Electrochemical Behavior and Corrosion Protection of Galvanized Steel Sheet Treated in Ce Based Solution

Yon-Kyun Song[1] and F. Mansfeld[†]

[1]Technical Research Laboratories, POSCO
1 Geodong-Dong, Nam-Gu, Pohang, Korea
Dept. of Materials Science, University of Southern California
3651 Watt Way, VHE714Los Angeles, CA90089, USA

A reaction and evaporation types of cerium based conversion coatings were developed for galvanized steel sheet. The corrosion loss $Q(Cb/cm^2)$ and protection efficiency P(%) were obtained using a polarization technique for cerium based conversion coatings on galvanized steel exposed to 0.5N NaCl for 7 days. The microstructure of coating layer was observed using SEM. An excellent corrosion reistnce of galvanized steel was obtained by two types of cerium basd conversion coating. Salt spray test was done to evaluate the corrosion resistance of three samples by visual inspection. The corrosion ranking of three samples-untreated and two treated-by electrochemical data was matched well with the results of salt spray test.

Keywords : *cerium based conversion coating, galvanized steel, corrosion*

1. Introduction

Galvanizing, i.e. the use of zinc coatings applied by electro-deposition or hot dipping, is widely used to protect steel from corrosion.[1] Zinc alloy coatings acts as a protective barrier between the steel and the corrosive environment. Zinc also provides galvanic protection by acting as a sacrificial anode where the steel is exposed to the environment due to defects or damages caused by handling. The galvanized steel sheets are usually protected from corrosive environments by conversion coatings that are produced by treatment with phosphoric acid (phosphate) or chromic acid (chromating),[2] which provides more efficient corrosion protection. Conventional chromate treatments are widely used to provide temporary corrosion protection due to their relatively low cost and good performance. However, since in its hexavalent form (Cr^{6+}) chromate is known to be a carcinogen and its compounds are environmentally hazardous as waste products,[3)-5)] it necessary to investigate alternative methods for corrosion protection. Recent environmental regulation is moving toward reducing and finally excluding Cr^{6+}. In the automobile industry, the workers who handle the chromated steel panels can be exposed to Cr^{6+} compound dust during the manufacturing process. Therefore successful development of alternative methods-"corrosion protection by green technology" or "Cr-free treatments"- to replace conventional chromate treatments has become urgent and critical.

Rare earth metal salts (REMs), such as cerium (Ce), yttrium (Y) and lanthanum (La) salts have received significant attention to as alternatives for chromate treatments on the metals such as steel, zinc and aluminum alloys.[6] The cerous ion (Ce^{3+}) has provided the best degree of protection against localized corrosion for Al7075 in NaCl,[7] therefore cerium has been studied intensively as inhibitor and coating as a Ce (hydr) oxide layer on the metal substrates.[8)-9)] The presence of cerous ions in the solution leads to the formation of protective film of Ce (hydr)oxide on the aluminum surface, which suppressed the oxygen reduction rate at the cathodic sites resulting in the reduction of the corrosion rate.[10] By dipping to cerium salts solution at room temperature could produce the protective Ce (hydr) oxide film, but this process takes at least 100 hours.[11] The treatment time was reduced within 30 min using cathodic polarization methods, but non-uniform and cracked film was obtained.[12] A modification of cerium-based coatings on Al and Zn has been developed by the addition of hydrogen peroxide in the so-called "cerating process".[13] The addition of sodium nitrite, lead acetate and Triton X-100 into cerating solution made the cerated layer on the mild steel smoother with less pores and cracks which resulted in reducing corrosion rate.[9] To enhance

the corrosion resistance, a Ce-Mo process using a two-step treatment for Al alloys has been introduced with a reduced treatment time of 2hrs.[8]

The elements of group VIa and VIIa of the periodic table such as chromium, molybdenum, manganese, tungstates and vanadates, including similar chemical states, polyatomic ions combining with oxygen, to chromium have been received attention to as candidates for Cr-Free treatments. Chromate coating layers protect the substrate from the corrosive environment by a Cr^{3+}-(hydr)oxide complex as a barrier combining mobile Cr^{6+} to repair defects in the layer by the formation of Cr^{3+}-(hydr)oxide film so-called "self-healing effect". These transition elements (VIa and VIIa) have at least two atomic states and can form oxide complexes which could be candidates to replace the present chromate treatment.

