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Electrochemical Noise analysis on Sputtered Chromium Nitride Coated D9 Steels

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Chromium nitride (CrN) films were coated on D9 steel substrates by reactive DC magnetron sputtering process. The corrosion properties were investigated in 3.5 % NaCl solution. Coated D9 steel showed higher R_{ct} values compared to bare D9 steel substrate. The corrosion current density (I_{corr}) was found to decrease considerably for CrN coated D9 steel specimen. The polarisation resistance was found to be higher for the coated specimens. The current transient as observed from electrochemical noise method was found to decrease with increasing the immersion time for CrN coated substrate. The noise resistance was found to be superior for coated specimen.

Keywords: Sputtered films, EIS, Polarization, Passive films

1. INTRODUCTION

In past decades, CrN films have shown a wide spread applications in engineering components due to their high hardness, resistance to wear, low friction coefficient and high temperature stability [1]. These characteristics make CrN an excellent protective candidate in forming tools, die casting dies, and wear protection applications as a replacement for Chromium electroplating [2]. The main advantage associated with the deposition of CrN film is the low deposition temperature, and this make it suitable for deposition onto temperature-sensitive material and low melting point metals [3]. A great advantage of CrN is that the internal stresses are very low, due to which coatings with thickness more than 40 μm can be obtained on a variety of engineering substrates [4]. In physical vapor deposition Cr-N film can grow in the form of CrN or Cr_2N phases, the Cr_2N phase exhibiting a higher hardness. On the other hand the CrN phase is interesting due to its magnetic, optical and electronic properties [5]. The CrN thin films were deposited by various methods such as ion-source-enhanced middle frequency magnetron sputtering [6], unbalanced magnetron sputtering [7], rf reactive sputtering [8], pulsed dc magnetron sputtering [9], metal vapor vacuum arc [10], arc discharge [11], e-beam PVD [12], Hollow cathode discharge gun [13]. Among these sputtering has advantages over other conventionally used high temperature techniques because of its simplicity, low thermal budget, low cost and its ability to produce good quality films with desired properties [14].

There are several electrochemical methods to study the inhibition characteristics of materials such as electrochemical impedance spectroscopy (EIS), scanning vibration electrode probe technique (SVET), potentiodynamic polarization, among these methods electrochemical noise measurements has also been successfully applied to the study of corrosion inhibiter performance [15]. Electrochemical noise (EN) method has gained popularity in the recent years and has emerged as a promising technique for corrosion analysis. Stochastic fluctuations of the potential or current occurring at the electrode interface could be described using a generic term called electrochemical noise. The methods based on electrochemical noise method do not need the any externally imposed perturbation to the electrochemical system that could be change its specific properties [16, 17].

There is no report found till date on electrochemical noise analysis of hard CrN thin films. In this paper, we put our pioneer attempt to investigate corrosion behavior of CrN films on D9 steel by electrochemical noise method. The results obtained from Electrochemical Noise method were compared with potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL PROCEDURE

CrN thin films of 2 μm thickness were deposited on well-cleaned D9 steel substrates using a dc magnetron sputter deposition unit. The composition of D9 steel substrate is given in Table.1.

Table 1. The composition of D9 substrate

Elements	Ni	Cr	Mn	Mo	Ti	Nb	Si	C	Fe
Wt %	14.7	15	1.5	2.2	0.3	0.167	0.67	0.05	Bal.

Only major elements are listed.

Table 2. Deposition parameters of CrN thin films

Objects	Specification
Target (2 " Dia)	Cr (99.9%)
Substrate	D9 Steel
Target to substrate distance	50 mm
Ultimate vacuum	1 x 10^{-6} m bar
Operating vacuum	2 x 10^{-3} m bar
Sputtering gas	Ar: 50 sccm N_2: 20 sccm
Power	50Watt
Substrate temperature	200°C

The high purity argon was fed into the vacuum chamber for the plasma generation. The substrates were etched for 5 minutes at a dc power of 50 W and an argon pressure of 10 m Torr (1.33 Pa). The optimized deposition parameters for CrN sputtering are summarized in Table.2.

X-ray analysis was conducted in PANalytical-X'Pert Pro using CuK_{α} (1.514Å) and a thin film attachment with a parallel plate collimator 0.18^{o}. The electrical studies were carried out by four probe set-up model DFP-20, #1223. The surface morphology of the coating was studied by scanning electron microscopy (SEM) using a Hitachi S 3000H microscope.

2.1. Electrochemical Impedance Spectroscopy and Potentiodynamic polarization

EIS measurements were carried out by using Autolab Potentiastat-Galvanostat (PGSTAT12.) and the FRA version 4.9.005 Beta software. A sinusoidal voltage signal of 10 mV was applied over a frequency range of 10 mHz-100 kHz. All EIS experiments were performed in an open circuit potential using a three electrode cell configuration consist of saturated calomel electrode as a reference, platinum sheet as a counter electrode and the sample as a working electrode. The working electrode was wounded using polyester such that the area exposed to a solution was 1 cm^2. All measurements were performed in 3.5% NaCl solution. After EIS measurements, the system was allowed to attain open circuit potential. After getting the stable open-circuit potential the upper and the lower potential limits of linear sweep voltametry were set at +200 and -200 mV respectively with the reference of OCP. The sweep rate was 1 mV/s. The Tafel plot was obtained after the electrochemical measurements.

