Cerium Conversion Coatings on Zinc Plated Steels

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Cerium based conversion coatings are done on the four galvanized (zinc plated) steel sheet in order to replace conventional chromate conversion coatings. Hydrogen peroxide and colloidal silica are employed to enhance the corrosion protection property. Electroplated zinc, hot dip zinc and electroplated zinc nickel steels are used as substrates. Samples are simply dipped into cerium conversion coating solutions at room temperature and oven baking process is followed. The corrosion protection property of treated samples are evaluated using by electrochemical techniques and corrosion accelration test (ASTM B-117). The characteristics of coating layer are done by SEM and SAM techniques. The cerium conversion coating on the zinc nickel based samples shows the excellent corrosion protection property comparison with electroplated and hot dip zinc steel. The cerium-based conversion coating layer is composed of Ce-O-C-Si complexes. All of treated galvanized samples passed 100 hrs without any white rust in the salt spray chamber. The treated EN showed the excellent corrosion resistance property. The cerium-based conversion coating used in this study has a high potential when applying it any galvanized steel without pre-treatment.

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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 necerssary to investigate alternative methods for corrosion protection. Recent environmental regulation is moving toward reducing and finally excluding Cr^{6+}. Therefore succesful development of alternative methods- “Cr-free treatments”- to replace conventional chromate treatments has become urgent and critical. Cerium-based with addition of silane and colloidal silicate conversion coating method to replace conventional chromate solution was applied for four different galvanized steels sheets which are most widely used in the industry. The corrosion resistance of treated galvanized samples was evaluated using electrochemical technique and salt spray test. The characteristics of coating layer were carried out using SAM depth profiling analysis.

2. Theoretical Background

Cerium-based conversion coating

Much research dealing with rare earth metal (REM) salts such as Ce, Y, Ru, etc. as corrosion inhibitors and conversion coatings has been performed [6-8]. 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, $Cerium^{3+}$ have been received the most detailed investigation as a corrosion inhibitor [9]. It has been reported that Ce^{3+} in aqueous

solutions suppresses the cathodic reaction associated with the metallic corrosion through precipitation of a thin cerium(hydr)oxide layer [10,11]. Hinton and coworkers reported that cerium-based conversion coating layers had a high potential to replace chromate treatments [12,13]. Hinton developed the so-called "cerating process" with a reduced treatment time using mixtures of cerium chloride and hydrogen peroxide. A cerium-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 [13].
The oxidation of Ce^{3+} to Ce^{4+} by hydrogen peroxide generates a peroxide complex at pH <2.5 [14]:

$$Ce^{+}(aq) + H_2O_2 \rightarrow Ce(H_2O_2)^{3+}(aq) \quad [1]$$

For pH> 2.5, a solution color changes from clear to golden yellow is observed [14] due to the following reaction:

$$2\,Ce^{3+} + 2OH^{-} + H_2O_2 \rightarrow 2Cer(OH)_2{}^{2+} \quad [2]$$

In the vicinity of the metal surface, the reduction of the hydrogen peroxide produce OH^-:

$$H_2O_2 + 2e \rightarrow 2OH^{-} \quad [3]$$

which causes precipitation of insoluble CeO_2 at cathodic sites [15]:

$$Ce(HO)_2{}^{2+} + 2OH^{-} \rightarrow CeO_2 + 2H_2O \quad [4]$$

For the cerium peroxide complex species, the precipitation reactions may occur [61]:

