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Corrosion Behavior of AISI 4140 Steel Surface Coated by Physical Vapor Deposition

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Abstract

The corrosion behavior of uncoated and CrN-coated onto AISI 4140 steel was studied by electrochemical technique. Firstly, the AISI 4140 steel samples were solution heat treated and oil quenched in order to achieve proper hardness. Then, they were surface-prepared with alteration of surface roughness by using SiC paper at different numbers of 180, 600, and 1200 prior to CrN coating. The samples were coated with CrN film by physical vapor deposition (PVD) technique. The corrosion behavior of the uncoated and CrN-coated samples was studied in air-saturated 3.5 wt% NaCl solution at the pH values of 2, 7 and 10 at room temperature. Before and after corrosion testing, the surface of the uncoated and CrN-coated samples was characterized by scanning electron microscopy (SEM) with chemical composition analysis by energy dispersive X-rays (EDX).The results showed that the CrN-coated samples exhibited lower corrosion rate than the uncoated samples at all pH values. In addition, it was found that corrosion rate of the uncoated and CrN-coated samples significantly altered with the surface roughness of the substrate prior to coating. The finer surface roughness is, the more corrosion resistance is.

Keywords: AISI 4140 steel, Chromium nitride coating, Electrochemical technique, 3.5-wt% NaCl solution.

Introduction

Low alloy steels have been commonly used in many engineering applications, especially parts in the automotive industry such as crankshaft, gear, pinion, bolt and various machine tool components because they have good mechanical properties and they are easily fabricated. In general, those parts are usually used for wear and abrasion applications. Therefore, the parts require high hardness of surface for increasing wear and abrasion resistance. The properties of the parts are focused on wear and hardness.[(1)] But, in several services they have been used in corrosive environments such as lubricant, gaseous and liquid environments resulting in reduction of performance and lifetime of those parts. As a result, surface modifications, i.e. Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD). Nitriding, Carbonitriding and Thermal spraying, are widely used to improve their surface in order to achieve better wear, abrasion and corrosion resistance. However, the PVD technique is a popular method used for improvement of surface because it is safe and clean technology.[(2)] PVD coatings are

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mostly composed of metal nitrides such as TiAlN, CrN and etc. that are employed as a protective film due to it has good hardness, chemically inert and thermal stability leading to improve corrosion resistance.[3] Properties of PVD coatings, such as corrosion, wear and abrasion resistance, depend on various parameters in accordance with type of substrates, microstructure of substrates, thickness and porosity of the PVD coatings. However, it still remains in question about the effective surface roughness of substrate prior to PVD coating on properties of the coating in particular for NaCl solutions with various pHs. In order to understand the effect of surface roughness of substrate on the corrosion behavior of AISI 4140 steel surface coated by physical vapor deposition (PVD) in air-saturated 3.5 wt% NaCl solution at pH 2, 7 and 10, the electrochemical technique has been used in this study. After electrochemical testing, the corroded surface of samples was investigated by scanning electron microscopy (SEM) with chemical composition analysis by energy dispersive X-rays (EDX).

Materials and Experimental Procedures

Sample Preparation

Low alloy steel with code name AISI 4140 was employed as the substrate in this study. The chemical compositions of AISI 4140 were measured and listed in Table 1. Firstly, the AISI 4140 steels were cut to obtain dimension 10x10x2 mm. After that, the samples were austenitized at 850°C for 30 minutes and oil-quenched. Then, the samples were polished by using SiC at various grit numbers, i.e. 180, 600 and 1200, in order to prepare difference of surface roughness. In addition, the surface roughness (R_a value) of the samples was measured by a profile-meter (Veeco) model as shown in Table 2. Then, the samples were rinsed by distilled water, acetone and were air-dried before PVD coating.

Table 1 : Chemical compositions of 4140 steel (in wt. %).

Grade	C	Mn	Cr	Si	Mo	Fe
4140	0.47	0.78	0.81	0.26	0.19	bal.

Table 2 : The average surface roughness (R_a).

Substrate	R_a (in nm)	
	Prior to coating	After coating
180 SiC	563.13	294.32
600 SiC	200.12	165.56
1200 SiC	31.14	30.92

Coating Preparation

The PVD sputtering process was employed to prepare chromium nitride (CrN) coating. The target used for coating process was made of chromium with 99.9% purity. The samples were cleaned in an ultrasonic cleaner for 20 minutes and were dried prior to coating process. The chromium nitride (CrN) coating was deposited onto the samples with the deposition conditions as shown in Table 3.

