



The Anti-Corrosion of Trivalent Chrome Conversion Coatings Containing Nano-Silica on Zinc Electroplated Steel

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ABSTRACT

A passive conversion layer was fabricated from C2 solution (with the composition of 5g Cr(III)/ L, compound producing complex 16 g/L, pH = 9) containing nano-silica particles with the content of 5 g/L, on zinc coated samples denoted as M9-5. In this condition, silica particles were dispersed well in the solution with the particles size of about 87 nm. M9-5 samples do not contain a toxic component of Cr(VI) and were significantly reinforced in anti-corrosion ability in comparison to the zinc coated samples. In addition, M9-5 samples have ability to self correct when it is scratched. This ability is the most important property of conversion layer which can reinforce the anti-corrosion property of the samples.

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Introduction

In the last decades, electroplated zinc coatings have been widely employed to protect metals and alloys from corrosion and have seen remarkable development due to the increase of demand from the automotive industry for coatings with better corrosion resistance. However, zinc is an electrochemically high reactive metal, therefore it can be corroded with a relatively high rate even under outdoor exposure conditions. Fortunately, the corrosion resistance of zinc coating can be increased by means of suitable chemical passivation treatments or organic coatings. Generally in industry, zinc coated articles are immersed in a bath of acidic solution containing chromate ion. Several surface reactions are taking place during immersion time leading to the formation of the passive film with the thick ranging from 10 to 100 nm composed of zinc oxides and hydroxides, zinc chromate, mixed Cr(III) and Cr(VI) oxides and hydroxides. Nevertheless, compounds containing Cr⁶⁺ are considered as carcinogenic substances for human health, cause a serious environmental pollution, have been increasingly forbidden by European standards.

For this reason, many chemicals including trivalent chromium conversion have been employed as alternative to chromate conversion coating. Trivalent chromium conversion coating is one of the most effective treatments, which provides more corrosion resistance and increases the adhesion between primer coatings and metal substrates [1, 2, 3]. Although the use of trivalent chromium conversion coating reduces the toxicity of the raw materials and of the produced wastes, it has several drawbacks including a low ability of self correction of the coating layer. It is believed that the addition of some compounds including nanosilica can overcome that problem. The self correction of layer depends much on the amount of silica in the layer and the size of silica particles. However, the dispersion of nanosilica in water to get small size is a

difficult procedure due to the ease of coagulation of nanosilica particles even at the ordinary conditions. In addition, suspension of nanosilica is unstable giving rise the difficulty in producing Cr(III) – nanosilica suspension.

In this work we present the investigation on factors affecting to the dispersibility of nanosilica in Cr(III) solution and characterization of passive chromium conversion coating on the electroplated zinc layer [4].

Materials and Methods

Chemicals: HNO₃, NH₄OH, NaCl and C12-14 alcohol ethoxylate (AE7) were purchased from China, the passive solution containing Cr(VI), UDYCRO 747 from Enthone, USA and nanosilica from Aerosil, Belgium. All chemicals were used as received without further purification.

SPHC steel samples were cut into the size of 100 × 50 × 1.2 mm. Chemical compositions of the SPHC steel sheet are accordance to JIS G3131. Before coating with zinc, the samples were mechanically polished with sandpaper of 600 grade, degreased, cleaned with 10% HCl solution. Zinc electrodeposition procedure was carried out according to the process proposed by Enthone [5] in a bath of 25 liters containing: ZnCl₂ 60 g/L, NH₄Cl 250 g/L, AZA 30 ml/L, AZB 1.5 mL/L, pH ranging from 4.8 to 5.4, using current density of 2A/dm² within 30 minutes under ambient condition. The average coating thickness of the zinc coatings was about 13 μm. The zinc coating surface was then activated with 0.5 % HNO₃ solution for 5 seconds and rinsed with deionized water before the conversion treatment. The block passive solution (C2) has composition of: Cr(III) (5g/L), compound which can produce complex (16g/L), pH = 1.5 ÷ 1.8. The passive conversion solution was prepared by mixing 10 mL of UDYCRO 747 and 100 mL of C2 then diluting to 1000 mL. pH of the conversion solution was adjusted using nitric acid and ammonium solution. The immersed time is 60 seconds under ambient condition and kept the same for every samples.