Previous studies of Cr-Free treatments have been remained on the laboratory scale due to relatively poor corrosion protection and long treatment times.[14] Therefore, the aim of this study was to develop a unique chromate-free conversion coating process for galvanized steels with reduced treatment time and enhanced corrosion protection required for the industrial applications. A modified cerium-based conversion coating process has been developed in this study.

Reaction(S1) and evaporation type(S3) cerium-based conversion coating processes for galvanized steels have been developed in this study. The protective properties of the cerium-based conversion coatings were evaluated by potentiodynamic polarization curves. SEM technique was done to analyze the characteristics of coating layer. The salt spry test for bare galvanized steels and galvanized steels treated in the reaction and evaporation type processes were carried out to compare with the industrial standard for corrosion resistance.

2. Thoeretical background

Galvanized steel sheet has been widely used for its sacrificial anode effect on the steel with cost effectiveness.. Electroplated galvanized steels are produced by passing coil steel continuously through an electrochemical cell with a speed of 80~150 m/min followed by a water rinsing zone and a chromate treatment zone. A conventional chromate treatment is applied after the galvanizing treatment to provide temporary corrosion protection during storage and handling. Different chromate treatments are used for different types of galvanized steel depending on the manufacturing parameters. Recent, environmental concern and legislative pressure to eliminate use of the carcinogenic chromate species (Cr^{6+}) have encouraged research to de-

velop environmental friendly methods to replace Cr^{6+}.

Much research dealing with rare earth metal (REM) salts such as Ce, Y, Ru, etc. as corrosion inhibitors and conversion coatings has been performed.[15]-[17] It has been generally accepted that REM cations act as cathodic inhibitors operating through precipitation of REM(hydro)oxide films.

Of all the REM cations, Ce^{3+} has been received the most detailed investigation as a corrosion inhibitor.[18] It has been reported that Ce^{3+} in aqueous solutions suppresses the cathodic reaction associated with the metallic corrosion through precipitation of a thin Ce(hydr)oxide layer.[19],[20] Hinton and coworkers reported that Ce-based conversion coating layers had a high potential to replace chromate treatments.[21],[22] Hinton developed the so-called "cerating process" with a reduced treatment time using mixtures of cerium chloride and hydrogen peroxide. A Ce-based coating layer on an Al-alloy formed in a $CeCl_3$ solution containing a mixture of Ce^{3+}-Ce^{4+} provided good corrosion resistance in the salt spray test.[22]

Hughes et al found that the cerated coating layer was composed mainly of hydrated cerium oxide and the main chemical species was Ce^{+4} as detected by X-ray photoelectron spectroscopy.[23] The cerated coating layer, complex of Ce^{4+}-Ce^{3+}-O-OH, was porous and non-uniform with a "cracked-mud" appearance. Therefore, a sealing treatment was required.

Mansfeld et al reported a Ce-based passivation process for Al alloys and Al-based metal matrix composites.[24] The corrosion resistance of Al6061-T6, Al7075-T6, Al-SiC, and Al-graphite metal matrix composites in 0.5N NaCl was greatly improved by exposure to a 1000 ppm $CeCl_3$ solution for one week. Sun found that the cerated film on mild steel was porous with a cracked-mud appearance and therefore needed to be sealed.[9] Sun optimized the cerating solution ($CeCl_3$+H_2O_2) for mild steel and improved the corrosion resistance provided by cerated film using additives such as Triton X-100 and lead acetate as well as a sealing treatment using a silicate or molybdate solution.[9]

3. Exerimental approach and data analysis

Two processes of cerium-based conversion coatings on galvanized steels were developed with cerium nitrate as the baseline solution containing different additives. Electroplated galvanized steel sheets manufactured by Pohang Iron & Steel Co. The base material was low-carbon steel with a thickness of 0.8 mm. Galvanized sheets were cut into 3.5 cm x 7 cm specimen for treatments. Cut substrates were degreased in an Alconox detergent solution using ultrasonic cleaning for 10 minutes and then fully rinsed