Table 3 : Deposition conditions of CrN coating.

Ar flow rate	9 sccm
N_2 flow rate	6 sccm
Base pressure	5.0 x 10^{-3} mbar
Working pressure	3.5 x 10^{-3} mbar
Current	800 mA
Voltage	-456 V
Deposition time	45 min
Target-to-substrate spacing	15 cm
Coating thickness	0.914 µm

Corrosion Testing

Electrochemical technique was used to study the corrosion behavior of the CrN coating onto the AISI 4140 steel and carried out by using a µ-Autolab software (General Purpose Electrochemical, GPES). A three-electrode cell was used for the polarization measurements. A silver/silver chloride (Ag/AgCl) electrode and graphite electrode were used as a counter and reference electrode, respectively. The study of corrosion behavior was firstly started by measuring the open circuit potential (OCP). Then, the samples were polarized to potentials ranking from -900 mV to +200 mV at a scan rate of 1.0 mV/s in air-saturated 3.5 wt% NaCl solution at pH 2, 7 and 10 and 27ºC. The pH of solution was adjusted by addition of hydrochloric acid (HCl) and sodium hydroxide (NaOH) for acidic and alkaline solutions, respectively. The tested areas of the samples were 0.85 cm^2. The polarization curves were used to evaluate corrosion behavior in terms of corrosion potential (E_{corr}) and corrosion current density (I_{corr}) on the basis of the Tafel analysis after potentiodynamic polarization measurements. The corrosion rate (R_{mmy}) was calculated from the corrosion current density after the Faraday's law. Before and after the electrochemical testing, the surface of the uncoated and CrN coated samples was examined by using scanning electron microscopy (SEM) with chemical composition analysis by energy dispersive X-rays (EDX).

Results and Discussion

Effect of CrN Coatings on the Corrosion Behaviour

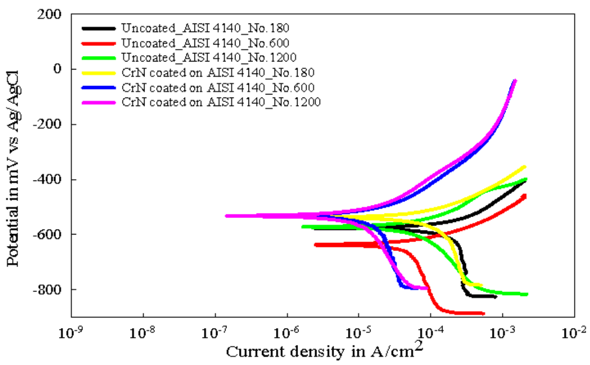
Figure 1 shows the polarization curves of the uncoated and CrN coated samples with alteration of surface roughness tested in air-saturated 3.5 wt% NaCl solution at pH 2, 7 and 10. The polarization curves were recorded from -900 mV to +200 mV with the scan rate of 1.0 mV/s. The important parameters estimated from the polarization curves are listed in Table 4.

Table 4 : Important values evaluated from the polarization curves of uncoated and CrN coated samples tested in air-saturated 3.5 wt% NaCl solution.

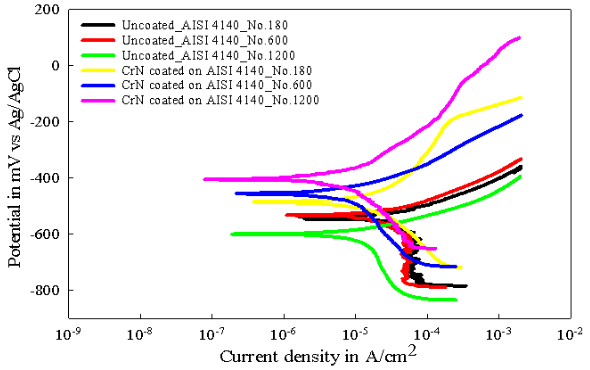
pH	Samples	Sic paper	E_{corr}	I_{corr}	R_{mmy}
pH2	Uncoated	No.180	-571	10.98	0.1289
		No.600	-636	5.55	0.0652
		No.1200	-572	5.19	0.0609
	CrN	No.180	-538	7.43	0.0219
		No.600	-531	2.00	0.0059
		No.1200	-532	0.89	0.0026
pH7	Uncoated	No.180	-533	8.11	0.0952
		No.600	-532	3.40	0.0399
		No.1200	-599	0.60	0.0071
	CrN	No.180	-485	0.77	0.0023
		No.600	-455	0.60	0.0018
		No.1200	-405	0.36	0.0011
pH10	Uncoated	No.180	-587	0.68	0.0080
		No.600	-596	0.67	0.0079
		No.1200	-560	0.45	0.0053
	CrN	No.180	-473	0.70	0.0021
		No.600	-423	0.59	0.0017
		No.1200	-354	0.10	0.0003