The porosity measurement was done on the assumption that the coating is electrochemically inert at low anodic over potential. The porosity of the coating is estimated using the relation.

$$P= (R_{ps}/ R_p) \text{ x } 10^{-|\Delta\, Ecorr| / \, ba} \text{ ----------------- } (1)$$

Where P is the total coating porosity, R_{ps} is the polarization resistance of the blank substrate, R_p is the polarization resistance of the coated steel, ΔE_{corr} is the difference between the free corrosion potential of the coated steel and blank steel substrate, and b_a is the anodic Tafel slope for the substrate [18].

2.2. Electrochemical Noise

Electrochemical noise data were recorded using an AUTOLAB potentiostat-galvanostat (PGSTAT 12) and GPES (General Purpose Electrochemical Software). Three electrode configuration consisting of two working electrodes (each other with 1 cm^2 surface area) and saturated calomel electrode as a reference electrode were used. The electrochemical current noise was measured between the two working electrodes and simultaneously the potential noise was measured between two coupled working electrodes (coupled through Zero Resistance Ammeter) and the reference electrode. All experiments were carried out in open circuit potential condition. For all experiments, a sampling interval of 0.5 s was chosen over a 2048 consecutive data points. The measurement was performed in 3.5 % NaCl solution.

In time domain, the most important parameter is noise resistance (R_n), that is, the standard deviation of potential noise (σ_v) to standard deviation of current noise (σ_i) which are linked by Zero resistance ammeter [19]. The noise resistance can be associated with polarization resistance (R_p).

$R_n = \sigma(v)/ \sigma(i)$ ------------------------- (2)

The protection afforded by the coating can be directly related to the value of noise resistance (R_n). The ratio 1/Rn is proportional to corrosion rate**.**

3. RESULTS AND DISCUSSION

3.1. Structural properties

The XRD results as shown in Fig.1.indicate that the crystallography structure of sputter-deposited CrN thin films depends on the nitrogen content in the sputtering process. The XRD pattern confirms that the deposited films are polycrystalline in nature.

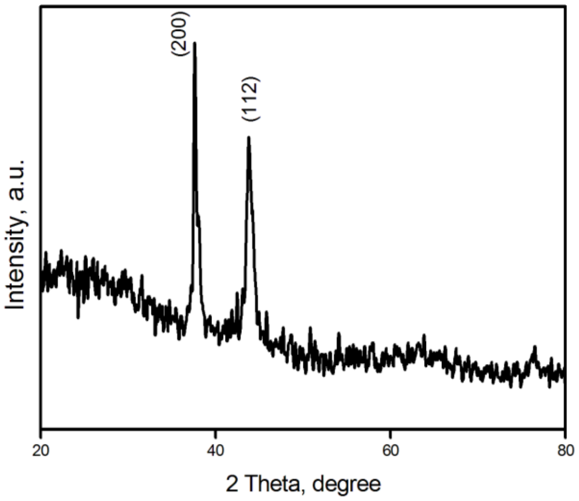


Figure 1. XRD pattern for CrN coated D9 steel

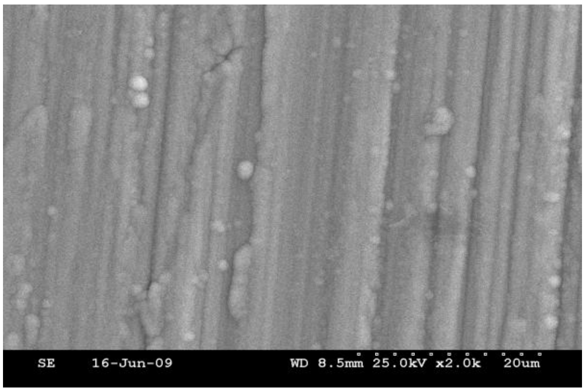


Figure 2. SEM micrograph of CrN film on D9 steel substrate

The mixed phases of face centered cubic CrN phase with preferred orientations along (200) and (400), orientation along (112) of hexagonal Cr_2N phases and Cr_2O_3 (214) were observed.

Fig.2. shows the SEM image of CrN on D9 steel containing the finer, denser equiaxed crystallites which are expected to provide more corrosion resistance [20]. This structure is related to the formation of the Cr_2N phase with broad diffraction peak as revealed in the XRD pattern.