$$Ce(H_2O_2)^{3+} \rightarrow Ce(HO_2)^{2+} + H^{+} \quad [5]$$

$$2Ce(HO_2)^{2+} + H_2O_2 \rightarrow 2Ce(O_2)^{2+} + H_2O \quad [6]$$

$$Ce(O_2)^{2+} + 2e \rightarrow CeO_2 \quad [7]$$

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 [16]. The cerate coating layer, complex of Ce^{4+}-Ce^{3+-}-O-OH, was porous and non-uniform with a “cracked-mud” appearance. Aramaki reported a hydrated Ce_2O_3 film formation process on pure zinc with addition of $Zn(NO_3)_2$ and Na_3PO_4 to a cerium nitrate solution [17-20]. The Ce_2O_3 coating layer containing a small amount of Ce^{4+} was remarkably protective had a “self-healing” effect during exposure to NaCl solution [21]. The release of Ce^{4+} into the sodium chloride solution was detected by UV absorption measurements and a Ce^{3+}-complex precipitation on the defects in the coating layer was observed [22]. This results supported the “self-healing “ effect of cerium-based conversion coating. Based on Davenport et al observed that Ce^{3+} was converted to Ce^{4+} in cerium-based coating layers applied to an Al-Mg alloy upon exposure to aerated chloride solution [23]. Boehm observed the cerium-film formation mechanism on Zn by in-situ ellipsometry and proposed that the rate determining step for cerium(hydro)oxide film formation was the hydrolysis of Ce^{3+} to precipitate $Ce(OH)_3$. Aqueous cation hydrolysis occurs in the region of high interfacial pH:10.5. $Ce(OH)_3$ may subsequently become oxidized to CeO_2 by H_2O_2 produce through the 2e- reduction of O_2 [9].

