

Preparation of chromium oxynitride and chromium nitride films by DC reactive magnetron sputtering and their material properties

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Thin films of $\sim 2 \mu\text{m}$ thick chromium nitride (CrN) were prepared by direct current (dc) reactive magnetron sputter deposition on steel substrates. XPS spectra showed the presence of chromium in the form of CrN with traces of Cr_2O_3 on CrN thin films. XRD spectrum shows CrN peaks at 37° and 43° which corresponds to (111) and (200) planes. Surface topography from atomic force microscope shows that films have continuous coverage of rectangular cell like patterns. Corrosion performance of these films on low carbon steel substrates in 3.5%NaCl solution was evaluated using electrochemical techniques. A less negative value of E_{corr} and lower value of I_{corr} signify an improvement in corrosion resistance of the CrON coating. Scanning vibrating electrode technique (SVET) was able to discretely map relative cathodic and relative anodic sites at a macroscopic defect and to record the changes of local electrode activities in a real time.

Keywords: Sputtered films, Chromium nitride, XPS, Corrosion, SVET

Introduction

The chromium based nitrides Cr_2N and CrN prepared by plasma deposition have been reported to have high hardness, enhanced wear and corrosion resistance and can be used as anti wear and anticorrosion films. It shows higher oxidation temperature together with a high ductility, which is desirable for mechanical applications.¹⁻³ Chromium nitride films have been increasingly used as a replacement for electroplated hard chromium in various applications including wear resistant films (hard chrome), corrosion resistant films and mirror-like films for cosmetic appearance in automobiles.³⁻⁵ CrN films have been used for injection moulding applications. CrN will form a dense and stable Cr_2O_3 thin film as a protective surface scale at the elevated temperature. Chromium oxynitride $[\text{Cr}(\text{N},\text{O})]$ films also exhibits higher hardness than CrN.^{6,7} It is presumed that $\text{Cr}(\text{N},\text{O})$ films has a low nitrogen content on the CrN structure.⁸ It is expected that $\text{Cr}(\text{N},\text{O})$ films can be produced by dissolving oxygen atoms into CrN lattice. Physical vapour deposition (PVD) of chromium nitride and its alloys with aluminium are emerging as a good alternative to other conventional surface treatments for tool protection.⁹ PVD CrN has good hardness and toughness, which allows deposition of films as thick as $20 \mu\text{m}$ without significant performance loss. Its friction

coefficient (in sliding contact with 100 Cr6 steel) is comparable to that of TiN. It shows high chemical stability making it appropriate for hot working applications, as its oxidation temperature is $\sim 700^\circ\text{C}$.⁹ In addition, its characteristic silver colour has extended its applications towards the decorative sector.

Because the electrochemical processes use hexavalent chromium $[\text{Cr}(\text{VI})]$ which has been found to be carcinogenic, whereas PVD processes offer an attractive alternative for producing chromium films in an environmentally friendly process. Deposition by reactive sputtering methods leads to the formation of various crystallite phases like Cr_2N , $\text{Cr}_2\text{N} + \text{CrN}$ and CrN depending on the nitrogen content and the degree of ion bombardment.¹⁰⁻¹³ However, for industrial applications, it is very important to have control of the crystal structure phase and preferred orientations, due to the strong influence these exert on the macroscopic mechanical properties.¹⁴

CrN, $\text{Cr}(\text{N},\text{O})$ and Cr_2O_3 films can be deposited with various technologies, including thermal spray,¹⁵ chemical vapour deposition,¹⁶ ion-implantation¹⁷ sputtering and cathodic arc deposition.¹⁸ $\text{Cr}(\text{N},\text{O})/\text{CrN}$ double layered films were prepared by cathodic arc deposition technology.¹⁹ CrN films have been deposited by the bipolar symmetric pulsed direct current (dc) reactive magnetron sputtering process at different temperatures and pulse substrate bias.²⁰ Growth of CrN films dc reactive magnetron sputtering at constant N_2/Ar_2 gas flow was reported by Forniés *et al.*²¹ Since mild steel (MS) is an important structural material used for industrial applications, it was chosen as the metal

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substrate for evaluating the applicability of CrN coating in the present study. For a protective coating material, the corrosion resistance of the film is one of the most important properties in addition to mechanical properties.

In this study, the authors have deposited Cr, CrN and Cr(N,O) on MS substrates using dc magnetron sputtering process and characterised their structural, microstructural, mechanical and corrosion properties. The effect of the addition of oxygen on the materials properties of the Cr based compounds is investigated. In this work, an array of experimental techniques were utilised, including X-ray diffraction (XRD), atomic force microscope (AFM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) and polarisation studies.

