

A Comparison of the Corrosion Resistance and Wear Resistance Behavior of Cr-C, Ni-P and Ni-B Coatings Electroplated on 4140 Alloy Steel

Hung-Hua Sheu^{1,*}, Jian-Huang Syu¹, Yih-Ming Liu¹, Kung-Hsu Hou², Ming-Der Ger^{1*}

¹ Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan City, Taiwan

² Department of Power Vehicle and Systems Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan City, Taiwan

*E-mail: shhccit@gmail.com, mingderger@gmail.com

Received: 1 January 2018 / Accepted: 18 February 2018 / Published: 6 March 2018

Different coatings such as Cr-C coatings (chromium sulfate bath), Cr-C coatings (chromium chloride bath), Ni-P coatings and Ni-B coatings are electrodeposited on 4140 alloy steel, respectively. The corrosion and wear resistance of these coatings are studied. The experimental results show that the Ni-B coatings has the highest hardness (approximately at 951 Hv) and the best adhesion strength (approximately at 11 MPa), these two excellent properties lead to the Ni-B coatings has the lowest wear rate (approximately at $0.66 \times 10^{-6} \text{ mm}^3/\text{Nm}$). According to the potentiodynamic polarization analysis results, it shows that Ni-B coatings has a better corrosion resistance ($i_{\text{corr}} = 9.62 \times 10^{-7} \text{ A/cm}^2$) than that of Cr-C coatings due to its crack-free structure and higher adhesion strength. All experimental results indicate that Ni-B coatings is the most suitable coatings which can be used to protect 4140 alloy steel substrates from corrosion and wear damages, and enhance the application of 4140 alloy steel in industry.

Keywords: adhesion strength; corrosion resistance; contact angle; Ni-B coatings

1. INTRODUCTION

4140 alloy steel has been widely used as materials for gear, blade, and many industrial applications due to its high strength and good ductility. However, the exposure of 4140 alloy steel in a harsh working condition will result in severe mechanical failures such as corrosion and wear, which is harmful to the service life of the critical parts and leading to a complete failure of machinery [1]. Therefore, surface modification techniques including physical vapor deposition (PVD) methods [2], arc evaporation [3], chemical vapor deposition (CVD) techniques [4] and electrodeposition [5] have

been performed to enhance the wear, abrasion and corrosion resistance. Electrodeposition has been considered as a useful technique for surface modification, owing to the advantages including low cost, and the capability to handle large-scale as well as complex workpieces.

In order to protect the substrate materials, many kinds of Ni-based coatings developed by electrodeposition method such as Ni-P [6], Ni-Co [7], Ni-W [8] and Ni-Mo [9] coatings were extensively used for various engineering applications due to their superior properties in corrosion and wear resistance. Conventionally, hard chrome electroplated from hexavalent chromium bath was extensively used in modern industry due to its high hardness, good corrosion resistance and excellent wear resistance [10]. However, the hexavalent chromium is highly toxic and banned by many countries. Among the possible alternatives to hexavalent chromium coatings, the trivalent chromium coatings electroplated from either CrCl_3 or $\text{Cr}_2(\text{SO}_4)_3$ bath have numerous environmental, health and technical advantages and appear to be an interesting choice for forming a protective layer on the surface [11-15].

Comparing candidate materials is one of the most important stages in choosing an optimal material for an engineering application. Therefore, a comparative study of the mechanical properties (including hardness and adhesion strength), corrosion resistance and wear resistance of four different coatings such as Cr-C coatings (chromium sulfate bath), Cr-C coatings (chromium chloride bath), Ni-P coatings and Ni-B coatings deposited on 4140 alloy steel, respectively, is presented in this study.

2. EXPERIMENTAL

2.1. Specimens preparation

A 4140 alloy steel plate of 50 mm \times 25 mm \times 2 mm was used as the substrate in the electroplating process. Before electroplating, the substrates were polished with SiC abrasive papers from #100 to #1200, degreased with acetone using an ultrasonic cleaner for 10 mins, blow-dried with nitrogen gas, and then kept in a vacuum pot to avoid an oxidation reaction on the surface of the 4140 alloy steel, activated the surface of samples using 10 wt.% NaOH aqueous solution at 40°C for 30 mins and soaked in a 50 vol. % HCl solution for 3 mins. Different coatings such as Cr-C, Ni-P and Ni-B coatings were deposited under the same experimental conditions on the 4140 alloy steel by electroplating process.

2.2. Characterization of Cr-C coatings (chromium sulfate bath), Cr-C coatings (chromium chloride bath), Ni-P coatings and Ni-B coatings

A scanning electron microscopy (SEM, HITACHI-3000S) was used to analyze the morphology of various coatings. The hardness of different coatings was measured by a Mitutoyo microhardness tester with a load of 100 g for 10 s.

The potentiodynamic polarization analysis of various samples were carried out by an Autolab-PGSTAT30 potentiostat/galvanostat analyzed by a GPES (General Purpose Electrochemical system) software. A platinum sheet and Ag/AgCl electrode were used as the counter and reference electrodes

in a saturated solution of 3.5% NaCl at room temperature. The linear polarization curves for the electrolyte were measured through potential scan from 0 to -0.3 V by scanning the potential at 0.5 mV/s.