Table 1. Ce-based treatment methods used in this study

Exp	Test No	Solution				Dipping time at RT (sec)	Hot Drying at 120℃ (sec)
		$Ce(NO_3)_3 \cdot 6H_2O$ (mM)	pH	H_2O_2 (g/L)	Additive (g/L)		
Reaction Type	S1	10	3.8	30	-	1800	
Evaporation Type	S3	20	3.3	20	60	10	60

with purified water One process is designated as the reaction type process(S1) with simple immersion of the test sample for a sufficient time. In the other process which is designated as the evaporation type(S3) the sample covered with a wet film was placed into a convection oven for drying in order to reduce the treatment time(Table 1).

After treatment, the samples were rinsed with purified water and immediately exposed to 0.5 N NaCl. A saturated calomel electrode (SCE) and a stainless steel plate were used as reference and counter electrode, respectively. The exposed area of the working electrode was 4.9 cm^2.

The corrosion protection provided by the Ce-based conversion coating layers on galvanized steels was evaluated during exposure to 0.5 N NaCl (open to air) for 7 days using corrosion potential (E_{corr}). A potential sweep with a scan rate of 0.167 mV/s was performed in the potential range $E_{corr} - 20$ mV $\leq E_{corr} \leq E_{corr} + 20$ mV. The polarization curves were analyzed using the POLFIT software[25] that results in the values of the anodic (b_a) and cathodic (b_c) Tafel slope as well as the corrosion current density i_{corr} according to the modified Butler-Volmer equation:[26),27)]

$$i = i_{corr}[\exp(2.303 \ \Delta E/ \ b_a) - \exp(-2.303 \ \Delta E/ \ b_c)] \quad (1)$$

where i is that net current density and $\Delta E = E-E_{corr}$.

The corrosion loss of Q (Cb/cm^2) was obtained by graphic integration of i_{corr}-time curves[28)]

$$Q = \int i_{corr} \ dt \quad (2)$$

3. Result and discussion

The corrosion behavior of bare galvanized steels and galvanized steels treated in the reaction type and evaporation type processes exposed to 0.5 N NaCl for 7 days were monitored using potentiodynamic polarization method.

The E_{corr} values of bare EG and EG treated in the optimum reaction type process S1 and evaporation type process (S3) were monitored in 0.5 N NaCl for two hours (Fig. 1). After exposure for two hours, E_{corr} for bare galvanized steel was about -1.06 V vs. SCE, while E_{corr}
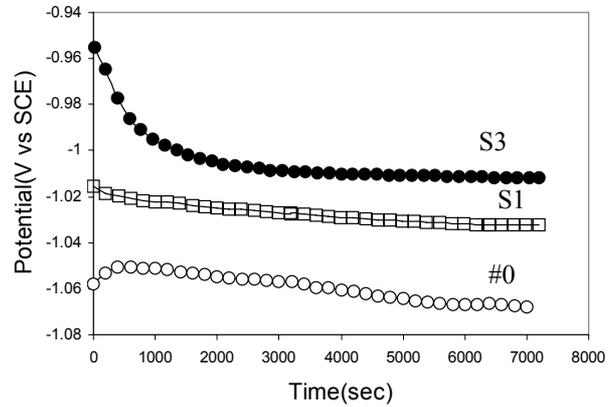
Fig. 1. The E_{corr} of three samples bare EG(#0) and treated in the reaction (S1) and evaporation processes (S3) and exposed to 0.5 N NaCl solution
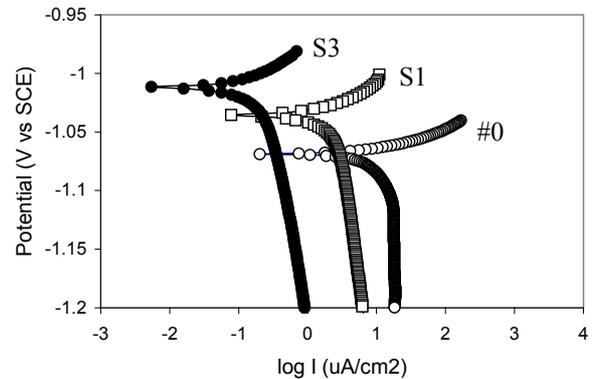
Fig. 2. Polarization curves of three samples used in this study

for the treated samples was more positive by more than 40 mV. The anodic and cathodic polarization curves obtained in a fairly wide potential region are shown in Fig. 2.