Experimental

The substrate used was MS, consisting of 0.37C–0.28Si–0.66Mn–98.69Fe. The substrates were cut into an appropriate size of 75 × 25 mm and ground with SiC paper to remove the heavy oxide and contamination. The polished substrates were degreased with acetone and then cathodically electrocleaned in alkali solution containing sodium hydroxide and sodium carbonate for 2 min at 70°C, followed by rinsing with distilled water. After cathodic cleaning, the substrates were dipped in 5 vol.-%H₂SO₄ solutions for 1 min.

The layers of CrN were deposited on ultrasonic cleaned substrates using a dc magnetron sputter deposition unit HINDHI VAC. The base vacuum of the chamber was below 1×10^{-6} torr (1.33×10^{-4} Pa) at the substrate temperature of 200°C. High purity argon was fed into the vacuum chamber for the plasma generation. (a high purity >99.9%Cr target of 5 cm in diameter was used as cathode). The deposition parameters for CrN are summarised in Table 1. The deposited films were analysed for crystallographic structure with a Philips X-ray diffractometer using Cu K_α line. The microstructure of the films was examined using a nanoscope AFM. TEM images were obtained using a 200 kV Tecnai-20 G2. Microhardness of the films on MS was evaluated by using a DM-400 microhardness tester from Leco with Vickers indenters. A dwelling time of 15 s and a load of 10 g were used for the measurement. The chemical nature of the outermost part of CrN film was obtained by XPS using MultiLab 2000.

Wear tests were carried out in a block-on-ring system. All tests were carried out at room temperature, ambient humidity and without lubrication. Steel ball bearing was used as a counter body. The ring material having the

diameter of 60 mm was made of high chromium high carbon tool steel with Vickers hardness 850 HV. The load applied on a specimen was 400 g (3.924 N) with the sliding speed of 100 rev min⁻¹. The wear rate was calculated by measuring the weight change of a specimen before and after the test. A conventional scratch tester (Ducom TR-101 M4 scratch tester) was used to determine the scratch resistance of the coated layers on the substrate. The radius of the diamond pin was 0.2 mm. The load applied on a specimen was increased from the initial 2 N to the final 100 N with the loading rate of 5 N mm⁻¹ and the loading velocity of 0.2 mm s⁻¹.

Electrochemical measurements were carried out using a conventional three-electrode cell, in which the exposed surface area of the test sample to the corrosive medium was ~1 cm², with platinum foil as a counter electrode and saturated calomel electrode as a reference electrode. The corrosion measurements were carried out in 3.5%NaCl aqueous solution at room temperature in non-stirred and free air conditions. Potentiodynamic polarisation and EIS measurements were performed using the Autolab PGSTAT12/30/302 galvanostat/potentiostat system. In order to establish the open circuit potential E_{OCP} or the steady state potential, before the measurements, the sample was immersed in the solution for ~60 min.

The spectrum was recorded in the frequency range 10 mHz–1 MHz. The applied alternating potential had root mean square amplitude of 10 mV on the open circuit potential. After getting the stable open circuit potential (OCP), the upper and lower potential limits of linear sweep voltammetry were set at ± 200 mV with respect to OCP. The sweep rate was 1 mV s⁻¹. After EIS measurements, the system was allowed to attain open circuit potential. After getting the stable OCP, the upper and the lower potential limits of linear sweep voltammetry were set at ± 200 mV with respect to the E_{OCP} . The sweep rate was 1 mV s⁻¹. The Tafel plot was obtained after the electrochemical measurements. The corrosion potential E_{corr} and the corrosion current density I_{corr} were deduced from the Tafel plot (log I v. E plot). The corrosion current is obtained using the Stern-Geary equation.²²