3.2. Electrochemical Studies

3.2.1. Polarization.

The potentiostatic polarization experiments provided some idea of the electrochemical activity of the material. However, this necessitated scanning across a wide range of electrode potentials so that the surface of the material at the end of such polarization was the result of cumulative effects at different potentials. To analyse the surface, the material was subjected to potentiostatic polarizations, one specified potential being impressed on the material at a time. The potentials were either anodic or cathodic with respect to the primary electrochemical process occurring on the surface as indicated by the potentiostatic polarization curves.

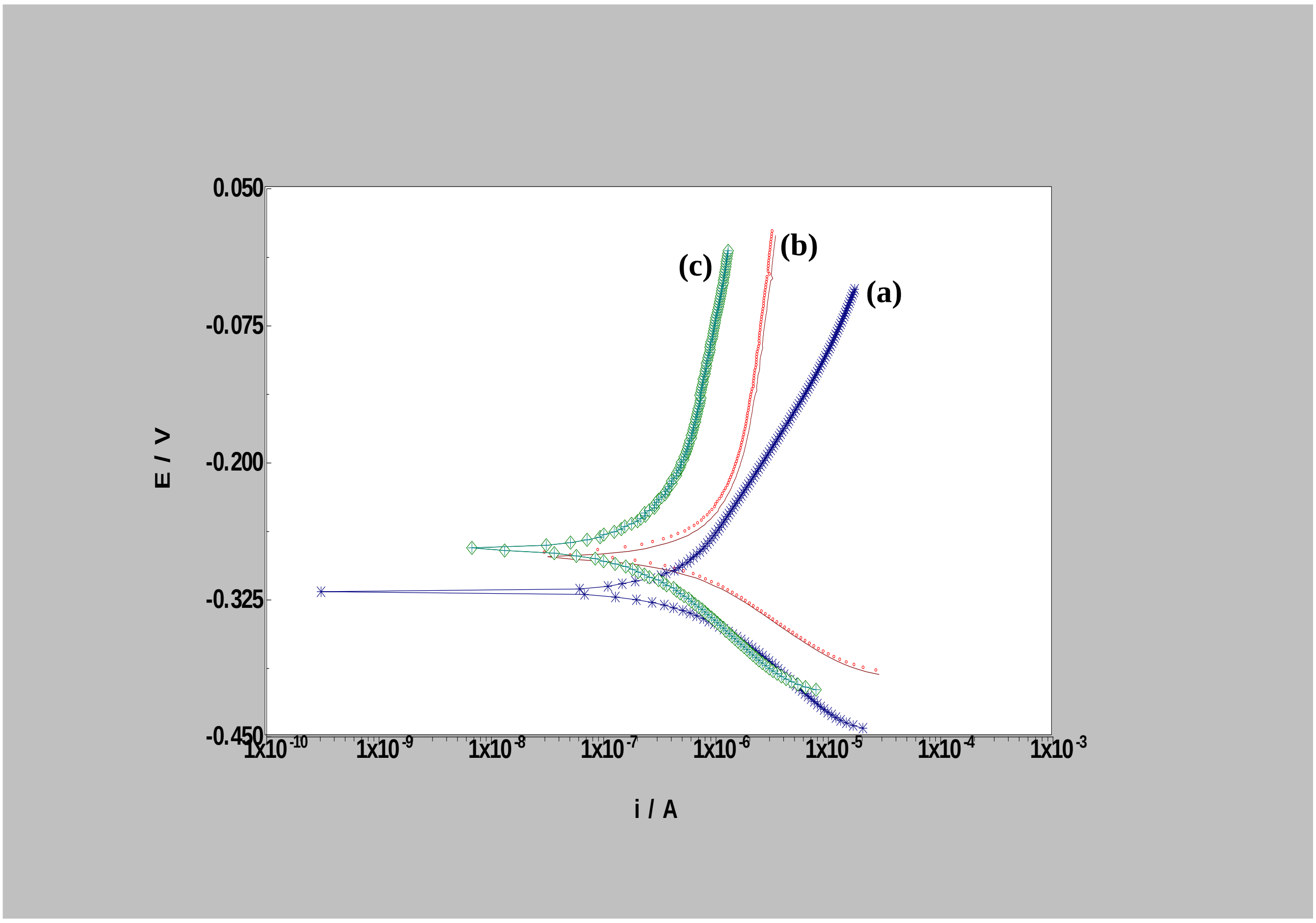


Figure 3. Potentiodynamic polarization curve for (a) blank D9 steel; (b) Cr/D9; (c) CrN/D9

The potentiodynamic polarization curves obtained for the D9 steel (substrate), Cr on D9 and CrN on D9 steel substrates in 3.5% NaCl electrolyte are presented in Fig.3. The current and potential of the corroding electrode is related by

$i= i_{corr} (e^{2.3\ \eta/ba} - e^{-2.3\ \eta/bc})$ . . . . (3)

Where i_{corr} - corrosion current; η - overpotential ($E-E_{corr}$), b_a and b_c -anodic and cathodic Tafel slopes.