E_{corr} Corrosion potential (mV, Ag/AgCl)
I_{corr} Corrosion current density (µA/cm^2)
R_{mmy} Corrosion rate (mm/year)

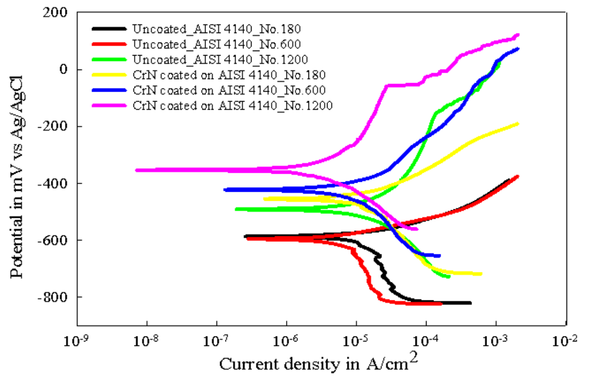
It is obvious that the CrN coating significantly affects corrosion properties of the AISI 4140 steel in particular the corrosion potential (E_{corr}) and corrosion current density (I_{corr}). From the comparison of the corrosion potential (E_{corr}) of the CrN-coated samples and uncoated samples, it is found that the corrosion potential (E_{corr}) is shifted to more positive value, if the samples were surface-coated by CrN.



a) at pH2



b) at pH7



c) at pH10

Figure 1 : The polarization curves of uncoated and CrN-coated samples tested in air - saturated 3.5 wt% NaCl solution.

For example, at pH 2 the corrosion potential (E_{corr}) of the uncoated sample with the highest surface roughness (No.180) is -571 mV, while the corrosion potential (E_{corr}) of the CrN-coated sample is increased to -538 mV. And, there is the same trend at pH 7 and pH 10. In addition, it is found that the CrN-coated samples have lower corrosion current densities (I_{corr}) than the uncoated samples at all pHs.[4] Those results indicate that after application of CrN coating onto the surface of bare steel, the corrosion resistance is better. The reason, why CrN enhances the corrosion resistance, is due to the fact that nitrogen atom in the nitride layer firstly dissolved into the solution, and it could repel the Chloride ion (Cl^-) away from the sample surface. The nitrogen anion (N^-) then combines with hydrogen ion (H^+) in the solution to form the ammonium (NH_4^+) resulting increase of solution pH. Finally, corrosion attack from the solutions decreases.[5,6]

Effect of pH of Solution on Corrosion Behaviour

In order to study the effect of pH of solution on corrosion behavior of the uncoated and CrN coated samples tested in air-saturated 3.5 wt% NaCl solution, the solution was pH adjusted by addition of hydrochloric acid (HCl) and sodium hydroxide (NaOH) for pH 2 and 10, respectively. Then, the corrosion testing was done at the same procedure. From the polarization curves, shown in Figure 1, corrosion rate in terms of millimetre per year (mm/yr) is calculated and plotted with various pHs of solution as shown in Figure 2.

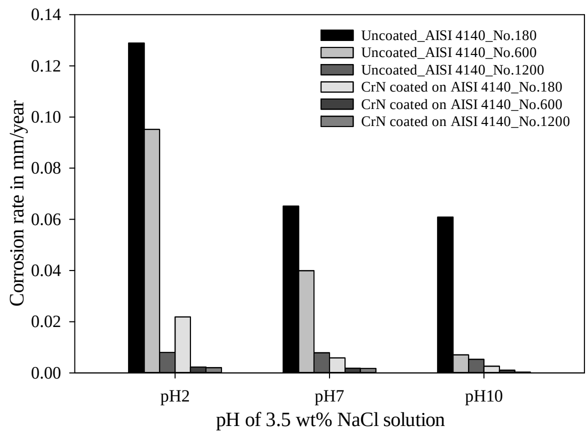


Figure 2 : Corrosion rate of uncoated and CrN coated samples with various pHs of solution.