Corrosion current density, i_{corr} and Tafel slopes for three samples (#0, S1 and S3) were obtained by analysis of the polarization curves obtained in the vicinity of E_{corr} (Fig. 3) with the POLFIT program.[26)] Qualitatively, Fig. 3 shows a large difference in $R_p = B/i_{corr}$ which is defined as the slope of the E - I curve at $i = 0$ for the treated and untreated samples. The time dependecne of i_{corr} obtained by the polariztion method for three samples is

shown in Fig. 4. The Q and P values for three samples are listed in Table 2. Samples treated in the S1 and S3 processes demosnstrated excellentt corrosion resistance
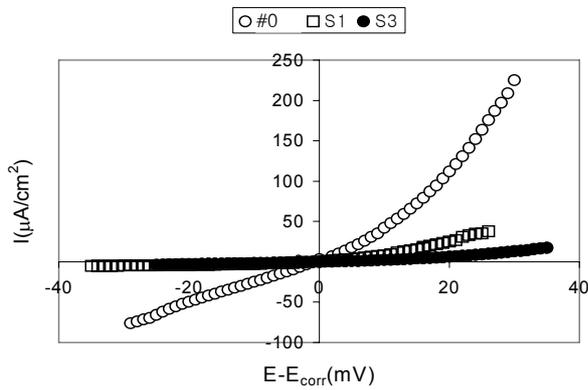
Fig. 3. Polarization curves for bare EG and EG treated in the S1 and S3 processes exposed to 0.5N NaCl for 2hrs

with P values close to 99%. The S3 process seems to provide a slightly better corroison resistance than S1 process.

The limiting current density (c.d) i_L for oxygen reduction for the treated samples was decreased compared to that for the untreated galvanized steel(#0). The anodic c.d. for the coated samples was also decreased which suggests that the corrosion protection provided by the Ce conversion film is due to reduction of the rate of both the anodic and the cathodic reactions. This is most likely due to the reduction of the area that is not covered by the conversion coating and at which corrosion occurs.