The coating samples were then rinsed with plenty of deionized water following by drying in an oven at 80 °C for 30 minutes. The passive conversion solutions containing nanosilica were prepared by mixing 800 mL dispersion of nanosilica with 1 gram of AE7, 100 mL distilled water and 100 mL of stock C2 solution under the magnetic stirring and ultrasonic conditions. pH of these solutions were adjusted using ammonia and nitric acid solutions.

The surface morphology of treated specimens was investigated by means of SEM, HITACHI S4800 and FT-IR spectroscopy, NEXUS-670, Nicotet – USA. Compositions of sample's surface was examined with the help of energy dispersive X-ray microscope. The salt spray testing of these treated samples was performed on Q-FOG CCT-600 according to the standard JIS H8502. The samples were exposed to 5 % NaCl fog (pH changing from 3.0 to 6.5 adjusted with NaOH or CH₃COOH solution by means of METERLAB PHM210) in a salt spray chamber at 35 °C. The coverage of the sample surfaces by the white corrosion products was recorded.

The corrosion behavior of the conversion coatings was evaluated by polarization tests. Polarization tests were performed at a scan rate of 2 mV/s in 5 % NaCl solution using a conventional three-electrode cell: specimen as a working electrode, saturated calomel electrode (SCE) as a reference electrode and a platinum counter electrode. All electrochemical experiments were performed using Autolab PGSTAT30.

Results and Discussion

Dispersion of nano-silica in water

In order to get the best dispersion of nanosilica in conversion solution, dispersion of nanosilica powders in water with at different pH values ranging from 1.5 to 10 and different contents of nanosilica was tested. Firstly, 1 gram of nanosilica was dispersed in 200 mL (or 5 g/L) water with pH value ranging from 1.5 to 10. The dispersions were observed with visual inspection. The results showed that, the precipitation took place immediately after dispersion of nanosilica in the water with pH value of 1.5, 2.0, 3.05, 4.0 and 5.0. At the other values of pH, the precipitation only appeared at least after 120 hours. With the case of pH = 9.0, the precipitation appeared after 480 hours. For this reason, the pH of 9.0 was chosen for the next step to study the effect of nanosilica content on dispersion.

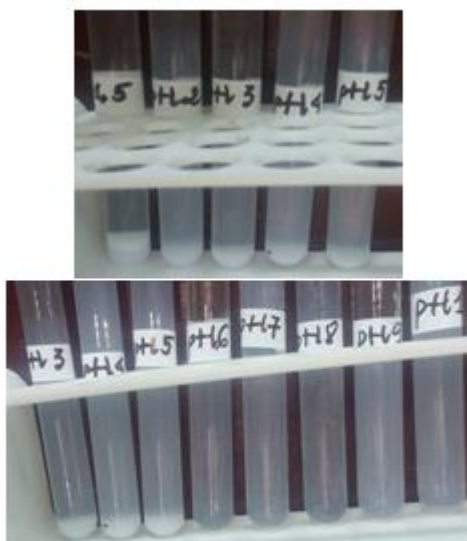
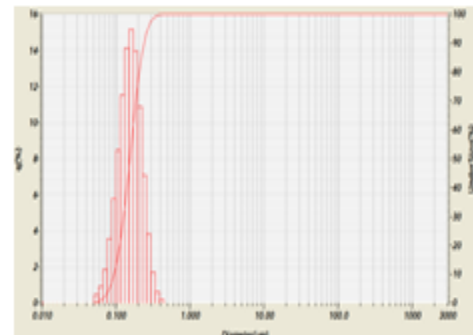
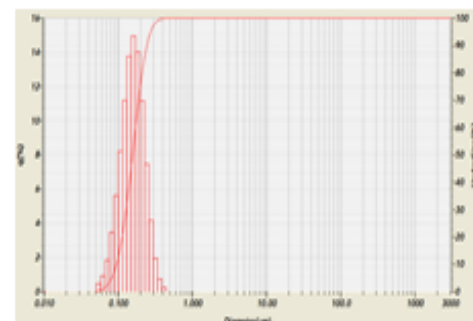


Figure 1. The dispersion of nano-silica particles in different pH values.