A ball-on-disk tribometer system (SENSE-7) which reported in our previous studies [16, 17] was used to analyze the average friction coefficient and wear resistance of various coatings. The commercially obtained steel balls ($\varnothing 6.25$ mm) were used as the counterpart. The friction tests were complied with a load of 6 N and sliding distance of 60 m under a reciprocating sliding velocity of 4 m/s. The average value for the friction coefficient and wear resistance is calculated after 3 tests. All the experiments were accomplished in ambient condition of temperature 25 ± 1 °C and no lubrication was applied during wear tests. The volumetric wear rate (R_w) of samples was computed by $R_w = V/F \cdot S$, where V is the wear volume (mm^3), F is the applied load (N), and S is the sliding distance (m). The wear volume was obtained by a non-contact surface mapping profiler (ADE Corporation, USA).

The adhesion strength was measured using an ELCOMETER-106 adhesion tester (the device is shown in Fig. 1). The coated sample was adhered to an aluminum dolly using an adhesive. After the adhesive has cured at 100 °C for 20 to 30 minutes, a tensile force was applied to the dolly axis. The force per unit area required to pull off the coating from the dolly was recorded as the value of adhesion strength.

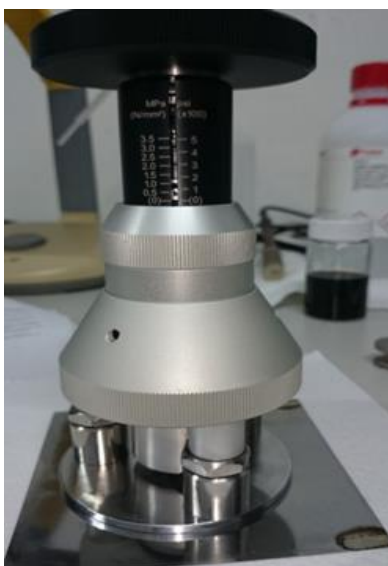


Figure 1. The actual photo of ELCOMETER-106 adhesion tester.

3. RESULTS AND DISCUSSION

3.1 Microstructure of different coatings electrodeposited on 4140 steel substrates

Fig. 2 shows the surface morphology of Cr-C coating (chromium sulfate bath), Cr-C coating (chromium chloride bath), Ni-P coating and Ni-B coating deposited on 4140 alloy steel, respectively. It has been reported that cracks were frequently observed on the Cr-C deposits [14, 18, 19]. As expected,

cracks appearing in networks were observed in both deposits plated from chromium sulfate bath (Fig. 2(a)) and chromium chloride bath (Fig. 2(b)). The formation of cracks can be ascribed to the release of internal stress during electroplating process. Moreover, it can be clearly seen from Fig. 2(b) that some pin-holes were also observed on the crack areas of the Cr-C deposit plated from chromium chloride bath. The presence of pin-holes might be related to a faster rate of hydrogen evolution during electroplating [20], suggesting the cathodic current efficiency is higher for deposit plated in chromium chloride bath than that in chromium sulfate bath. The scanning electron micrograph of Ni-P and Ni-B coatings is shown in Fig. 2(c) and Fig. 2(d), respectively. Cracks were hardly observed in the Ni-P (Fig. 2(c)) and Ni-B (Fig. 2(d)) deposits. However, the surface topographies of these coatings are different. A smooth surface appeared in Ni-P coating, while Ni-B coating showed a granular morphology. The formation of granular structure can be attributed a faster electrodeposited rate [21]. As can be seen from Figure 2, in comparison with Cr-C coatings, both Ni-P and Ni-B coatings show a crack-free structure, and this can be attributed to a smaller accumulated internal stress during electroplating process [22].