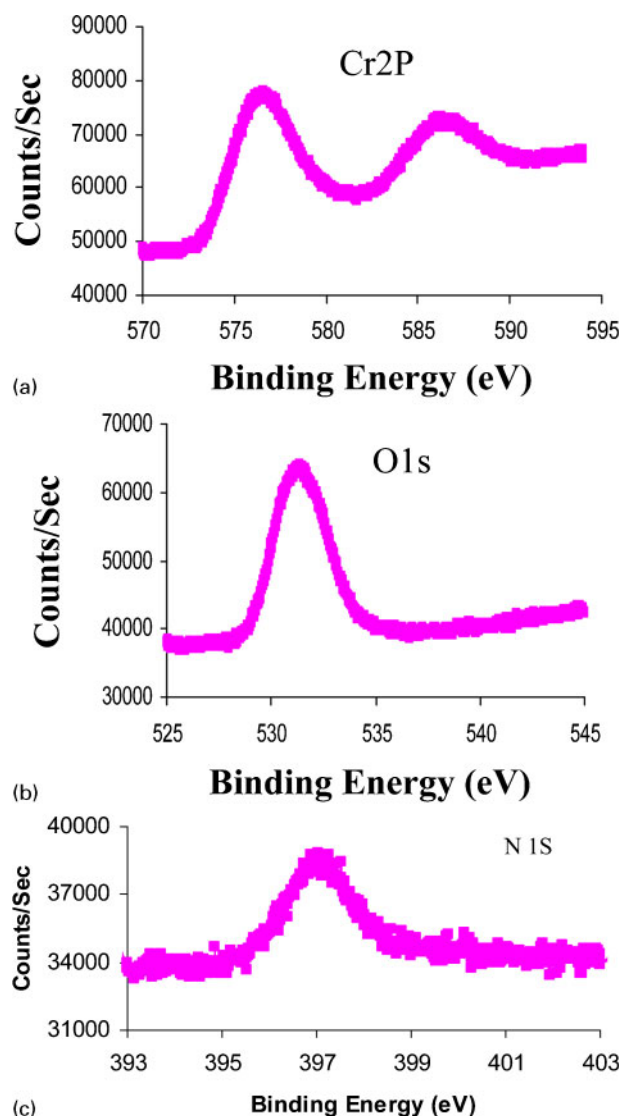
Results and discussion

Composition and structural analyses

The high resolution XPS core level spectra of CrN films are shown in Fig. 1, which shows a clearer result of the possible chemical bonding states of Cr with N individual XPS signal. The peaks centred at 576.7 and 586.3 eV originate from Cr2P_{3/2} and Cr2P_{1/2} respectively. Peaks centred at 576.7 and 586.3 eV are attributed to the formation of CrN compound by a reaction between Cr and N during sputtering. A similar observation was made by Fu *et al.*²³ Deconvolution of Cr 2P_{3/2} peak indicated that it consisted of two peaks centred at 576.7 and 577.6 eV. The peak centred at 577.6 eV could be due to the formation of Cr₂O₃.²⁴ Peaks pertaining to free Cr at 574.3 eV and Cr₂N at 574.5²⁵ were not observed, indicating that the bonding state of chromium was in the form of CrN with traces of Cr₂O₃. The N1s spectra revealed the presence of a peak characteristic of nitrogen in CrN and a weak peak which is assigned to Cr(O,N),

Table 1 Deposition parameters for CrN reactive sputtering

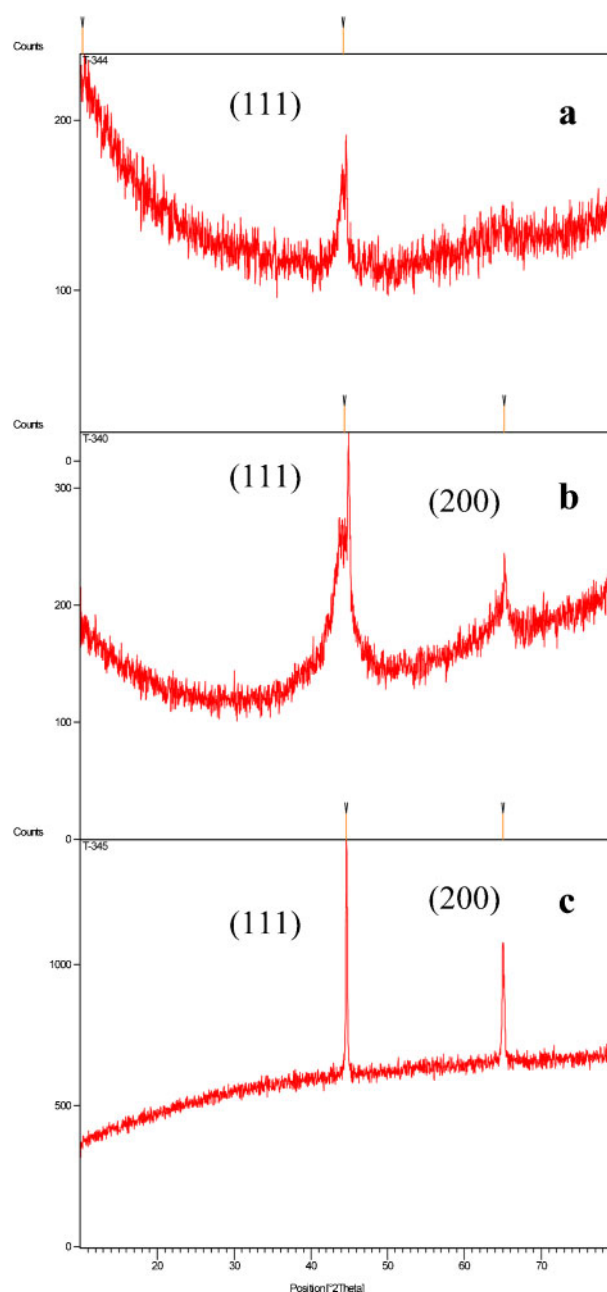
Objects	Specification
Target	Cr (99.95%)
Substrate	Mild steel (MS)
Target to substrate distance, mm	50
Ultimate vacuum, mbar	1×10^{-6}
Operating vacuum, mbar	2×10^{-3}
Sputtering gas (Ar/N ₂)	60:40
Power, W	50
Substrate temperature, °C	300