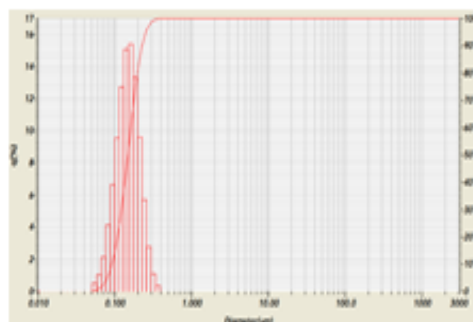
In addition, the measurement of dispersion of nanosilica showed that at this pH value of 9.0 and nanosilica content of 5 g/L, the dispersion contains the highest amount of small particles with the size of 58 nm. Therefore in the second step of dispersion study, different contents of nanosilica ranging from 2 g/L to 6 g/L were dispersed in water with pH value of 9.0. The dispersion measurement revealed that with the content of 5g /L, the dispersion has the highest amount of small particles with the size of 58 nm as shown in Table 1 and the nanosilica particles dispersed relatively well in water with zeta potential of – 32.6 mV. Dispersions of nano-silica are denoted as TX-Y in which X stands for pH of aqueous solution silica particles dispersed in and Y is content of silica measured in g/L.



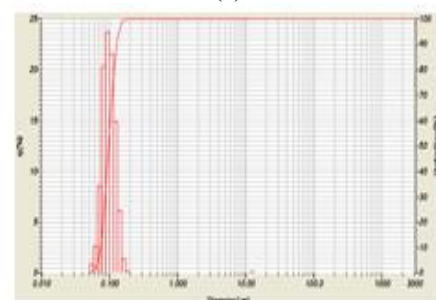
(a)



(b)



(c)



(d)

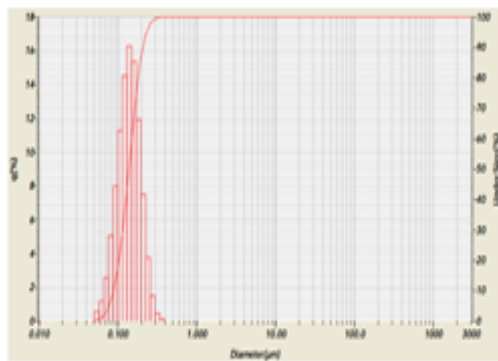


Figure 2. Distribution of nano-silica in different aqueous solution with different pH values, pH = 2 (a), pH = 3 (b), pH = 4 (c), pH = 5 (d) and pH= 6 (d).

Table 1. Percentage of particles having the size of 58 nm at different pH values.

Sample	% particles with size of 58 nm
T9-2	0.451
T9-3	0.457
T9-4	0.155
T9-5	0.113
T9-6	0.145

Characterization of passive conversion layers

All samples passivated with Cr(III) were dried at 80°C and samples passivated with Cr(VI) were dried at 50°C for 30 minutes following by keeping at ordinary condition for 48 hours. Samples are symbolized as MX-Y (X is pH of solution, Y is content of dispersed nanosilica measured in g/L) and samples passivated with C2 and UDYCRO 747 solutions without dispersed nanosilica are denoted as M1 and M2, respectively. Samples passivated with UDYCRO 747 solution appear with two main colors: green and yellow and samples passivated with by C2 and C2 containing silica particles appear with two main colors: purplish-green and purplish-pink. Both types of samples look bright and iridescent.