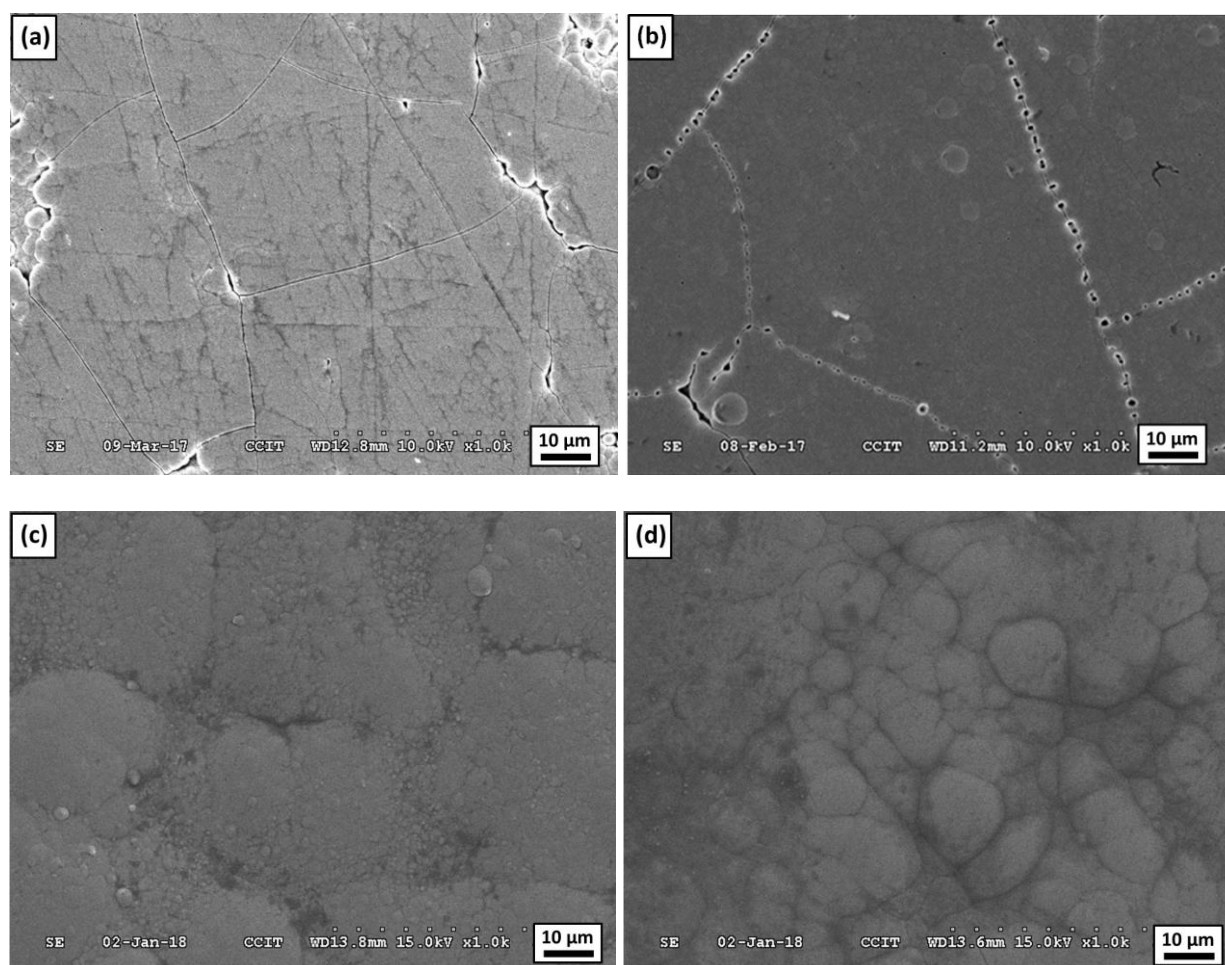


Figure 2. SEM morphologies of different coatings deposited on 4140 alloy steel substrates: (a) Cr-C coatings (chromium chloride bath), (b) Cr-C coatings (chromium sulfate bath), (c) Ni-P coatings, (d) Ni-B coatings.

Fig. 3 shows the cross-sectional SEM images of Cr-C (chromium chloride bath), Cr-C (chromium sulfate bath), Ni-P and Ni-B coatings electrodeposited on 4140 alloy steel. The average thickness of Cr-C coatings electroplated from chromium sulfate and chromium chloride bath is approximately at 4.8 and 7.6 μm , respectively (Fig. 3(a) and (b)). In addition, cracks penetrating through the deposit were clearly seen on both Cr-C coatings. It might have negative impact on the corrosion resistance of the coatings. The average thickness of Ni-P and Ni-B coatings is approximately at 14.8 and 21.2 μm , respectively (Fig. 3(c) and (d)). The thickness of Ni-P and Ni-B coatings are much greater than these of Cr-C coatings, indicating the deposition rate of Ni-based coatings is higher than that of Cr-C coatings. Although the Ni-B coating has the largest electrodeposition rate, it still remain a crack-free structure within coating, this can be attributed to the Ni-B coatings has lower accumulated internal stress during electroplating. Moreover, it should be pointed out that the Ni-based coatings are attached to the surface of 4140 alloy steel substrate firmly, implying the adhesion strength will be improved dramatically.

Table. 1 presents the adhesion strength of different coatings electroplated on 4140 alloy steel substrates, both Cr-C coatings deposited from chromium chloride and chromium sulfate bath have lower adhesion strength (approximately at 7 and 5.5 MPa), the Ni-based coatings have higher adhesion strength and the highest adhesion strength is approximately at 11 MPa for Ni-B coatings. The result of adhesion strength test confirms the Ni-based coatings indeed have better adhesion behavior in 4140 alloy steel substrates.

Table 1. The adhesion strength of various coatings deposited on 4140 steel substrate

Deposited coatings	Adhesion strength (MPa)
Cr-C coatings (chromium chloride bath)	7
Cr-C coatings (chromium sulfate bath)	5.5
Ni-P coatings	9.5
Ni-B coatings	11