Colloidal Silica. Micro-fine particles of silicon dioxide(SiO_2) dispersed in the water are called colloidal silica. The silica surface is negatively charged by hydroxyl ions formed by the loss of protons from water molecules in the space between the oxygen atoms of the SiO_2 structure which makes it gelatin and colloidal. The stability of colloidal silica depends on the particle size and pH. Generally, the higher the concentration and the smaller the size, the greater is the effect of pH changes. The colloidal silica is extraordinarily stable at pH:2, where the zeta potential is zero and becomes increasingly unstable at higher pH. Colloidal silica has been widely used in industrial application as a binding agent, oil ink dispersing agent and anti-soiling surface agent. Addition of colloidal silica into a chromate solution can provide improved corrosion protection due to its hydrophobic effect. Some authors have tried to form a silicate film on galvanized steel using sol-gel methods [24-26].

```Silane. The most commonly used silanes are organotrialkoxysilanes, titanates, zirconates and organic acid-chromium chloride coordination complexes, which act as coupling agents to enhance bond strength between organic and inorganic materials. Silanes may also bond inorganic fillers or fibers to organic resins to form or promote a stronger bond at the interface. Silane plays a role as a chemical bridge between resin and glass fiber in the composite material. The inhibiting efficiency of silane on Al corrosion in sodium chloride solution was studied by Zucchi et al. who found the optimum pH range for each silane[27]. The silane film was formed on Al by simple immersion in the BTSE solution and the treated samples were exposed to 0.1N NaCl to obtain potentiodynamic polarization curves. The cathodic current density was forward to the decreased about a factor of 4 compared to a sample without treatment [27]. Silane apparently produces a thin organic film which reduces the oxygen reduction reaction rate.
Ferreira et al reported the silane (BTESPT) treatment for hot dip galvanized steels to replace the conventional chromate treatment [28]. A simple immersion in a silane(BTESPT) solution and heat treatment at 120 $C^o$ for 40 min produce a carbon rich film on the substrate, which showed some improved corrosion protection comparing untreated hot dip galvanized steels based on the analysis of the EIS data.