FT-IR spectroscopy: To prove the presence of nanosilica, Cr(III) and Cr(VI) in the passive conversion film, samples were characterized by Fourier Transmission Infrared Spectroscopy (FT-IR). Spectra of samples are depicted on the Figure 3. As shown in Figure 3, peaks appear at 1111 cm⁻¹, 808 cm⁻¹ and 474 cm⁻¹ are three main characteristic of peaks of silica attributed to -Si-O-Si vibration modes. The peaks at 1111 cm⁻¹ and 808 cm⁻¹ were related to the network -Si-O-Si asymmetric (Si-O) and symmetric (Si-OH) bond stretching vibration, respectively. While the peak at 474 cm⁻¹ was assigned to the network -Si-O-Si bond bending vibration (Si-O-Si, siloxane) [6, 7]. The O-H stretching vibration modes appearing in the range of 3200–3700 cm⁻¹ was attributed to the consequence of silanol groups (-OH) and water bound to the silica surface by hydrogen bonding [8, 9]. The peaks at 3466 cm⁻¹ and 1645 cm⁻¹ were due to the -OH absorption band which is caused by physically adsorbed water. The broad absorption band at 3466 cm⁻¹ and the peak at 1645 cm⁻¹ were assigned to the H-O-H stretching and bending modes of the adsorbed water, respectively.

It can be seen in all coated samples that a new peak appearing at around 605 cm⁻¹ which was characteristics of Cr(III) present in the sample. However, the peak characteristic for the presence of Cr(VI) at around 950 cm⁻¹ do not appear in the spectra. This proves that Cr(VI) species does not exist in all sample.

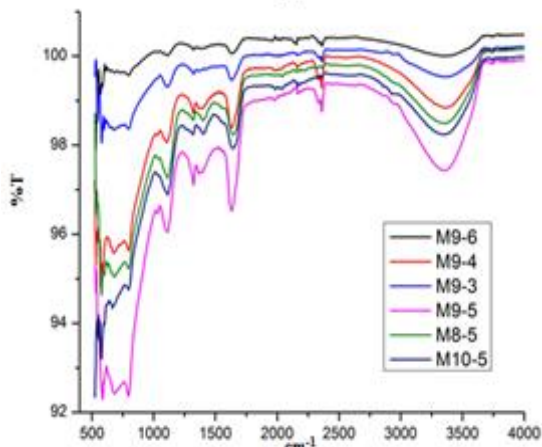
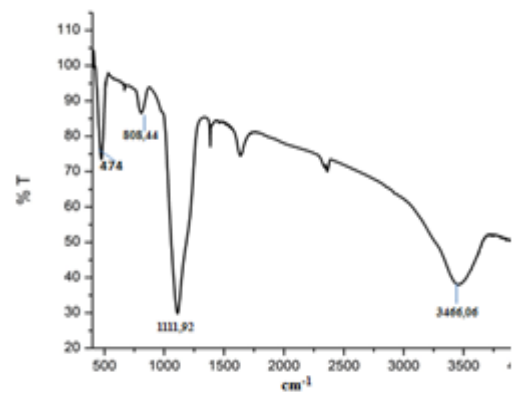


Figure 3. FTIR spectra of nano-silica and passive conversion layer containing nano-silica.

Morphological study of coated samples Images shown in Figure 4 are samples zinc coated sample without passivation of C2 solution and with passivation of C2 and C2 containing dispersed nanosilica particles.

As shown in Figure 4, it is clear that the samples passivated with C2 solution with and without dispersed nanosilica particles have the smoother surface in comparison to surface of zinc coated sample. The surface of the zinc coated sample is porous with homogeneous crystals having the sizes ranging from 30 to 100 nm (Figure 4a). The trivalent chrome conversion coatings didn't appear cracks or cloud on the surface (Figure 4b and Figure 4c).