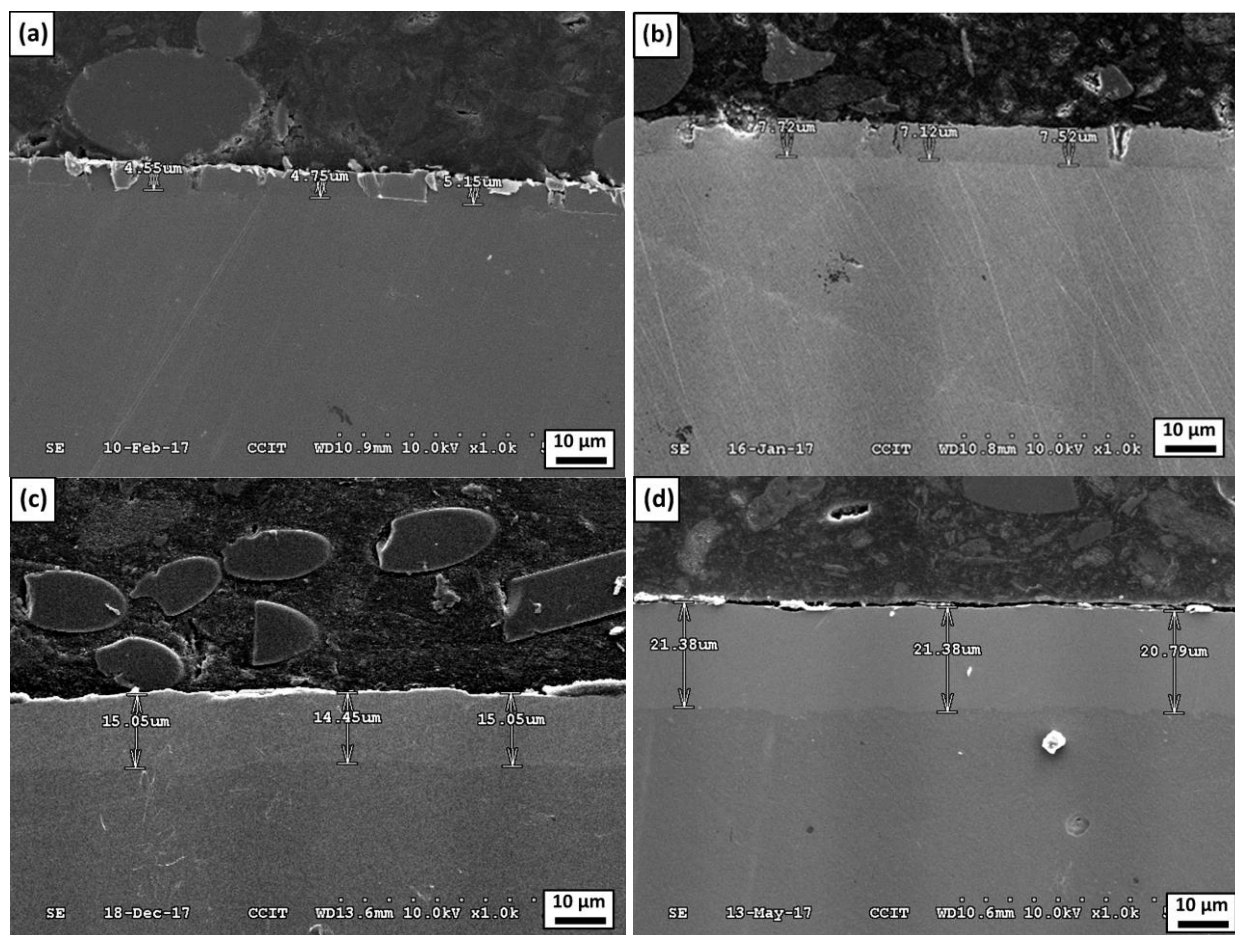


Figure 3. SEM cross-sectional images of different coatings electrodeposited on 4140 alloy steel substrates: (a) Cr-C coatings (chromium chloride bath), (b) Cr-C coatings (chromium sulfate bath), (c) Ni-P coatings, (d) Ni-B coatings.

3.2 Corrosion resistance of different coatings electrodeposited on 4140 alloy steel substrates

Table 2. Corrosion characteristics of 4140 alloy steel substrate, Cr-C coatings (chromium chloride bath), Cr-C coatings (chromium sulfate bath), Ni-P coatings, and Ni-B coatings in 3.5 wt.% NaCl solution.

Sample	β_a (V/ decade)	β_c (V/ decade)	i_{corr} (A/cm ²)	E_{corr} (V vs. SCE)
4140 alloy steel substrate	0.235	-0.347	1.45×10^{-5}	-0.92
Cr-C coatings (chromium chloride bath)	0.265	-0.376	1.67×10^{-6}	-0.54
Cr-C coatings (chromium sulfate bath)	0.271	-0.314	1.54×10^{-6}	-0.58
Ni-P coatings	0.322	-0.387	3.52×10^{-6}	-0.51
Ni-B coatings	0.173	-0.115	9.62×10^{-7}	-0.50

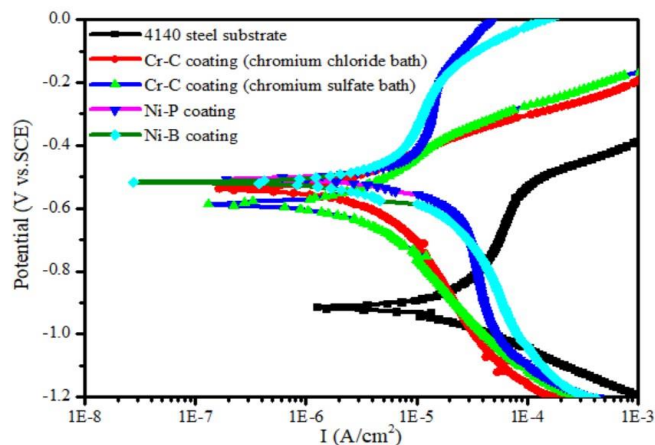







Figure 4. Polarization curves of 4140 alloy steel substrate, Cr-C coatings (chromium chloride bath), Cr-C coatings (chromium sulfate bath), Ni-P coatings, and Ni-B coatings.