## 3. Experimental Approach

### Materials.

Four different galvanized steel sheets manufactured by POSCO in Korea were used in this study with coating thicknesses between 3 and 70 µm. The base material was low-carbon steel with a thickness of 0.8mm. The chemical composition of galvanized steel layer is shown in Table 1. Galvanized sheets were cut into 3.5cmx7cm specimen for treatments. Cut substrates were degreased in an Alconox detergent solution using ultrasonic cleaning for 10 minutes and then fully rinsed with purified water.

### Treatments

Degreased four galvanized samples were dipped into the Cerium-based solution
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Table 1 Coating thickness and chemical composition of four different galvanized steel sheets

	EG	EN	GA	GI
	(electroplated Zn/Steel)	(electroplated Zn-Ni/Steel)	(hot dipped Zn/Steel)	(hot dipped Zn-Fe/Steel)
Coating Thickness (μm)	3~5	3~5	50~60	50~70
Chemical Composition (wt%)	Zn: >99.99	Ni:10~15 Zn:bal	Al:0.3~0.4, Zn:bal	Al:0.2~0.3 Fe:9~13 Zn;bal.

Table 2. The chemical composition of cerium-based conversion coating solution used in this study

(g/L)

Cerium	H_2O_2	Silane	Silicate
12.5	5	20	30

including silane and silicate for three seconds and put into the convection oven at 120^{o}C for 1minute. The cerium-based conversion coating solution used in this study is shown in Table 2.

Evaluation

Electrochemical techniques were employed to evaluate the corrosion protection of galvanized steels by the coatings developed in this study. The corrosion protection provided by the cerium-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}) and potentiodynamic polarization measurements using impedance measurement unit(IM6, Zahner). 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 [29] 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 [30,31]:

$$\boldsymbol{i} = \boldsymbol{i}_{corr}[\exp(2.303\ \Delta E/ b_a) - \exp(-2.303 \Delta E/ b_c)] \qquad [8]$$

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

The parameter $B = b_a b_c / 2.3(b_a + b_c)$ was used to convert the polarization resistance The corrosion loss of Q (Cb/cm^2) was obtained by graphic integration of $\boldsymbol{i}_{corr}$-time curves [32]:

$$Q = \int \boldsymbol{i}_{corr}\ dt \qquad [9]$$