The microstructure of galvanized steel (#0) and that of treated in the S3 process are shown in Fig. 5. A very thin cerium based layer was deposited on galvanized steel sheet. SST results of three samples are shown in Fig. 6. Excellent corrosion resistance of galvanized steel was obtained by S1 and S3 process. S3 process gives much higher corrosion resistance property of galvanized steel sheet than
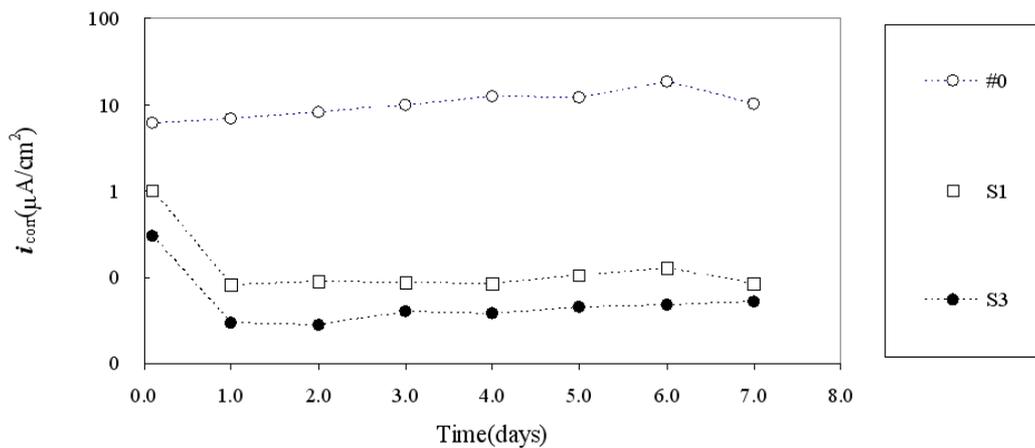
Fig. 4. Time dependence of icorr for bare galvanized steel (#0) and treated in the S1 and S3 processes exposed to 0.5N NaCl
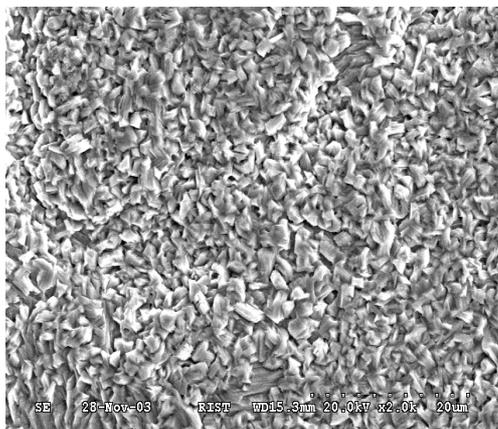
(a)
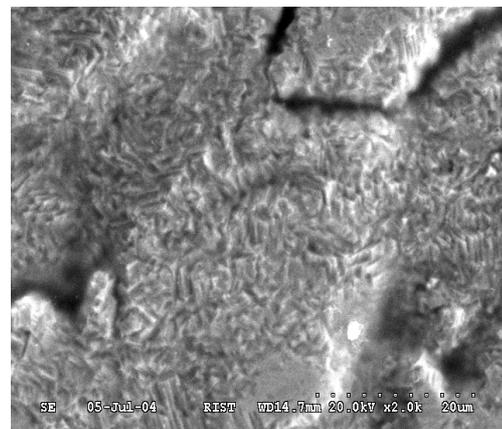
(b)

Fig. 5. SEM of bare galvanized steel (a) and that of treated in S3 process(b)

(a)   (b)   (c)
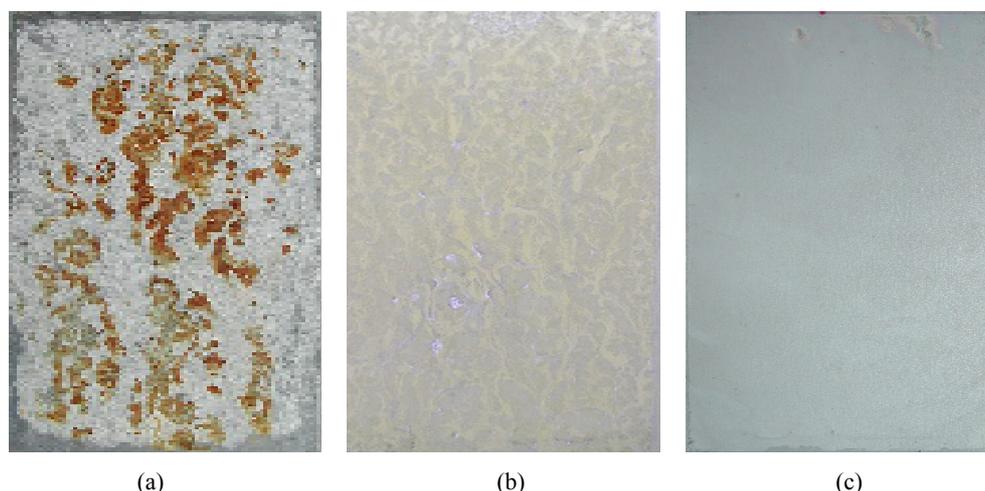
Fig. 6. SST results of bare galvanized steel (a), those of treated in the S1(b) and S3(c) process for 24 hrs

Table 2. Comparison of Q and P values obtained for three samples exposed to 0.5N NaCl for 7 days

	Q(Cb/cm^2)	P(%)
#0	6.9	-
S1	0.12	97.5
S3	0.03	99.6

S1 process. The corrosion ranking of three samples by polarization method is well matched with that by SST.