Fig. 4 shows potentiodynamic polarization curves of 4140 alloy steel substrate, Cr-C coating (chromium chloride bath), Cr-C coating (chromium sulfate bath), Ni-P coating and Ni-B coating. The values of corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c) derived from the potentiodynamic polarization curves of coated and uncoated samples are presented in Table 2. The uncoated 4140 alloy steel exhibited a corrosion potential of -0.936 V vs SCE and a corrosion current density of approximately $1.21 \times 10^{-5} \text{ A/cm}^2$. The corrosion current densities of the Cr-C coating (chromium chloride bath), Cr-C coating (chromium sulfate bath), Ni-P coating and Ni-B coating are $1.67 \times 10^{-6} \text{ A/cm}^2$, $1.54 \times 10^{-6} \text{ A/cm}^2$, $3.52 \times 10^{-6} \text{ A/cm}^2$, and $9.62 \times 10^{-7} \text{ A/cm}^2$, respectively. All the coated specimens exhibit a corrosion current density which is one order of magnitude less than that of bare 4140 alloy steel. On the other hand, the corrosion potentials of the Cr-C coating (chromium chloride bath), Cr-C coating (chromium sulfate bath), Ni-P coating and Ni-B coating are -0.541, -0.585, -0.526 and -0.514 V, respectively. It is recognized that a less negative of E_{corr} and lower value of i_{corr} mean a lower corrosion rate and better corrosion resistance. The corrosion resistance of the Ni-B coating is superior to other test samples. Previous studies had reported that the Cr-C coatings have an excellent corrosion resistance, but their corrosion resistances will be reduced by cracks due to the higher internal stress within coatings [23-26]. In this study, however, the corrosion resistances of both Cr-C coatings electroplated from chromium chloride and chromium sulfate bath are only slightly inferior to that of Ni-B coating.

SST duration	4140 alloy steel substrates	Cr-C coating (CrCl_3)	Cr-C coating (CrS_2O_4)	Ni-P coating	Ni-B coating
0 h					