1 X-ray photoelectron spectroscopy spectra of *a* Cr2P, *b* O1s and *c* N1s

with binding energies at 397.1 and 399.7 eV respectively. A similar observation has been made on Cr(O,N) films, and no significant shift in peak position could be observed. The C1s peaks in the spectra at 285.8 eV may be the contribution from organic carbon which is unavoidable when using oil diffusion pump for evacuating the deposition chamber and XPS sample holding compartment.²⁶

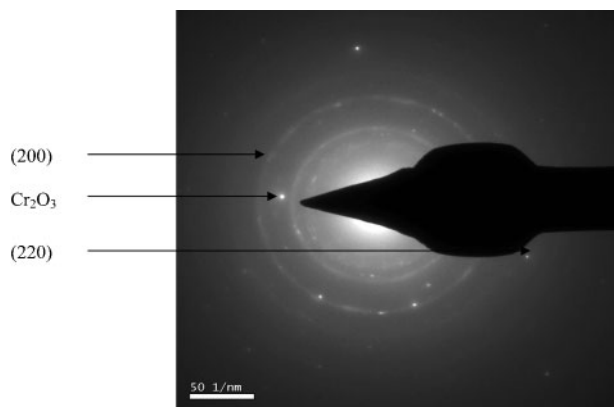
Figure 2 reveals the crystal structure of Cr, CrN and Cr(O,N) deposited films in terms of XRD patterns. A peak is observed for the Cr coating on MS. Planes are oriented at peak positions of $2\theta=43.5$, 37.7 and 76.16° corresponding to the (111), (200) and (311) planes respectively for CrN. The high intensity peak centred at $2\theta=37.7^\circ$ is assigned to cubic CrN (111) and the peak with the lower intensity at $2\theta=43.5^\circ$ is assigned to cubic CrN (200). After oxygen atoms were introduced with the CrN films, Cr(O,N) films remain the NaCl structure, which is the same as the CrN film. The presence of oxynitride phase in the surface layer can be attributed to the reaction of chromium and oxygen, whose affinity is more favourable than that of chromium and nitrogen, thus resulting in easy replacement of nitrogen by oxygen during the reactive process.



2 Patterns (XRD) of *a* Cr, *b* CrN and *c* CrON films on MS

Figure 3 illustrates the TEM-SAED patterns obtained for the CrN films. There is no significant change in the pattern as obtained for CrON film. The pattern is indexed as a NaCl structure according to the occurring diffraction rings, which confirms that the Cr (O,N) film remains in the same structure as CrN film, matching the XRD analysis carried out for these samples. The addition of oxygen atoms does not remarkably change deposition rate of the films. The target poisoning effect,²⁷ common in the reactive sputtering process when reactive gas partial pressure is high, does not happen under such preparation condition used in this paper.

The AFM pictures of the MS, Cr/MS, CrN/MS and CrON/MS coatings are shown in Fig. 4 in three- and two-dimensional (inset) views. The top view of the three-dimensional pictures recorded in area of $5 \times 5 \mu\text{m}$ shows the presence of rectangular grain on the top of homogeneous granular surface for CrON/MS. Cr coatings are oriented along the substrate cleavages.