It is obvious that the corrosion rate decreases as the pH of solution increases. The highest corrosion rate is observed at pH 2 because the solution was adjusted by HCl acid that significantly increased chloride (Cl^-) ion and hydrogen ion (H^+) in the solution. This means that the solution at pH 2 is more aggressive than that at pH 7 and pH 10. The corrosion attack is more severe in the uncoated samples than in the CrN-coated samples. Even though the Cl^- ion still attacks the CrN coating as the same in the uncoated samples, corrosion appearance is not the same. Because the Cl^- ion attacks at the specific area of CrN coating i.e. pore and crack, then it penetrates to the substrate resulting in pitting corrosion.(7) Moreover, there is more available hydrogen ion (H^+) in solution causing H_2 evolution resulting increase in the corrosion rate at pH 2 more than pH 7 and 10. At pH 10, it was found that the uncoated sample with the smoothest surface shows passive behavior. This is due to the fact that iron can form hydroxide film at basic pH more than 7.(8) As a result, the corrosion resistance in basic solution is better than in acid solution.

Effect of Surface Roughness on Corrosion Behavior

In order to investigate the effect of surface roughness on corrosion behavior, the samples prior to PVD coating were surface-prepared by using different SiC numbers. The average surface roughness in R_a values of each sample both before and after coating was measured by using the profile-meter (Veeco) model as listed in Table 2. It clearly demonstrates that the average surface roughness (R_a) of the samples prior to coating decreases with the number of grinding paper increases. Moreover, it is obvious that the surface roughness of sample prior to coating also affects the surface roughness of the CrN-coated samples. The effect of surface roughness of uncoated samples on corrosion rate at pH 2, 7 and 10 is shown in Figure 3. It is obvious that corrosion rate significantly increases with the surface roughness of the substrate, especially at pH 2 and pH 7. In case of pH 7, surface roughness slightly affects the corrosion rate. Figure 4 also shows effect of surface roughness on corrosion rate of the CrN-coated samples. It is obvious that the CrN coated onto the rougher surface has a higher corrosion rate than the CrN coated onto the smoother surface. The evidence of increasing corrosion rate can be observed at pH 2. In contrast to pH 2, there is slightly increasing of corrosion rate at pH 7 and 10. This is due to the fact that higher surface roughness leads to a higher number of defects in the coating and also results in lower complete coverage of the sample by the coating. Those results also have the same trend as shown in the uncoated samples. And, those can be used to confirm that the surface roughness of substrate prior to coating significantly effects on the deposition of CrN film.(9,10)

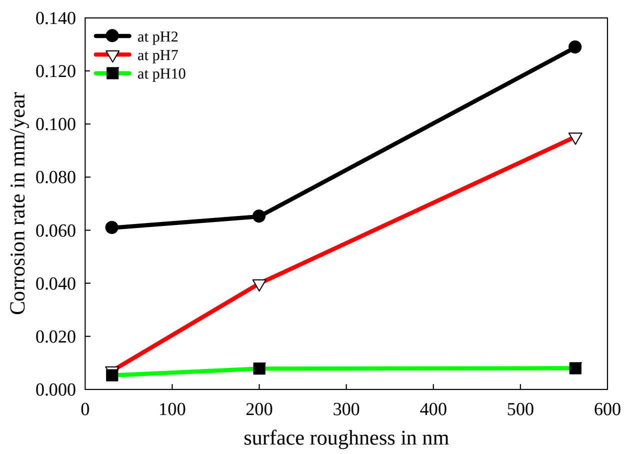


Figure 3: Corrosion rate of uncoated samples with different surface roughness in air - saturated 3.5 wt% NaCl solution at pH 2, 7 and 10.