5. Summary

In this study, cerium based conversion coating on galvanized steel is investigated using electrochemical method. Corrosion current densities of two different treated galvanized steel samples were monitored in 0.5 N NaCl solution. Corrosion loss and protection efficieny of bare and treated samples were evaluated. Evaporation process gives higher corrosion resistance than reaction type process based on the electrochemical data. The corrosion ranking of three samples (bare and two treated) obtained by electrochemical methods is well matched with salt spray test results.

References

1. K. E. Aeberli and Y. H. Lee, Bokamper, Helmut, Metallurgical plant and technology international, MPT 23, 58 (2000).
2. Conversion coating,Alubook< http://www.alu-info.dk/Html/alulib/modul/A00197htm>
3. H. J. Ashmead, *J. Appl. Nutrition*, **24**, 8 (1972).
4. M. S. Vukasovich and J. P. G. Farr, *Materials Performances*, **25**, 9 (1986).
5. N. Zaki, *Metal Finishing*, **88**, 99 (1990).
6. B. R. W. Hinton, D. R. Arnott, and N. E. Ryan, *Metals Forum*, **7**, 211 (1984).
7. B. R. W. Hinton, D. R. Arnott, and N. E. Ryan, *Mater. Forum*, **9**, 162 (1986).
8. You Wang, Ph. D. Thesis, University of Southern California, 1994.
9. Z. Sun, Ph.D. Thesis, University of Southern California, 2001.
10. B. R. W. Hinton and L. Wilson, *Corros, Sci.*, **29**, 967 (1989).
11. International Patent WO 88/06639.
12. M. Geary and C. B. Breslin, *Corr. Sci.*, **39**, 1341 (1997).
13. G. D. Wilcox, D. R. Gabe, and M. E. Warwick, *Corros. Sci.*, **28**, 577 (1988).
14. G. D. Wilcox and D. R. Gabe, *Brit. Corros. J.*, **22**, 254 (1987).
15. A. C. Cross land, G. E. Thompson, P. Skeldon, G. C. Woof, C. J. E. Smith, H. Habazaki, and K. Shimizu, *Corrosion Sci.*, **40**, 871 (1998).
16. F. Mansfeld, C. Chen, C. B. Breslin, and D. Dull, *J. Electrochem.Soc.*, **145**, 2792 (1998)
17. F. M. Seon, *J. Less Common Metals*, **148**, 73 (1989).
18. S. Boehm, R. Greef, H. N. McMurray, S. M. Powell, and D. A. Worsley, *Jr. Electrochem. Sci.*, **147**, 3286 (2000).
19. A. J. Aldykiewicz, A. Z. Davenport, and H. S. Issacs, *J. Electrochem. Soc.*, **143**, 147 (1996).
20. A. J. Davenport, H. S. Isacs, and M. W. Kendig, *Corros. Sci.*, **32**, 653 (1991).
21. B. R. W. Hinton, D. R. Arnott, and N. E. Ryan, *Metals Forum*, **7**, 211 (1984).
22. B. R. W. Hinton and L. Wilson, "Effect of Cerous Chloride Concentration on Corrosion Rate", Australian patent, PCT/AU88/00060.
23. A. E. Hughes, R. J. Taylor, B. R. W. Hinton and L. Wilson, *Surf. Inter. Anal.*, **23**, 540 (1995).

24. F. Mansfeld, S. Lin, S. Kim, H. Shih, *Corrosion*, **45**, 615 (1989)

25. F. Mansfeld, H. Shih, H. Greene and C. H. Tsai, *ASTM STP*, **1188**, 27, (1993).

26. J. A. V. Butler, *Transactions of the Faraday Society*, **19**, 729 (1924).

27. T. Redey-Gruz and M. Volmer, *Zeitschrift fur Physikund Chemie*, **150A**, 203 (1930).

28. V. Barranco, C. Feliu Jr. and S. Feliu, *Corros. Sci*., **46**, 2221 (2004).