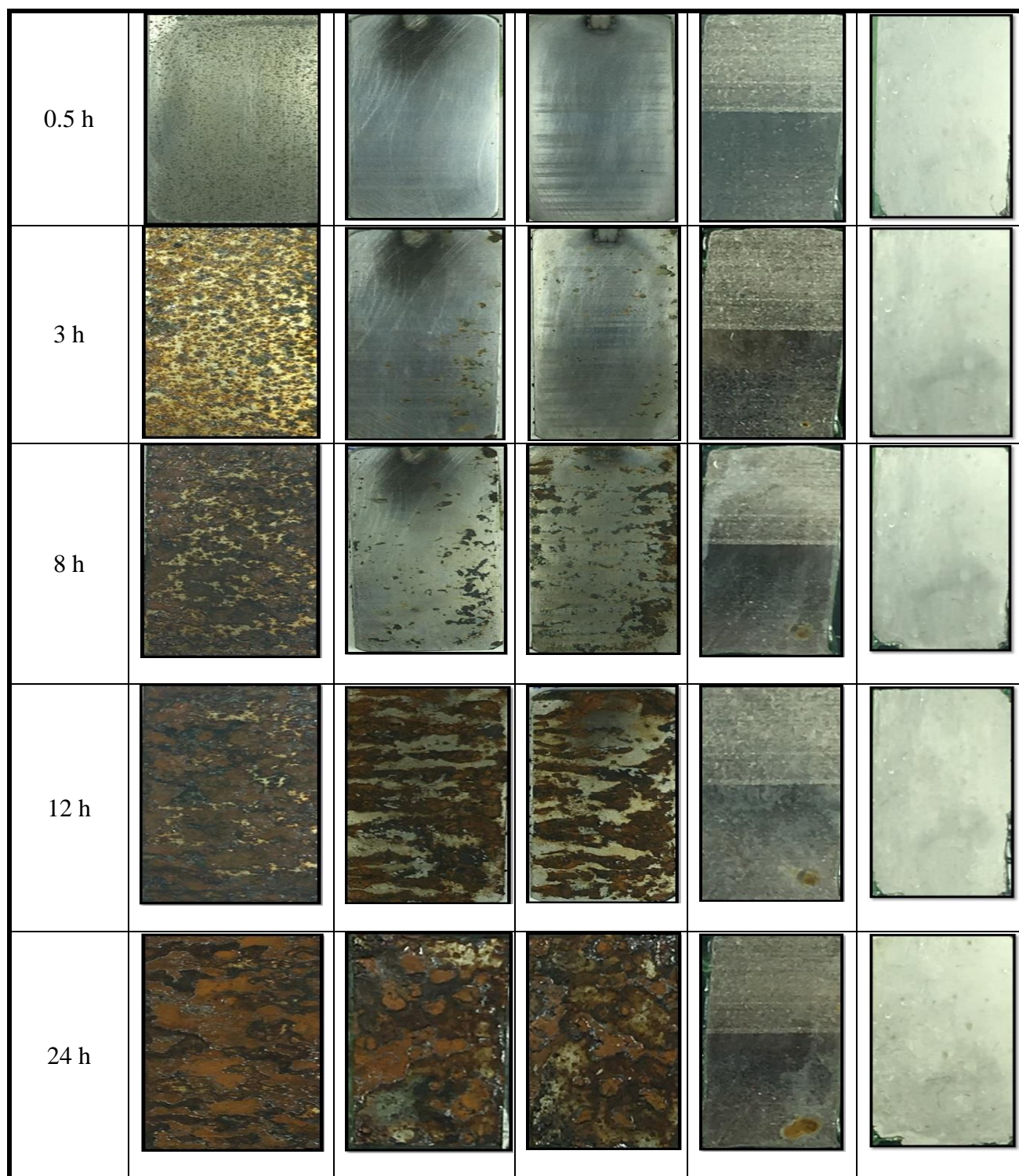


Figure 5. Optical images of different coatings deposited on 4140 alloy steel substrates after salt spray test for various durations.

In order to study the corrosion performances further, the corrosion behaviors of different coatings deposited on 4140 alloy steel substrates were evaluated by salt spray test (SST) again. The surface macroscopic morphologies of various coatings during the 24 h salt spray test time are represented in Fig. 5. According to the ASTM D610-08 standard, the Ni-B coatings deposited on 4140

alloy steel specimens show that there is no rust point (rust grade 10) on the surface after 12 h of the SST, the Cr-C coating (chromium chloride bath) is approximately at rust grade 0 (percent of surface rusted greater than 50%), the Cr-C coatings (chromium sulfate bath) is approximately at rust grade 1 (percent of surface rusted greater than 33% and up to 50%), the Ni-P coating is approximately at rust grade 8 (percent of surface rusted greater than 0.03% and up to 0.1%). However, the 4140 alloy steel is already at rust grade 0 just after salt spray test for 3 h, indicating the poor corrosion resistance of 4140 alloy steel. After salt spray test for 24 h, both Cr-C coatings electroplated from chromium chloride and chromium sulfate bath are at rust grade 0, the Ni-P coating still maintains at rust grade 8, the Ni-B coating still keeps at rust grade 10. The result of salt spray test indicates that the Ni-B coating has the best corrosion resistance than others coatings. This result was in a good agreement with the potentiodynamic polarization analysis result.

3.3 Mechanical property and wear resistance of different coatings electrodeposited on 4140 alloy steel substrates

Fig. 6 displays the hardness of 4140 alloy steel substrate, Cr-C coating, Ni-P coating, and Ni-B coating. The average hardness of 4140 alloy steel is only 163 Hv. This result indicates that 4140 alloy steel is too soft to be applied in the industrial sliding parts without any surface treatment process. Compared with the bare 4140 alloy steel, the hardness of all the coated specimens studied increase significantly. The hardness of the Cr-C coating, Ni-P coating, and Ni-B coating reaches to 820, 618 and 951 Hv, respectively. Among these coatings, Ni-B coating has the highest hardness (951 Hv) and should have a better wear resistance behavior.

The friction coefficient curves for different coatings during the wear test are shown in Fig. 7. The average friction coefficient of Cr-C coating (chromium chloride bath), Cr-C coating (chromium sulfate bath), Ni-P coating, and Ni-B coating is approximately at 0.244, 0.239, 0.283 and 0.329, respectively (see Table. 3). It is noted that the surface of the Ni-B coating (Fig. 1(d)) is rougher than that of other coatings. The higher friction coefficient of Ni-B coating in this study may be caused by its high surface roughness [27]. Generally, the anti-wear behavior of deposits is influenced by their hardness, strength and friction coefficient, etc.; the high hardness and low friction coefficient of coatings will enhance their wear resistance [28, 29]. The average friction coefficient of Ni-B coatings is about 0.329 and is only slightly higher than that of Cr-C and Ni-P coatings.

