on the hardness and wear resistance of nickel–alumina composite coatings," *Surf. Coatings Technol.*, vol. 192, no. 2–3, pp. 154–163, 2005.

[5] M. Sajjadnejad, M. Ghorbani, and A. Afshar, "Microstructure-corrosion resistance relationship of direct and pulse current electrodeposited Zn-TiO_2 nanocomposite coatings," *Ceram. Int.*, vol. 41, no. 1, pp. 217–224, 2015.

[6] M. Sajjadnejad, N. Setoudeh, A. Mozafari, A. Isazadeh, and H. Omidvar, "Alkaline Electrodeposition of Ni–ZnO Nanocomposite Coatings: Effects of Pulse Electroplating Parameters," *Trans. Indian Inst. Met.*, vol. 70, no. 6, pp. 1533–1541, 2017.

[7] M. Sajjadnejad, A. Mozafari, H. Omidvar, and M. Javanbakht, "Preparation and corrosion resistance of pulse electrodeposited Zn and Zn–SiC nanocomposite coatings," *Appl. Surf. Sci.*, vol. 300, pp. 1–7, 2014.

[8] C. J. Chen and C. C. Wan, "A study of the current efficiency decrease accompanying short pulse time for pulse plating," *J. Electrochem. Soc.*, vol. 136, no. 10, pp. 2850–2855, 1989.

[9] Y. Yang and Y. F. Cheng, "Fabrication of Ni–Co–SiC composite coatings by pulse electrodeposition—Effects of duty cycle and pulse frequency," *Surf. Coatings Technol.*, vol. 216, pp. 282–288, 2013.

[10] A. K. Pradhan and S. Das, "Pulse-reverse electrodeposition of Cu–SiC nanocomposite coating: effect of concentration of SiC in the electrolyte," *J. Alloys Compd.*, vol. 590, pp. 294–302, 2014.

[11] M. Sajjadnejad, H. Omidvar, M. Javanbakht, and A. Mozafari, "Textural and structural evolution of pulse electrodeposited Ni/diamond nanocomposite coatings," *J. Alloys Compd.*, vol. 704, pp. 809–817, 2017.

[12] P. C. Tulio and I. A. Carlos, "Effect of SiC and Al 2 O 3 particles on the electrodeposition of Zn, Co and ZnCo: II. Electrodeposition in the presence of SiC and Al 2 O 3 and production of ZnCo–SiC and ZnCo–Al 2 O 3 coatings," *J. Appl. Electrochem.*, vol. 39, no. 8, pp. 1305–1311, 2009.

[13] G. Roventi, T. Bellezze, and R. Fratesi, "Electrodeposition of Zn–SiC nanocomposite coatings," *J. Appl. Electrochem.*, vol. 43, no. 8, pp. 839–846, 2013.

[14] T. Frade, V. Bouzon, A. Gomes, and M. I. da Silva Pereira, "Pulsed-reverse current electrodeposition of Zn and Zn-TiO_2 nanocomposite films," *Surf. Coatings Technol.*, vol. 204, no. 21–22, pp. 3592–3598, 2010.

[15] I. Suzuki, "The behavior of corrosion products on zinc in sodium chloride solution," *Corros. Sci.*, vol. 25, no. 11, pp. 1029–1034, 1985.