Results of visual inspection of coated galvanized steels after exposing to 0.5N NaCl were compared to the electrochemical results. Surface analysis of coatings was performed and the salt spray test was carried out according to ASTM B-117. Surface analyses using SEM and SAM were carried out to define surface morphology and chemical composition of the coating layers formed on the galvanized steel sheets..

4. Results and Discussion

Corrosion current density, $\boldsymbol{i}_{corr}$ and Tafel slopes for the four bare substrates EG and EG treated in the Cerium-based solution were obtained by the analysis of the polarization curves in the vicinity of E_{corr} (Fig. 1) with the POLFIT program [29]. Open circle and squire indicates the experimental measured data . Solid and dotted lines are simulated data by POLFIT program. Qualitatively Fig.1. Shows a large difference in R_p which is defined as the slope of the E – I curve at $\boldsymbol{i} = 0$ for the bare and treated samples. The corrosion current densities of bare and treated samples exposed to 0.5N NaCl were monitored for 7 days. (Fig. 2.) Open markers are untreated samples (EG,EN,GA,GI) and solid markers are treated samples.

Corrosion current densities of treated samples are much lower than those of bare samples. The corrosion loss, Q (Eq.9) obtained by integration of $\boldsymbol{i}_{corr}$ vs time and the protection efficiency P defined as:

$$P(\%) = (1 - Q_{corr} / Q_{corr}^{\ o})\ 100 \qquad [10]$$

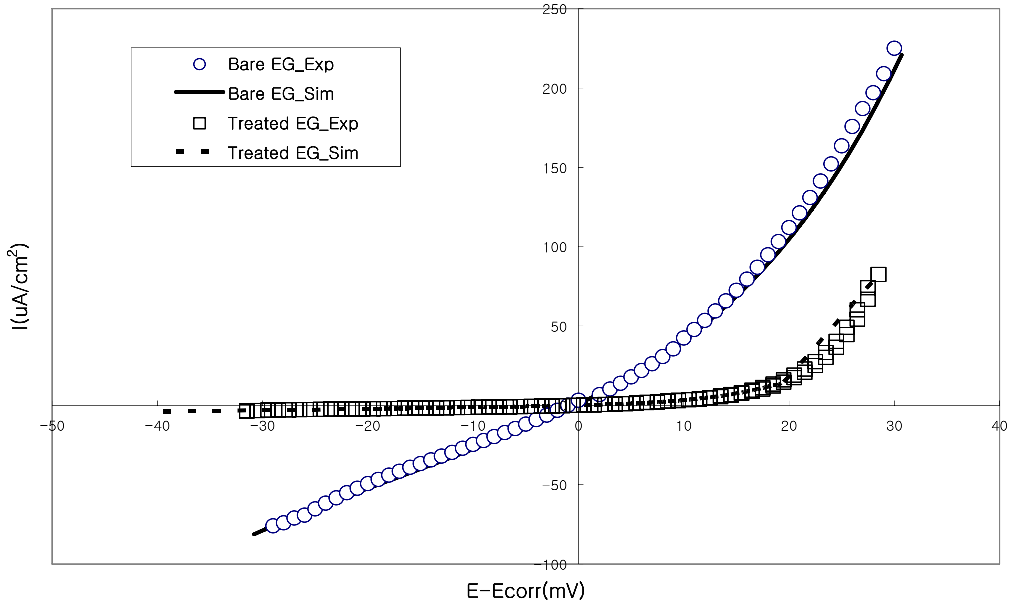


Fig. 1. Polarization curves for bare EG and treated EG exposed to 0.5N NaCl for 1 day

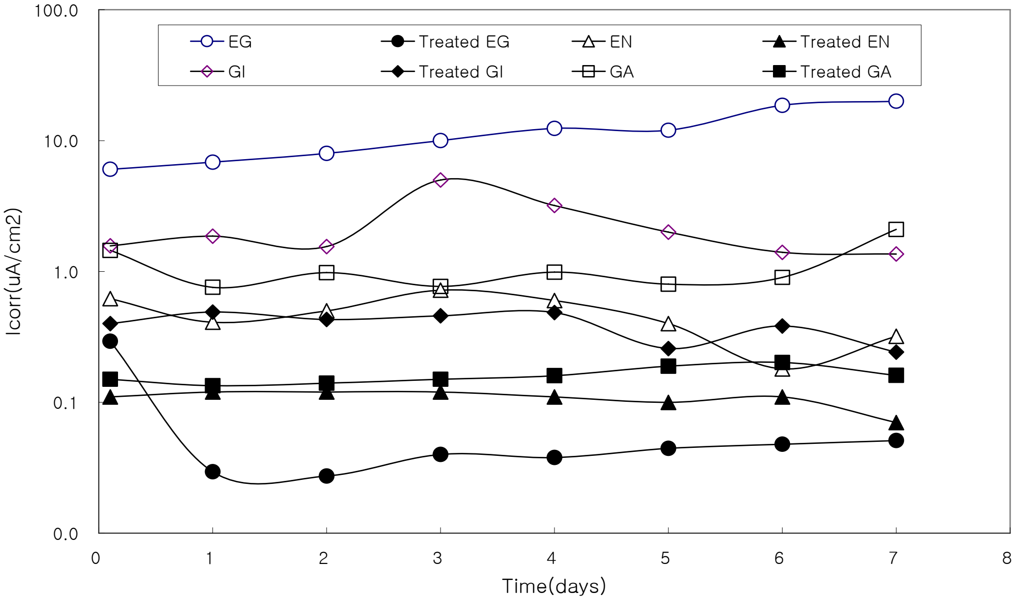


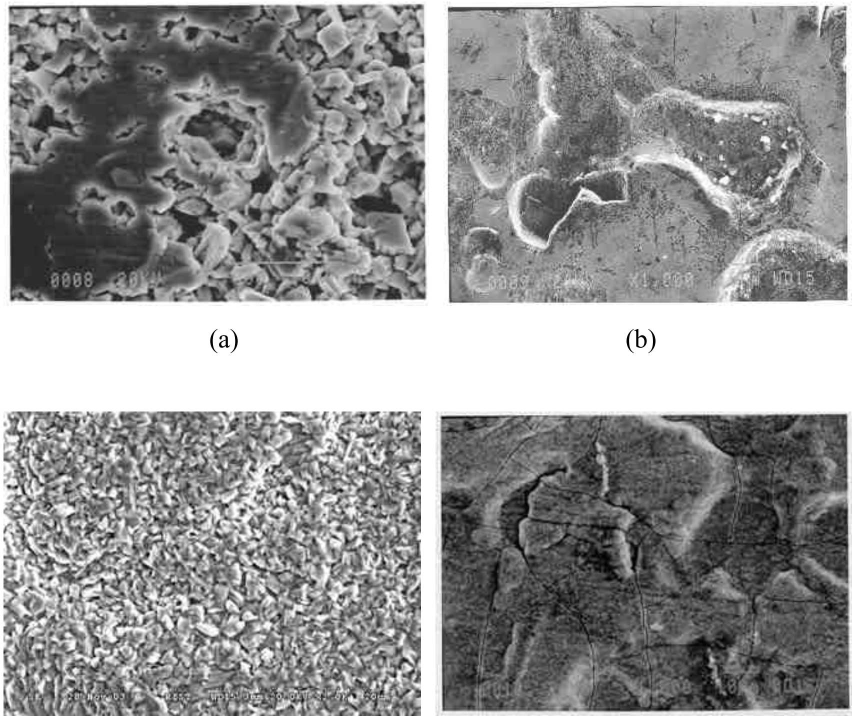
Fig. 2. Time dependence of $\boldsymbol{i}_{corr}$ *for bare and treated samples exposed to 0.5N NaCl*

are shown in Table 2 where Q^{o}_{corr} and Q_{corr} refers to the bare and treated samples, respectively [33]. The ranking order of the corrosion resistance for bare galvanized samples based on Q values is EN>GA>GI>EG. It can be said that the corrosion resistance of bare galvanized steels seemed to be attributed to the surface chemical composition and roughness, etc. The SEM morphologies of bare galvanized samples are shown in Fig.3. The surface morphologies of galvanized samples seem to depend on the manufacturing process. The ranking of corrosion protection for treated samples based on Q values is treated EN> treated EG > treated GI > treated GA.