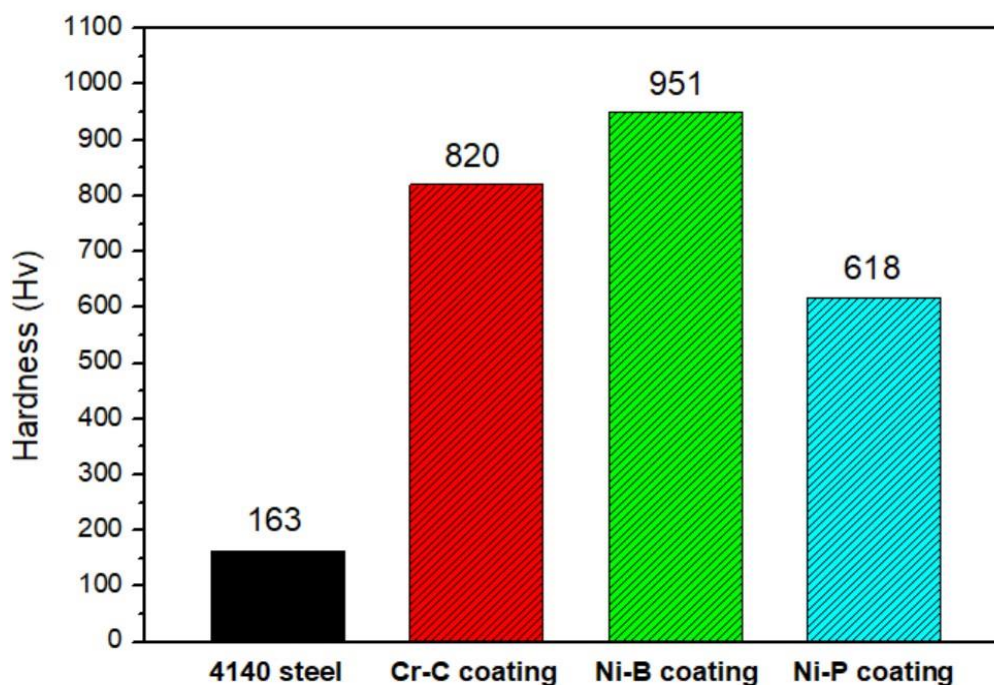


Figure 6. The hardness of 4140 alloy steel substrate, Cr-C coatings (chromium chloride bath), Cr-C coatings (chromium sulfate bath), Ni-P coatings, and Ni-B coatings.

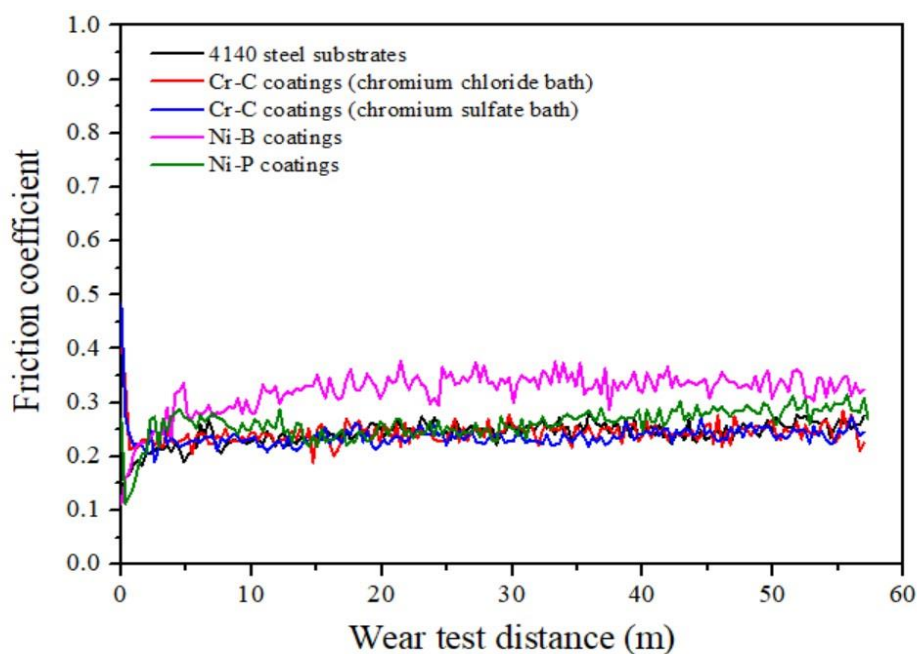


Figure 7. The friction curves of 4140 alloy steel substrate, Cr-C coatings (chromium chloride bath), Cr-C coatings (chromium sulfate bath), Ni-P coatings, and Ni-B coatings.

Therefore, in this study, the wear resistance of Cr-C, Ni-P and Ni-B coatings will be mainly affected by their hardness. Table 3 presents the wear rate of different coatings electrodeposited on 4140 alloy steel substrate. From Table 3, it can be seen that the Ni-B coatings has the lowest wear rate approximately at $0.66 \times 10^{-6} \text{ mm}^3/\text{Nm}$ due to its higher hardness (about 951 Hv). Although the Cr-C

coatings electrodeposited from chromium sulfate bath also has a higher hardness (about 820 Hv), but the cracks and pinholes (see Fig. 2(b)) cause the Cr-C coatings to peel off during wear test; therefore, the Cr-C coatings electrodeposited from chromium sulfate bath has the highest wear rate approximately at $4.88 \times 10^{-6} \text{ mm}^3/\text{Nm}$. Moreover, the Ni-P coating has a higher wear rate ($2.60 \times 10^{-6} \text{ mm}^3/\text{Nm}$) due to its lower hardness (only about 618 Hv).