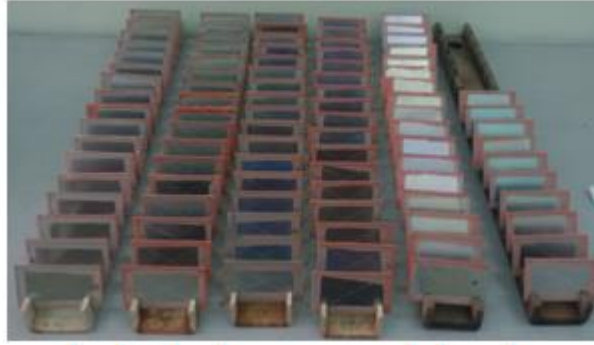
Table 2. Testing condition (JIS 8502:1999).

pH	6.5-7.2
NaCl	5wt.%
Spray pressure	1.0 atm
Temperature	35 ± 2°C
Spraying speed	2 mL/hour 80 cm ²

Testing results are listed in Table 3 and Figure 5

Table 3. Duration for appearing white rust.

Sample	Duration/ hour
M0	3
M1	24
M2	216
M8-5	144
M10-5	240
M9-3	144
M9-4	144
M9-5	288
M9-6	96



Zinc coated with and without passivation before salt spray testing

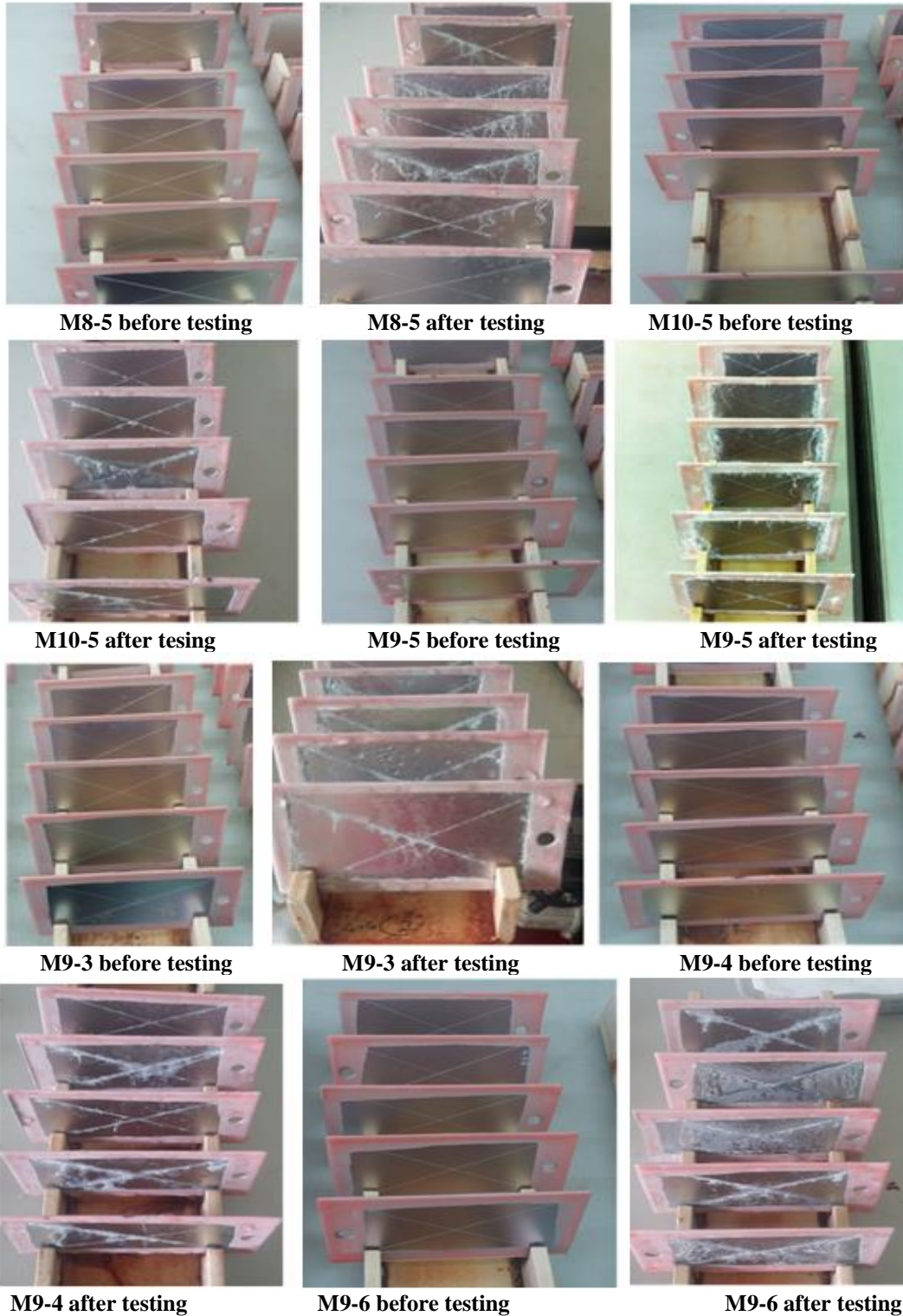


Figure 5. Zinc Coating and Zinc coating with passive conversion layer before salt spray.

The obtained results show that the white corrosion product appears very fast after 3 hours of salt spray for zinc coating. While, The time interval appearing the white rust in the case of 747 conversion passive layer with scratching is 72 times (216 hours) longer than time interval in the case of zinc coating. For conversion passive layer containing silica particles, the time interval for appearing the white rust is even longer. It takes 288 hours for appearing white rust. As listed in Table 2, if sample was passivated with C2 solution after coated by zinc, the time for appearing the white rust is 24 hours, 4 times longer than that of pure zinc coating. When the sample was passivated with C2 solution contains dispersed silica particle, the time interval needed to appear white rust continues increasing and reaches value of 288 hours. The introduction of nanosilica particle into the coating layer increases the stability of the coating layer in corrosive environment. With the same amount of nanosilica, but time duration times for appearing the rust are different. Duration