Table 2. Comparison of Q and P values obtained by polarization method for bare and treated samples exposed to 0.5N NaCl

		EG	EN	GI	GA
Q(Cb/cm2)	Bare	6.9	0.27	1.6	0.5
	Treated	0.1	0.06	0.17	0.21
P(%)		98.5	77.8	89.4	58.1

The corrosion resistance of the bare substrates was reflected in that of coated sample. Bare EN has the highest corrosion protection based on Q values, which makes the high corrosion protection for cerium-based coating on EN. EG showed the highest P value (98%) while GA showed the lowest value (58.1%). The cerium-based conversion coating used in this study is suitable for EG. Some modification of the solution composition or use of pre-treatment is necessary for GA. However, a unique process can be applied to the different galvanized steels with good corrosion protection, which has a high potential to apply for working mills in terms of productivity. The cerium-based conversion coating used in this study It can be inferred that the different chemical status and morphologies of each bare sample shows the different corrosion behavior. SAM depth profiling analyses of treated galvanized samples were performed with Ar^{+} sputtering (Fig. 4.) The major component of cerium-based conversion coating layer is a complex of Ce-O-Si. Considering the same sputtering rate, the thickness of coating layers

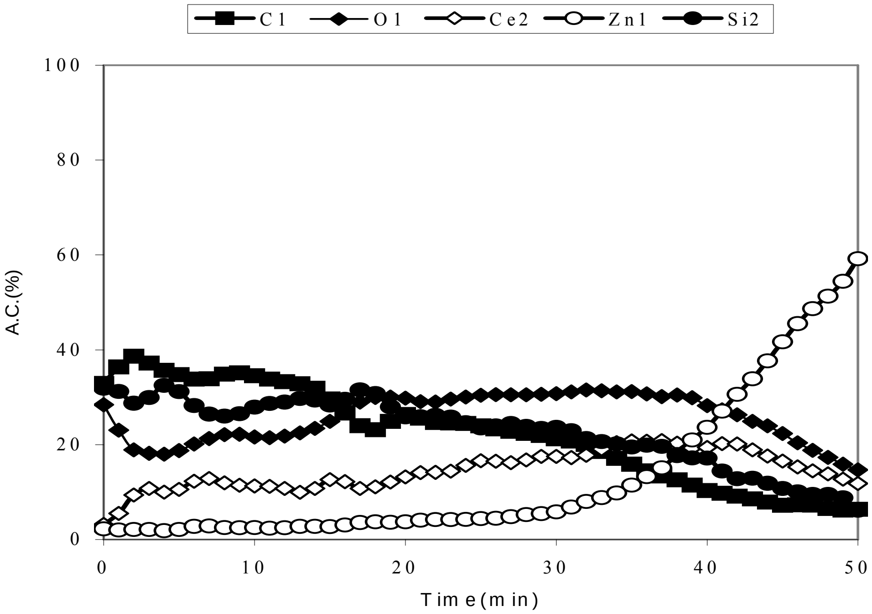


(a) (b)

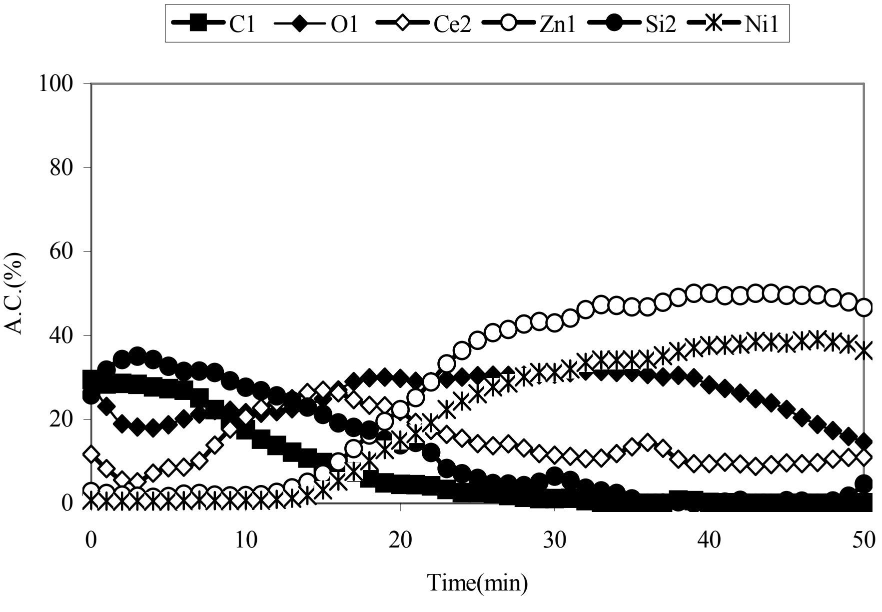
(c) (d)

Fig. 3. SEM morphologies for bare EG(a), EN(b), GI(c) and GA(d)

on galvanized steels are little bit different. Salt spray results for treated galvanized steels are shown in Fig. 5. All of the test samples passed 100hrs without the appearance of white rust and some tarnished area was found on the surface for all samples after 100 hrs. White rust appeared on the treated GI after 120 hrs and was observed on treated EG and treated GA after 160 hrs. The treated EN showed excellent corrosion resistance passing 200 hrs without the appearance of white rust, which indicates the developed cerium-based conversion coating layer is very useful in terms of short treatment time (70sec) providing excellent salt spray test results(100hrs). The cerium-based conversion coating with the addition of silane and silicate also has significant advantages that it can apply to the different galvanized steels without any pre-treatment. The ranking of corrosion protection for treated galvanized steels are treated EN >> treated EG > treated GA > treated GI based on the time for white rust appear on the surface. The ranking of the corrosion based on the electrochemical data does not completely agree with that