Table 3. The wear characteristics of different coatings

Samples	Average friction coefficient	Wear rate (mm^3/Nm)
Cr-C coatings (chromium chloride bath)	0.244	1.66E-06
Cr-C coatings (chromium sulfate bath)	0.239	4.88E-06
Ni-P coatings	0.283	2.60E-06
Ni-B coatings	0.329	0.66E-06

4. CONCLUSIONS

In this study the Cr-C coating (chromium chloride bath), Cr-C coating (chromium sulfate bath), Ni-P coating, and Ni-B coating were electrodeposited on 4140 alloy steel substrate. The corrosion behavior and mechanical properties of these coatings were investigated, the following conclusions can be drawn:

- (1) The Ni-B coatings has the best corrosion resistance ($i_{\text{corr}} = 9.62 \times 10^{-7} \text{ A/cm}^2$) that can protect 4140 alloy steel substrate from corrosion environment due to a crack-free structure within Ni-B coatings and the highest adhesion strength.
- (2) The Ni-B coatings has the lowest wear rate ($0.66 \times 10^{-6} \text{ mm}^3/\text{Nm}$) due to its higher hardness and adhesion strength.
- (3) Among the Cr-C coatings (chromium chloride bath), Cr-C coatings (chromium sulfate bath), Ni-P coatings, and Ni-B coatings, Ni-B coatings is the most suitable coatings to protect 4140 alloy steel substrates from corrosion and wear damages, and enhance the application of 4140 alloy steel in industry.

References

1. S. Glodež, M. Šraml, J. Kramberger, *International Journal of Fatigue*, 24 (2002), 1013.
2. A. Jellad, S. Labdi, T. Benameur, *J. Alloy. Compd.*, 483 (2009) 464.
3. A.M. Neves, V. Severo, L. Cvrček, T. Polcar, C. Louro, A. Cavaleiro, *Surf. Coat. Technol.*, 202 (2008) 5550.
4. F. Maury, *Electrochim. Acta*, 50 (2005) 4525.
5. F. I. Danilov, V. S. Protsenko, V. O. Gordienko, S. C. Kwon, J. Y. Lee, M. Kim, *Appl. Surf. Sci.*, 257 (2011) 8048.
6. K.H. Hou, M.C. Jeng, M.D. Ger, *J. Alloys Compd.* 437 (2006) 289.
7. M. Srivastava, V.K. William Grips, K.S. Rajam, *Appl. Surf. Sci.* 253 (2007) 3814.

8. K.H. Hou, H.T. Wang, H.H. Sheu, M.D. Ger, *Appl. Surf. Sci.* 308 (2014) 372.
9. E. Beltowska-Lehman, A. Bigos, P. Indyka, M. Kot, *Surf. Coat. Technol.* 211 (2012) 67.
10. L. Gianelos, *Plating and Surface Finishing*, 66 (1979) 56.
11. C.A. Huang, C.K. Lin, C.Y. Chen, *Surf. Coat. Technol.* 203 (2009) 3686.
12. H.H. Sheu, C.H. Lin, S.Y. Jian, H.B. Lee, B.R. Yang, M.D. Ger, *Int. J. Electrochem. Sci.*, 11 (2016) 7099.
13. C.E. Lu, J.L. Lee, H.H. Sheu, K.H. Hou, C.C. Tseng, M.D. Ger, *Int. J. Electrochem. Sci.*, 10 (2015) 5404.
14. Z. Zeng, L. Wang, A. Liang, J. Zhang, *Acta Electrochimica*, 52 (2006) 1366.
15. S. Ghaziof, K. Raeissi, M.A. Golozar, *Surf. Coat. Technol.*, 205 (2010) 2174.
16. C. I. Hsu, K. H. Hou, M. D. Ger, G. L. Wang, *Appl. Surf. Sci.*, 357 (2015) 1727.
17. H. H. Sheu, S. Y. Jian, M. H. Lin, C. I. Hsu, K. H. Hou, M. D. Ger, *Int. J. Electrochem. Sci.*, 12 (2017) 5464.
18. K.S. Nam, K.H. Lee, S.C. Kwon, D.Y. Lee, Y.S. Song, *Materials Letters*, 58 (2004) 3540.
19. V. Protsenko, F. Danilov, *Electrochimica Acta*, 54 (2009) 5666.
20. M.E. Bahrololoom, A. Hoveidaei, *Surf. Eng.* 15 (6) (1999) 502.
21. I. Mizushima, P.T. Tang, H.N. Hansen, M.A.J. Somers, *Electrochim Acta*, 51 (2006) 6128.
22. H.H. Sheu, C.E. Lu, K.H. Hou, M.L. Kuo, M.D. Ger, *Journal of the Taiwan Institute of Chemical Engineers* 48 (2015) 73.
23. S. Surviliene, L. Orlovskaja, G. Bikulcius, S. Biallozor, *Surf. Coat. Technol.*, 137 (2001) 230.
24. A. Baral, R. Engelken, *J. Electrochem. Soc.*, 152 (2005) C504.
25. S.K. Ibrahim, A. Watson, D.T. Gawne, *Trans IMF*, 75 (1997) 181.
26. S.C. Kwon, M. Kim, S.U. Park, D.Y. Kim, D. Kim, K.S. Nam, Y. Choi, *Surf. Coat. Technol.* 183 (2004) 151.
27. A. Bigos, E. Beltowska-lehman, P. Indyka, M.J. Szczerba, M. Kot, M. Grobelny, *Archives of Metallurgy and Materials*, 58 (2013) 247.
28. H. Ogihara, H. Wang, T. Saji, *Appl. Surf. Sci.*, 296 (2014) 108.
29. S. T. Aruna, C. Anandan, V. K. William Grips, *Appl. Surf. Sci.*, 301 (2014) 383.

© 2018 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).