At high over potentials ie

$\eta >> RT/F$

$i = i_{corr}\ e^{2.3\ \eta/ba}$

$\log i = \log i_{corr} + \eta/b_a$

In the plot of η versus log i, extrapolation of linear line to corrosion potential gives a straight line and the slope gives both b_a and b_c and the intercept gives the corrosion current.

The E_{corr} and I_{corr} values have been calculated using the Tafel extrapolation method and they are given in Table 3. The corrosion potential of blank D9 steel is about -0.318 V. The corrosion potential goes to positive region for Cr and CrN coated D9 steels, which indicates the better corrosion resistance of all coated samples. The corrosion rate is normally proportional to the corrosion current density (i_{corr}). The corrosion current density of blank D9 steel substrate is about $1.31\text{x}10^{-7}$ A/cm^2, which decreases to $1.88\text{x}10^{-8}$ A/cm^2 for CrN/D9. The polarization resistance also increases in the same manner.

Table 3. Potentiodynamic polarization data for the CrN coated D9 steel substrate

Materials	I_{corr} X10^{-7} (A cm^{-2})	E_{corr} (V/SCE)	b_c V dec^{-1}	b_a V dec^{-1}	R_p kΩ	Porosity (%) x10^{-3}	Corr.rate x10^{-7} mills y^{-1}
Blank D9 Steel	3.20	-0.318	0.129	0.015	6.9	----	1.42
Cr/D9	1.35	-0.287	0.015	0.035	33.6	8.57	0.59
CrN/D9	0.18	-0.278	0.009	0.012	117.0	0.12	0.08

The transition metal nitride coatings are electrochemically inert and thus their polarization resistance is very high [21]. The coating may suffer from corrosive attack due to inherent coating defects (such as pores, cracks, etc.) and inhomogeneties [4]. The porosity values were measured from polarization data as shown in Table.3. The porosity is very low for CrN/D9 film when compared to metallic Cr coated D_9 steel.

The corrosion rate (CR) is expressed in mills per year.

$CR= 0.1288\ \text{x}\ i_{corr}\ \text{x}\ w/\rho$ . . . . (4)

where i_{corr} = corrosion current in amp / cm^2, w = equivalent weight of metal, ρ = density

The corrosion rate as observed on CrN coated D9 steel sample was significantly lower than that of the bare substrate and Cr species on the substrate exhibiting the lowest corrosion rate of sputtered CrN film on D9 steel.