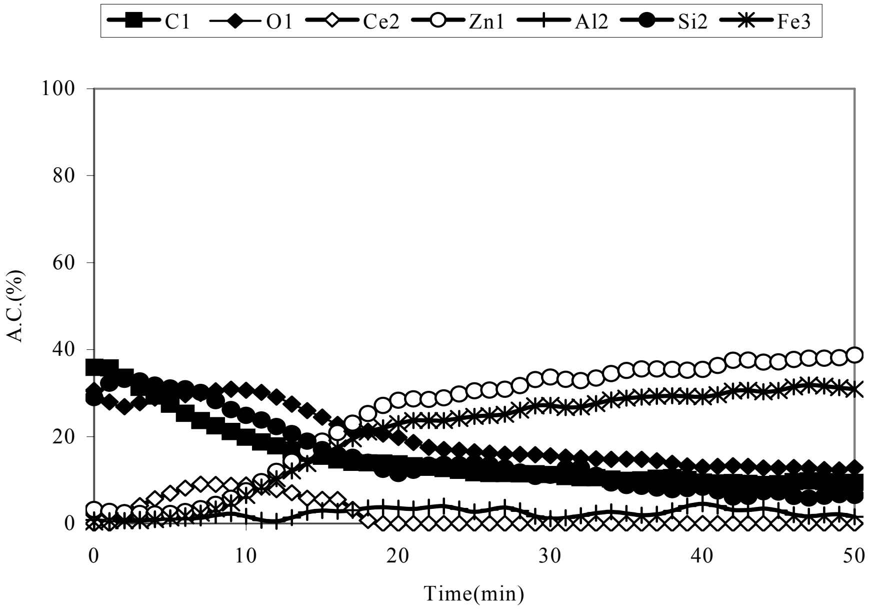


(a)

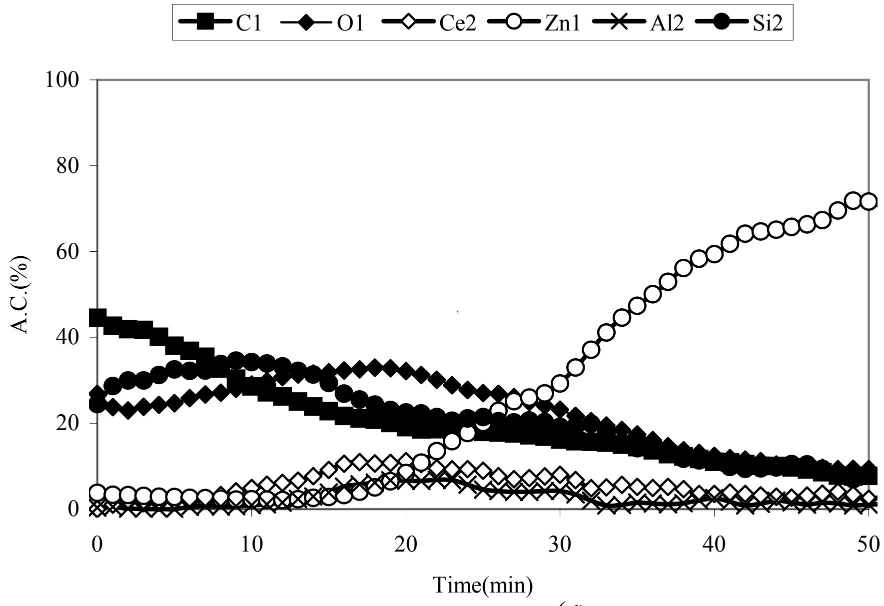


(b)

Fig. 4. SAM depth profiles of treated EG (a), treated EN(b), treated GI(c) and treated GA(d) with sputtering rates of 2nm/min for 0~30min and 10nm/min for 30~50min



(c)



(d)

Fig. 4. continued

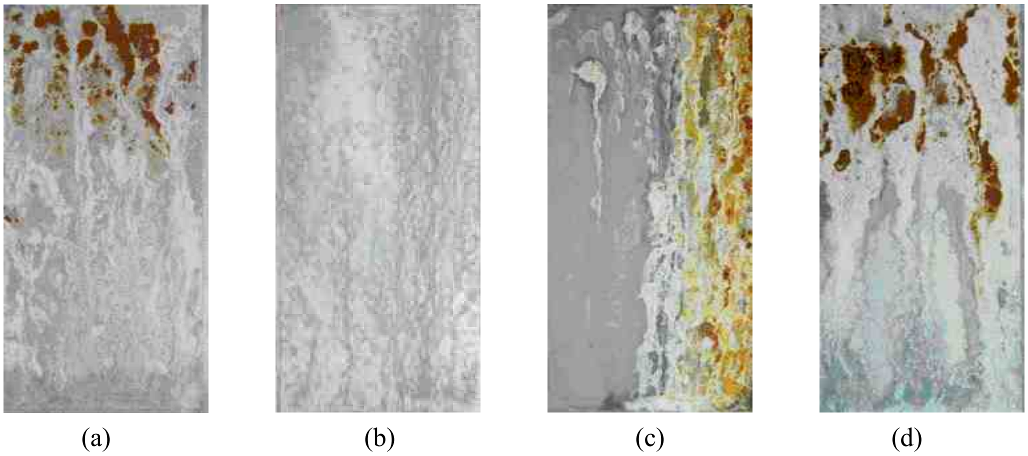

(a) (b) (c) (d)

Fig. 5. Salt spray results for treated EG(a), treated EN(b), treated GI(c) and treated GA(d) for 200 hrs

obtained by salt spry test results. However, it can be said that the tendency of corrosion resistance for treated samples obtained by electrochemical data for evaluation almost matches with that obtained by salt spray test results.

5. Conclusions

Cerium-based conversion coating with the addition of silane and silicate was applied for four galvanized steel. Electrochemical data of treated samples were used to evaluation the corrosion protection property for treated galvanized samples. Electrogalvanized steel(EG) seems to be most suitable for the cerium-based conversion coating used in this study. The cerium-based conversion coating layer is composed of Ce-O-C-Si complex. The coating thickness of layers depends on the kinds of galvanized substrate. The ranking of corrosion resistance obtained by monitoring Q and P values does not completely agree with that obtained by salt spray test result. It can be said that the tendency for the order of corrosion protection obtained by electrochemical date would almost match with the salt spry test results. All of treated galvanized samples passed 100 hrs without any white rust in the salt spray chamber. The treated EN showed the excellent corrosion resistance property. The cerium-based conversion coating used in this study has a high potential when applying it any galvanized steel without pre-treatment.

REFERENCE.

1. Aeberli, Karl Edward; Lee, Young Ho; Bokamper, Helmut, Metallurgical plant and technology international: MPT. 23, no. 4, (2000): 58 (8 Pages).
2. POSCO Automotive steel application center, Products development http://www.poscoauto.co.kr/docs/eng/rnd/rnd_material3_09.jsp