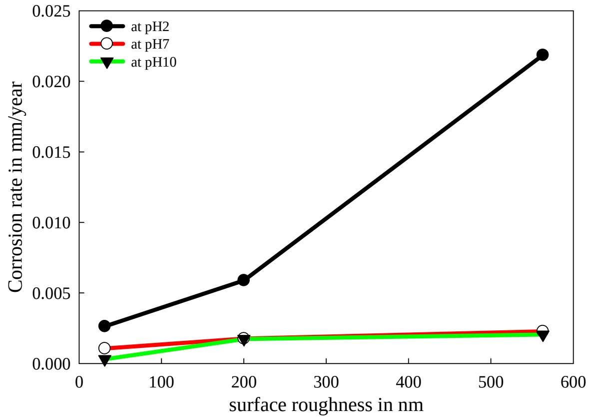
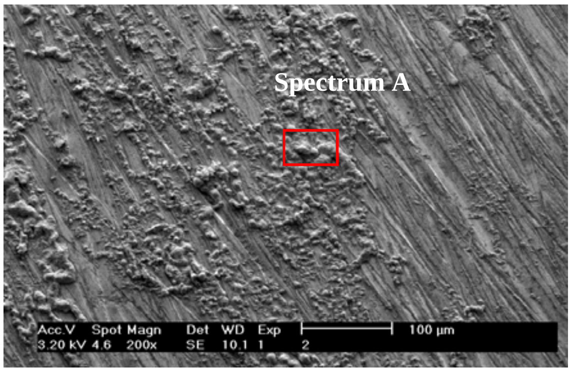


Figure 4 : Corrosion rate of CrN - coated samples with different surface roughness in air - saturated 3.5 wt% NaCl solution at pH 2, 7 and 10.

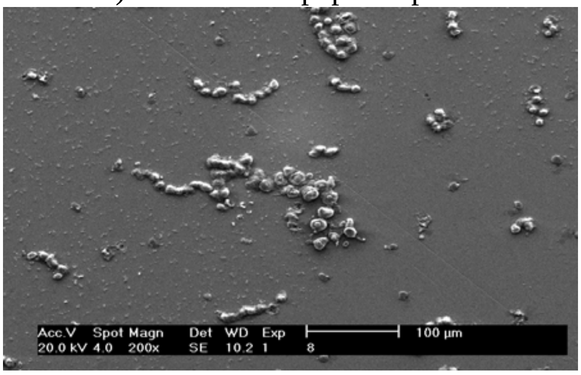
Corrosion Morphology

The SEM images of the uncoated samples after corrosion testing in air-saturated 3.5 wt% NaCl solution are shown in Figure 5. Corrosion products appear on corroded surface of all samples, but there is different in the amount and location of corrosion products. There are more corroded areas in the sample with the highest surface roughness than in the sample with the finest surface roughness. This is certainly true, if the pH of solutions is 2. And, it can be observed in Figure 5a and the corrosion products appear along the scratch of grinding.

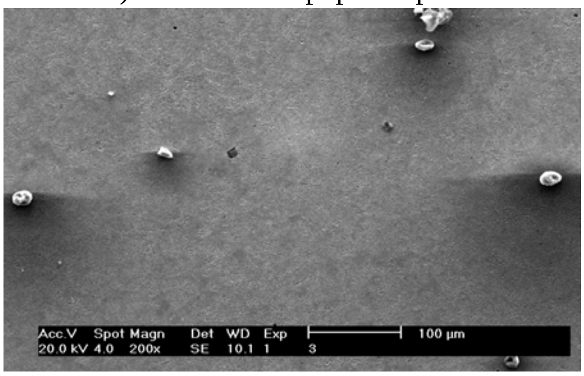
Moreover, it is found that the uncoated samples with the finest surface have a little amount of corrosion products in particular at pH 10 and they represent the best corrosion resistance. The compositions of corrosion products evaluated by EDX are shown in Figure 6. From the EDX analysis, it reveals the content of Fe and O representing the corrosion products.



a) No. 180 SiC paper at pH 2



b) No. 600 SiC paper at pH 7



c) No. 1200 SiC paper at pH 10

Figure 5 : SEM images of the uncoated samples after corrosion testing in air - saturated 3.5 wt% NaCl solution at pH 2, 7 and 10.