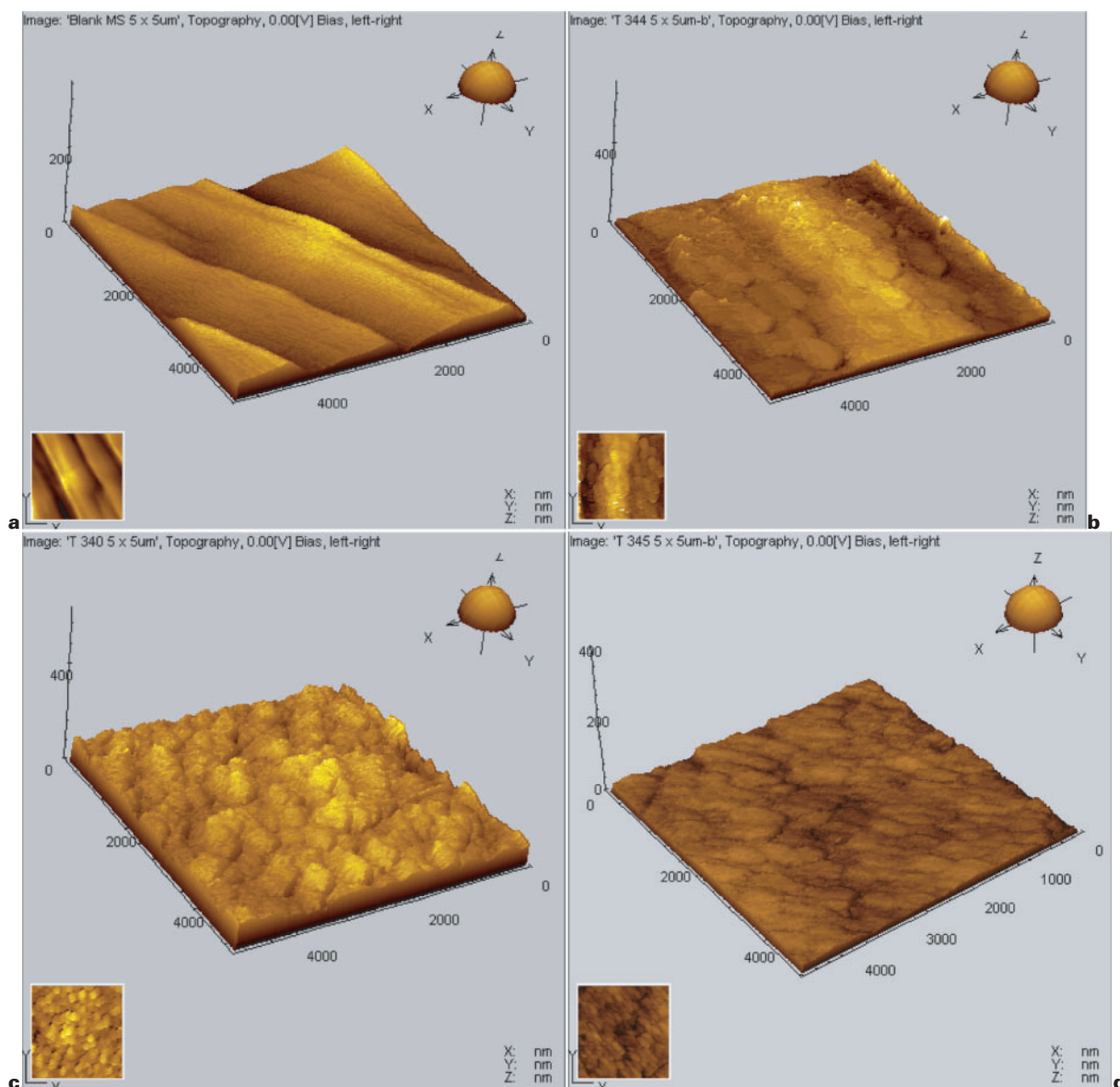
3 TEM-SAED pattern obtained for CrN on MS

However, CrN images are recorded with continuous, homogeneous hill like structure on top surface. The sputtered atomic or molecular species on the substrate surface acquire a large thermal energy and hence a large mobility. This enhances the diffusion distance of the evaporated species. As a result, the collision process