3. Conversion coating,Alubook < http://www.alu-info.dk/Html/alulib/modul/A00197htm>
4. H.J. Ashmead, J. Appl. Nutrition, 24, 8 (1972).
5. M.S. Vukasovich and J.P.G. Farr, Materials Performances, 25, 9 (1986).
6. 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).
7. F. Mansfeld, C. Chen, C. B. Breslin and D. Dull, J. Electrochem.Soc., 145, 2792 (1998).
8. F. M. Seon, J. Less Common Metals, 148, 73 (1989).
9. S. Boehm, R. Greef, H. N. McMurray, S. M. Powell and D. A. Worsley, Jr. Electrochem. Sci., 147, 3286 (2000).
10. A. J. Aldykiewicz, A. Z. Davenport and H. S. Issacs, J. Electrochem. Soc., 143, 147 (1996).
11. A. J. Davenport, H. S. Isacs and M. W. Kendig, Corros. Sci., 32, 653 (1991).
12. B. R. W. Hinton, D. R. Arnott and N. E. Ryan, Metals Forum, 7, 211 (1984).
13. B. R. W. Hinton and L. Wilson, “Effect of Cerous Chloride Concentration on Corrosion Rate”, Australian patent, PCT/AU88/00060
14. A. E. Hughes, S. G. Hardin, R. M. Peter and W. W. Klaus, paper no. 111, NACE 2000, Orlando, Florida (2000).
15. A. J. Aldykewicz, Jr. A. J. Davwnport and H. S. Isaacs, J. Electrochem. Soc., 143, 147 (1996).
16. A. E. Hughes, R. J. Taylor, B. R. W. Hinton and L. Wilson, Surf. Inter. Anal., 23, 540 (1995).
17. K. Aramaki, Corros. Sci., 44, 2621 (2002).
18. K. Aramaki, Corros. Sci., 45, 1085 (2003).
19. K. Aramaki, Corros. Sci., 43, 1573 (2001).
20. K. Aramaki, Corros. Sci., 43, 2201 (2001).
21. K. Aramaki, Corros. Sci., 45, 1085 (2003).

22. J. Zhao, G. S. Frrenkel and R. L. McCreey, J. Electrochem. Soc., 145, 2258 (1998).

23. A.J. Davenport, H.S. Isaacs and M. W. Kendig, Corros. Sci., 32, 653 (1991).

24. A. Barducci, M. Delucchi and G. Gerisola, Progress in Organic Coatings, 33, 131 (1998).

25. R. L. Twite and G.P. Bierwagen, Progress in Organic Coatings, 33, 91 (1998).

26. M. Khobaib, L. B. Reynolds and M.S. Donley, Surface and Coatings technology, 140, 16 (2001).

27. F. Zucchi, G. Trabanelli, V. Grassi and A. Frignani, 15th International Corrosion Council, Granada, Spain, Sept. 22, 2002, p. 222.

28. M. G. S. Ferreria, R. G. Durate, M. F. Montemor and A. M. P. Simoes, Electrochim. Acta, 49, 2927 (2004).

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

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

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

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

33. K. Aramaki, Corros. Sci., 45, 1085 (2003).