3.2.2. Electrochemical impedance spectroscopy

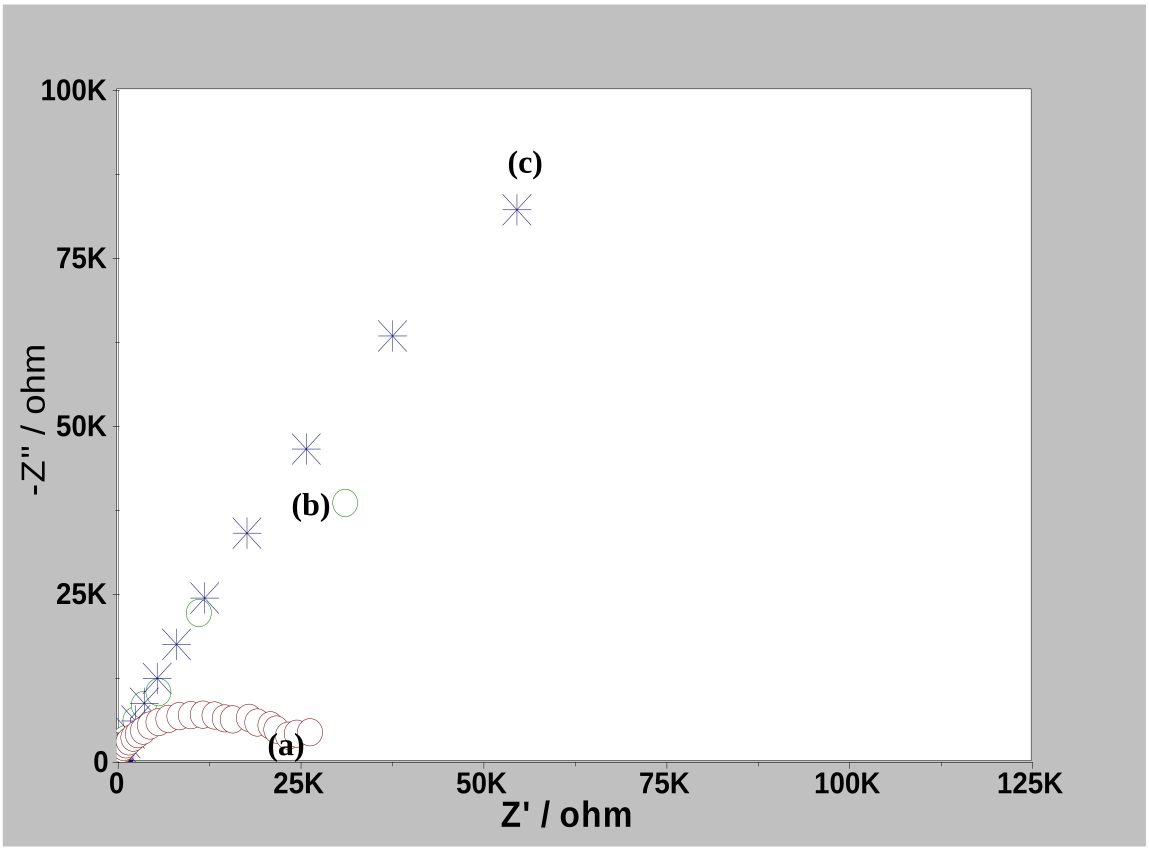
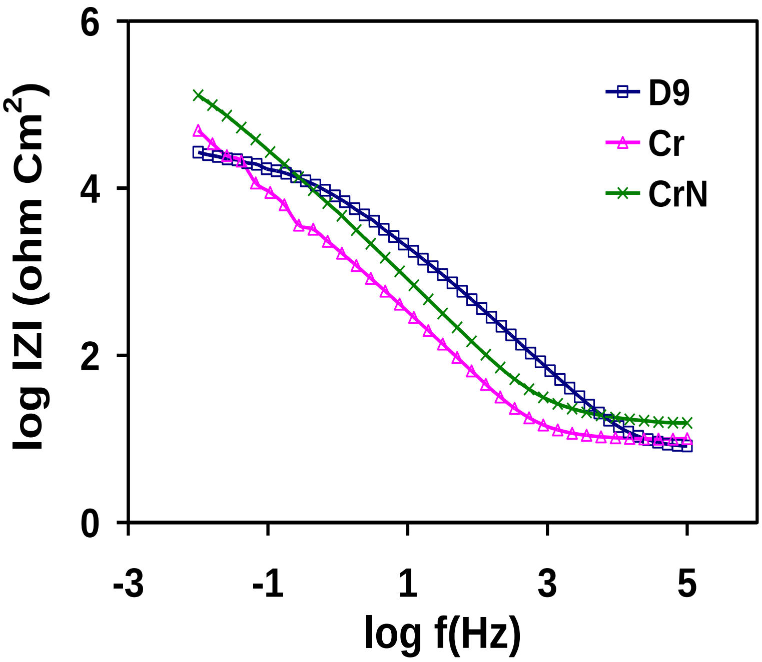
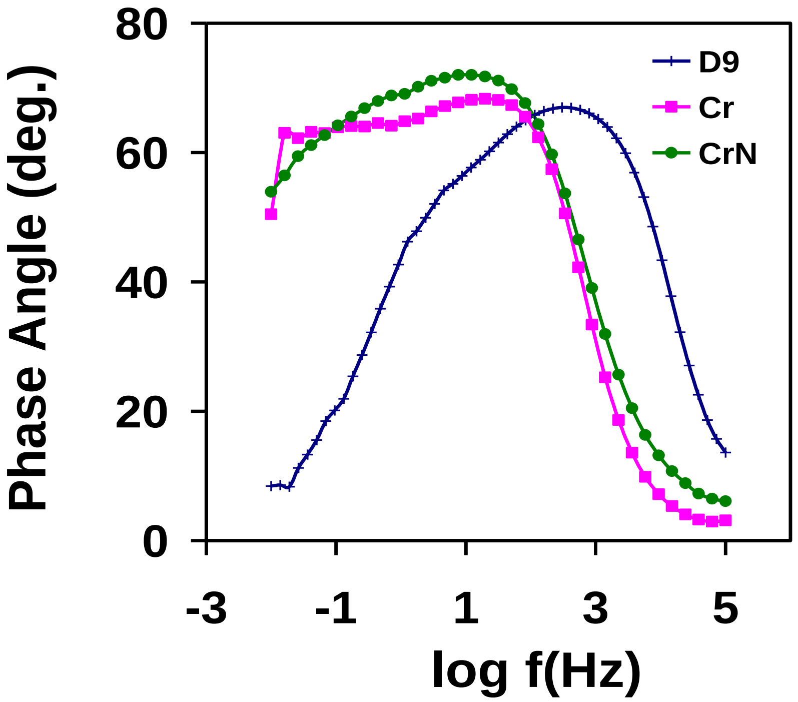


Figure 4. Nyquist plot for (a) blank D9 steel (b) Cr/D9 (c) CrN/D9



(a)



(b)

Figure 5. Bode plots (a) log f Vs log | Z | (b) log f Vs Phase angle of blank D9 steel, Cr/D9 and CrN/D9

Table 4. Electrochemical impedance data for the CrN film on D9 steel

Materials	R_{ct} (kΩ)	C_{dl} (µF cm $^{-2}$)
Blank D9 Steel	11.59	692
Cr/D9	73.9	204
CrN/D9	146.7	58.8

The electrochemical impedance spectra of the specimen were measured in the same three electrode assembly, as used for the potentiodynamic polarization experiments. The impedance results obtained from Nyquist and Bode plots for the samples used for corrosion tests in 3.5% NaCl solution are shown in Table.4 and in Fig. 4 and Fig.5.