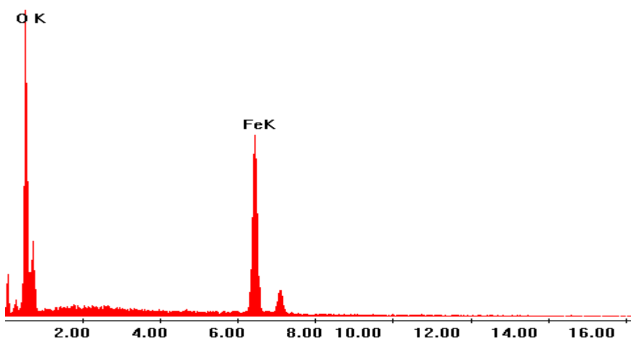
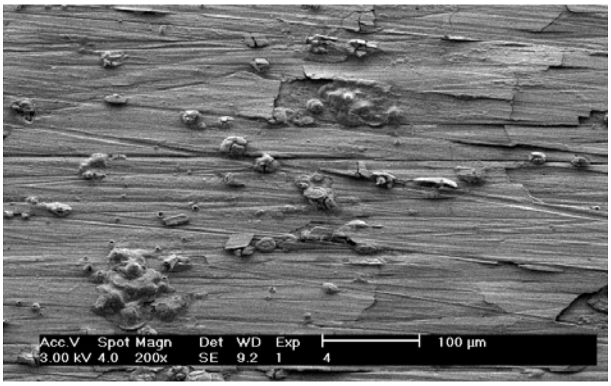
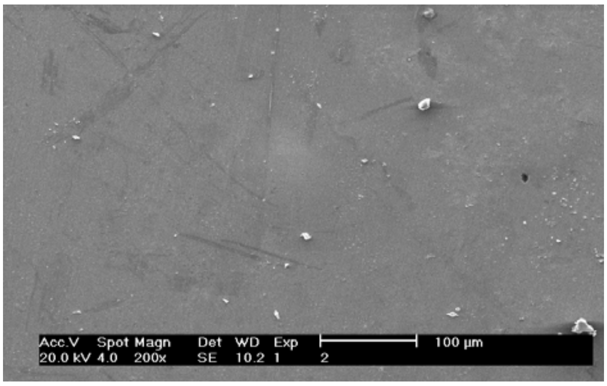


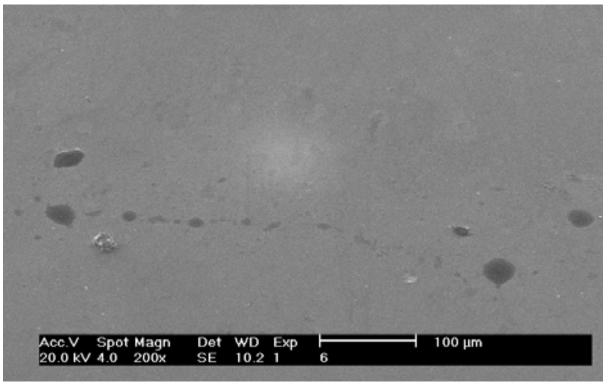
Figure 6: The EDX analysis of spectrum A.



a) No. 180 SiC paper at pH 2



b) No. 600 SiC paper at pH 7



c) No. 1200 SiC paper at pH 10

Figure 7 : SEM images of the CrN coated samples after corrosion test in air-saturated 3.5 wt% NaCl solution.

Figure 7 shows the SEM images of the CrN coated samples after corrosion testing in air-saturated 3.5 wt% NaCl solution. It is obvious that the CrN-coated samples have less corrosion products in comparison with the uncoated samples (Figure 5) at the same condition for testing. From the results, it is shown that the CrN film represents as a protective film which can be used to reduce corrosion attack of NaCl solution. In addition, the results show that the corrosion resistance of the CrN film drastically depends on the roughness of substrate and pH of solution. For example, the CrN coated samples with the highest surface roughness and tested in solution at pH 2 (Figure 7a) exhibit the worst corrosion resistance. This is due to the fact that some parts of the CrN film break and remove from the substrate resulting in the ion penetrates easily into the CrN coating and attacks the surface of substrate. The breakdown of the CrN film is a result from an imperfection of adhesion between the CrN coating and substrate. In contrast, the CrN coated samples with smoother surface and tested at pH 7 and 10 almost have no corroded area as shown in Figure 7b and 7c. From those results, it is corresponding to the previous results [11] that corrosion resistance of the samples is better, if the surface of samples is smoother and pH of solution is higher.

Conclusions

The corrosion behavior of AISI4140 steel surface coated with chromium nitride (CrN) film by physical vapor deposition (PVD) was studied. The following conclusions are:

1. The CrN coated samples exhibited better corrosion resistance than the uncoated samples in 3.5 wt% NaCl solution at all pH values.

2. The corrosion resistance of the uncoated and CrN coated samples significantly altered with pH of solution. And, the corrosion resistance of the samples at pH 10 was better than at pH 7 and pH 2 respectively.

3. The surface roughness of substrate prior to coating significantly effected on the deposition and breakdown of CrN film during corrosion testing. And, the

corrosion rate increased with increasing surface roughness of substrate.

4. The corroded area in the CrN-coated samples was less than that in the uncoated samples.

Acknowledgments

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