time is 144 for M8-5, 288 for M9-5 and 240 for M10-5. The difference in duration is also observed when amount of nanosilica varies from 3 to 6 mg/L. The small values of duration time for appearing white rust can be explained due to the flocculation of nanosilica particles when they are introduced to this solution. The flocculation of silica particles reduces its dispersibility in the solution and affects to the stability of passive conversion layer.

The stability of coating increases as the duration time for appearing white rust increases. This increase can be explained because the presence of nanosilica particles produces the self correction of the passive conversion layer [10]. When samples are scratched, the hydrolysis process is taking place at the scratching place with the help of water in salt solution. The Si-OH groups are formed and adsorbed on the metal surface. Then, metallosiloxane (-Me-O-Si) bonds are formed and the solidification process is taking place. The solidification produces hydrophobic Si-O-Si bonds. The hydrophobicity of Si-O-Si bonds is a good property which can protect metals from aqueous oxidative species [11].

Polarization measurements

Anti-corrosion of coatings was tested by polarization measurements. All measurements are measured in aqueous solution of 3.5% wt NaCl. Results are depicted on the Figure 6. As can be seen, the corrosion rate reaches the smallest value on the sample of M9-5. This means that sample M9-5 is the most stable in the medium of sodium chloride solution. This result is in good agreement with the result in salt spray study.

Table 4. Values of E_{corr} and i_{corr} on different samples.