The R_{ct} can be related to i_{corr}

$R_{ct} = b_a \times b_c / 2.3 (b_a + b_a) i_{corr}$ . . . . (5)

R_{ct} -- charge transfer resistance

b_a and b_c - anodic and cathodic tafel slopes

The double layer capacitance C_{dl} value is obtained from the frequency at which Z imaginary is maximum

$\omega (Z_{(im)} \max) = 1 / C_{dl} R_{ct}$ .. . . (6)

The Nyquist plot showed a single semi circle for all the samples. These behaviors of the samples are due to the short exposure time (30 minutes), which is not sufficient to reveal the degradation of the substrate [22]. The CrN/D9 has higher charge transfer resistance (R_{ct}) than blank D9 steel substrate.

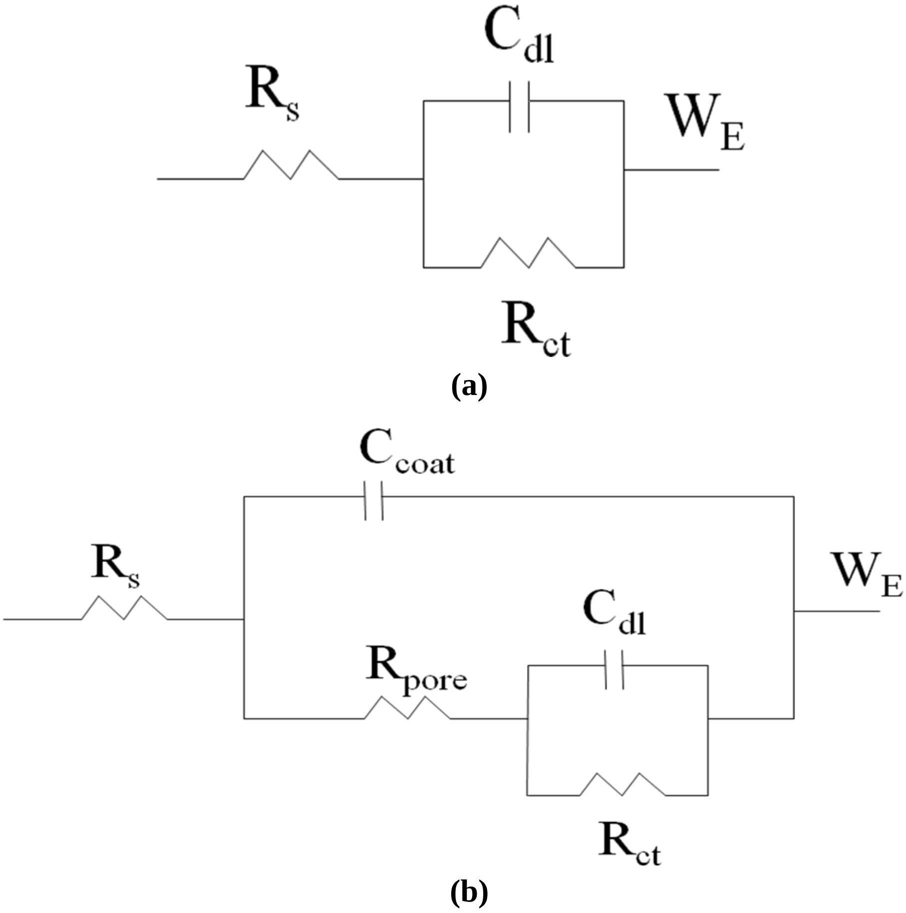


Figure 6. Equivalent circuit for fitting the electrochemical impedance data of (a) Blank D9 steel substrate (b) Coated D9 steel substrate

The same behavior was observed from the Bode plot (log f Vs log Z). The corrosion behavior of the samples is further illustrated by Bode plots as shown in Fig. 5a where it can be seen that the bare D9 steel has the lowest absolute impedance. The values of |z| of the coated D9 substrates are significantly higher than that of the bare substrate. Fig. 5.b (log frequency (f) Vs Phase angle) shows that, for D9 steel has a narrow peak with single time constant for corrosion process at the substrate/electrolyte interface was observed for bare D9 substrate. The Cr and CrN coated samples have shown the broad peak, which is indicating the presence of two interfaces (Cr and CrN coating/electrolyte and substrate/electrolyte) due to the formation of pitting corrosion. The equivalent circuits for these systems are shown in Fig.6.

3.2.3. Electrochemical Noise studies

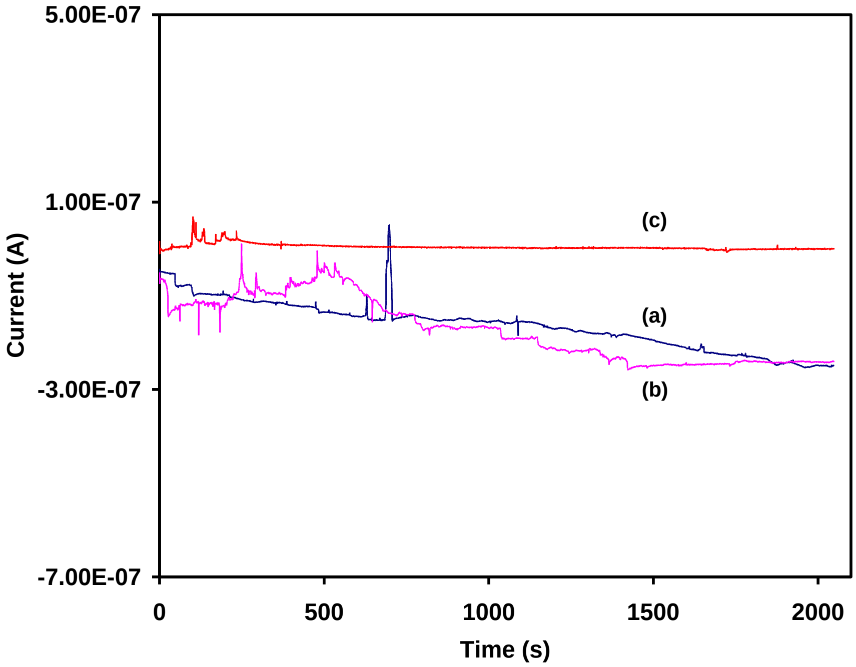


Figure 7. Current noise as a function of time of (a) D9 steel (b) Cr/D9 (c) CrN/D9.

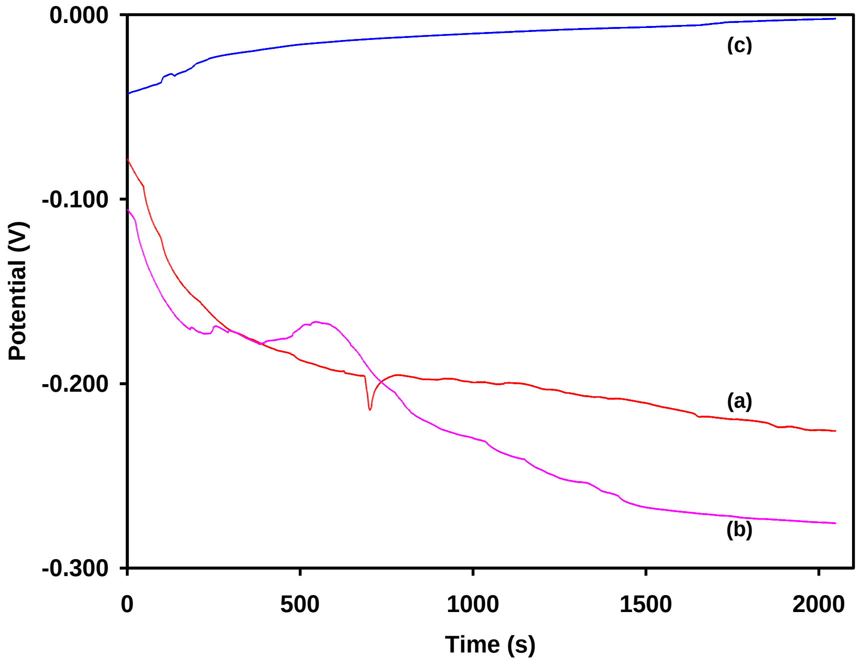


Figure 8. Potential noise as a function of time for (a) D9 steel (b) Cr/D9 (c) CrN/D9.

Fig.7. shows current noise of blank D9 steel, Cr/D9, and CrN/D9. The current transient of D9 steel is about -0.06X10^{-5} A in the cathodic region. The current transient decreases with increasing the time. The sudden rise in current transient approximately at 700 second refers to pit formation [23]. The

periodic transient could be associated with hydrogen evolution. The current noise of the Cr Coated D9 steel initially increases to approximately -0.01x10^{-6} A with increasing the immersion time up to 500 seconds in the cathodic region, then the current noise decreases with increasing immersion time to 1400 seconds. The decreasing current transient refers to stable film formation [24]. The saturation of current was observed after 1400 seconds. The current noise of the CrN coated D9 steel shows that the current transient is high about 0.70X10^{-7} A in anodic region. Then the current transient decreases with increasing the immersion time. The current transient between 500 second and 2048 seconds, small and periodic, in the order of 0.15x10^{-7} A is associated with hydrogen evolution. The smaller amplitude of current refers to stable film formation [25].