Sample	E_{corr} , mV/SCE	i_{corr} (A/cm ²)
M8-5	-1077.6	6.57×10^{-6}
M10-5	-1084.9	5.26×10^{-6}
M9-6	-1081.5	9.73×10^{-6}
M9-5	-1061	2.83×10^{-6}
M9-4	-1077.4	6.08×10^{-6}
M9-3	-1089.3	8.13×10^{-6}
M1	-1035.6	2.07×10^{-5}

Conclusion

The pH = 9 was the best value to disperse nano-silica particles and chosen to make the passive conversion solution producing passive conversion layer. The nano-silica content of 5 g/L was optimum content for dispersion of silica particle without precipitation and the nano-particle has the size of about 87 nm. When samples coated with zinc and then with passive conversion layer of M9-5 containing silica particles without a toxic component of Cr(VI), the anti-corrosion was reinforced significantly in comparison to the samples coated with only zinc layer. In addition, the this passive layer has

ability to self correct when it is scratched. This ability is the most important property of conversion layer which can reinforce the anti-corrosion property of the samples.

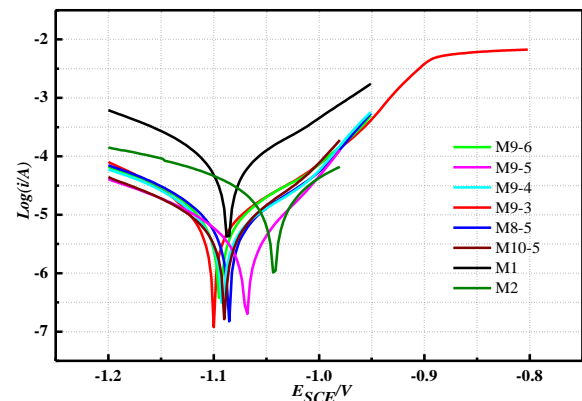


Figure 6. Tafel plot for different sample in 3.5%wt NaCl solution.

References

- [1] P. C. Wynn and C. V. Bishop, *Replacing hexavalent chromium*, Transactions of the Institute of Materials Finishing, 2001, 79(B) 27-30.
- [2] J. García-Antón, R. M. Fernández-Domene, R. Sánchez-Tovar, C. Escrivà-Cerdán, R. Leiva-García, V. García, A. Urriaga. *Improvement of the electrochemical behaviour of Zn-electroplated steel using regenerated Cr (III) passivation baths*, Chemical Engineering Science, 2014, 111, 402-409.
- [3] A. R. Di Sarli, J. D. Culcasi, C. R. Tomachuk, C. I. Elsner, J. M. Ferreira-Jr, Costa I. *A conversion layer based on trivalent chromium and cobalt for the corrosion protection of electrogalvanized steel*, Surface & Coatings Technology, 2014, 258, 426-436.
- [4] Japanese Standards Association - JIS H 8502: Methods of corrosion resistance test for metallic coatings (1999).
- [5] Enthone-OMI Inc. - Technical Manual, 2008.
- [6] G.M. Gao, H.F. Zou, S.C. Gan, Z.J. Liu, B.C. An, J. J. Xu, G.H. Li, Preparation and properties of silica nanoparticles from oil shale ash, Powder Technol. 191 (2009) 47–51.
- [7] D. An, Y. Guo, Y. Zhu, Z. Wang, A green route to preparation of silica powders with rice husk ash and waste gas, Chem. Eng. J. 2010, 162, 509–514.
- [8] T.H. Liou, H.S. Lin, *Synthesis and surface characterization of silica nanoparticles from industrial resin waste controlled by optimal gelation conditions*, J. Ind. Eng. Chem. 18 (2012) 1428–1437.
- [9] H. E. Bergna, W. O. Roberts, *Colloidal Silica: Fundamentals and Applications*, surfactant Science Series, vol. 131, CRC Press, New York, 2005.
- [10] X. Zhang, C. Van den Bos, W.G. Sloof, A. Hovestad, H. Terryn, J.H.W. de Wit, *Comparison of the morphology and corrosion performance of Cr(VI)-and Cr(III)-base conversion coatings on zinc*, Surface and Coatings Technology, 2005, 199, 92-104.
- [11] D. C. H Nevison. (1987), *ASM Handbook*, ASM International, Materials Park, Ohio (13), 755.