Fig.8. shows the potential noise of blank D9 steel, Cr/D9, and CrN/D9. The potential noise of the blank substrate is initially at -0.08 V and then the potential noise exponentially decreases with increasing the immersion time in the cathodic region. This decreasing trend may be due to the occurrence of corrosion [26]. The potential noise of Cr coated D9 steel decreases initially from -0.100 V to -0.275 V with increasing the immersion time to 1700 seconds, then the potential passivate, with increasing immersion time to 2048 seconds. The potential noise for CrN coated D9 steel is initially -0.05 V in the cathodic region. Then the potential noise exponentially increases with increasing the immersion time and goes to positive direction. This increasing trend refers to passive film formation [27].

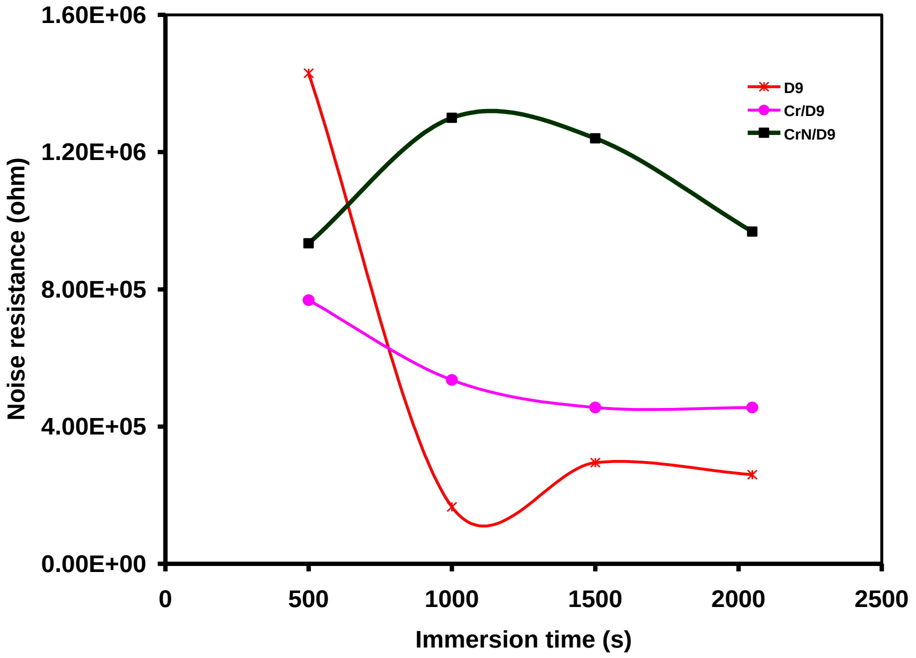


Figure 9. Noise resistance as a function of immersion time for the blank D9 steel, Cr/D9 and CrN/D9.

Fig.9. Shows the variation of noise resistance as a function of immersion time .The graph shows the noise resistance varies with immersion time. The noise resistance was found to decrease with increasing the immersion time for uncoated and Cr coated D9 steel samples. Whereas for the CrN coated D9 steel it initially increases with increasing immersion time and decreases thereafter. A higher

noise resistance value was observed for the CrN coated specimen than uncoated and Cr coated D9 steel. This enhanced noise resistance of the CrN coating is due to the simultaneous contributions of metallic, covalent, and ionic bonding between metal-metal pairs of atoms and metal-nonmetal pairs of atoms in transition metal nitride compounds [28].

Table 5. Electrochemical noise data for the CrN film on D9 steel

Materials	Noise resistance(R_n) (kΩ)
D9 steel	190
Cr/D9	684
CrN/D9	1470

Table.5. shows that the noise resistance of coated D9 steel substrates was higher than the uncoated D9 steel. The rapid increase in noise resistance (Rn) was observed because the protective passive film formation has increased the polarization resistance and this will lead to a drastic decrease in corrosion rates [19]. The similar behavior was also observed in charge transfer resistance (R_{ct}) and polarization resistance (R_p) from electrochemical impedance spectroscopy and Potentiodynamic polarization, but not equal because the noise resistance (R_n) was calculated from raw data [15].

4. CONCLUSIONS

Chromium nitride films of 2 μm thickness were coated on D9 steel substrates by reactive DC magnetron sputtering process. The XRD pattern confirmed the grown films have polycrystalline nature and exhibited CrN and Cr_2N phases. The coated D9 steel showed higher charge transfer resistance values compared to bare substrate. The corrosion current density (I_{corr}) was found to decrease from 1.31 $x10^{-7}$A for bare substrate to 1.88 x 10^{-8} A for CrN coated D9 steel specimen. A decrease in the porosity value was noticed for coated substrate. The polarisation resistance was found to be higher for the coated specimens. From electrochemical noise analysis, the current transient was found to decrease with increasing the immersion time for CrN coated substrate and potential noise shifted to the positive direction. The noise resistance was found to be higher for coated specimen than bare substrate. Considering the better corrosion resistance of the coating, we anticipate a wide range of applications, including biomedical applications, for CrN coatings.

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