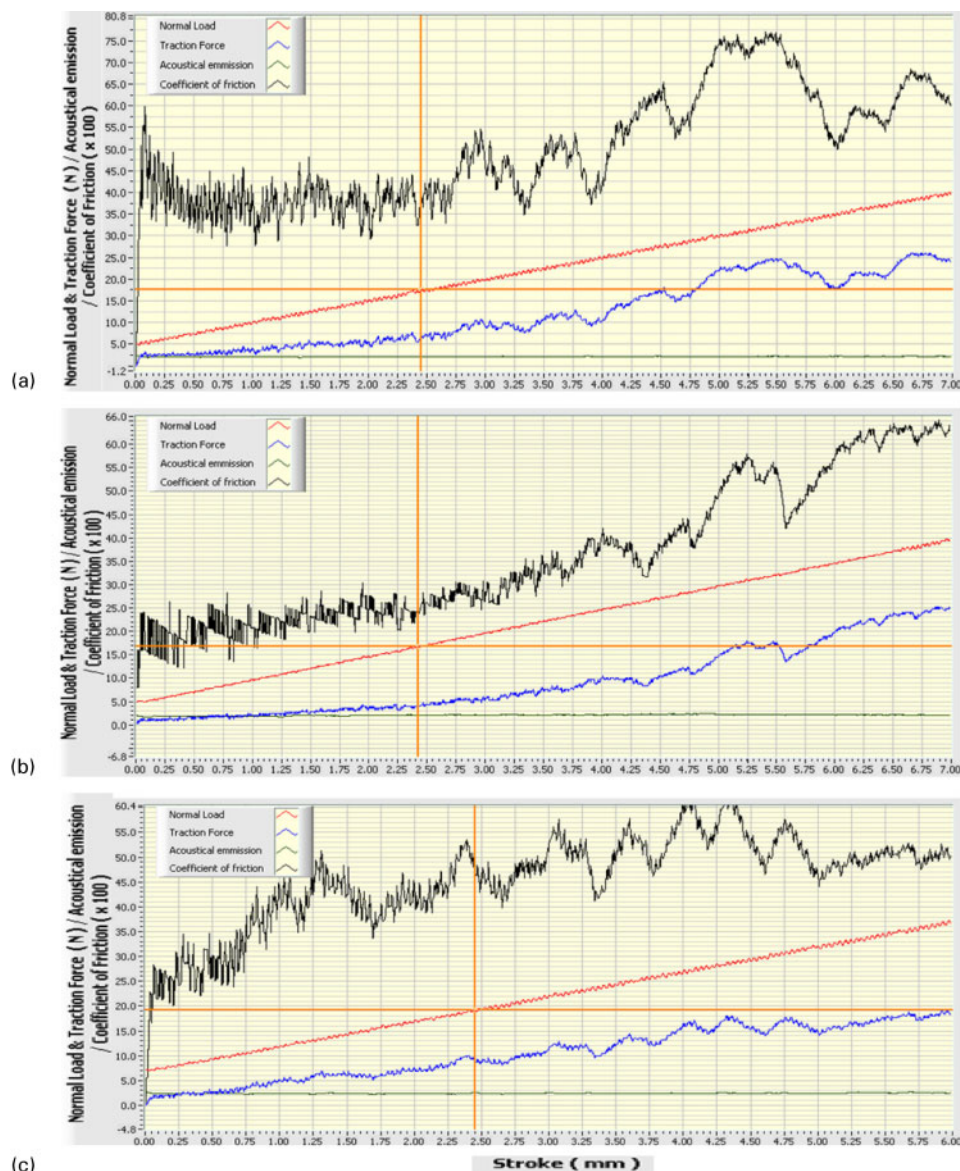
initiates the nucleation and enhances the island formation in order to grow continuous film with larger grains.

Mechanical properties

The microhardness values of Cr/MS, CrN/MS and CrON/MS samples were measured with an average of minimum three readings taken at each load. The microhardness values are 620, 1750 and 2257 HV for Cr/MS, CrN/MS and CrON/MS respectively. With the incorporation of oxygen, the microhardness of CrON/MS is found to increase to 2257 HV(10 g) which may be due to the load support provided by the oxynitride. When a normal load is applied on the film, it introduces a shear stress at the interface between the substrate and the film which, in turn, causes the film to come off. These are two main factors causing the peeling-off. One is that the Fe substrate is rather soft, and another is due to the poor adhesion between the CrN coating and Fe substrate (MS). The improvement in the hardness when the oxygen is introduced into CrN on MS can be attributed to the fact that the CrON coating has good adhesion because of its compatibility in thermal expansion coefficient.²⁸



4 Topographies of a MS, b Cr/MS, c CrN/MS and d CrON/MS films



5 Scratch results of a Cr/MS, b CrN/MS and c CrON/MS

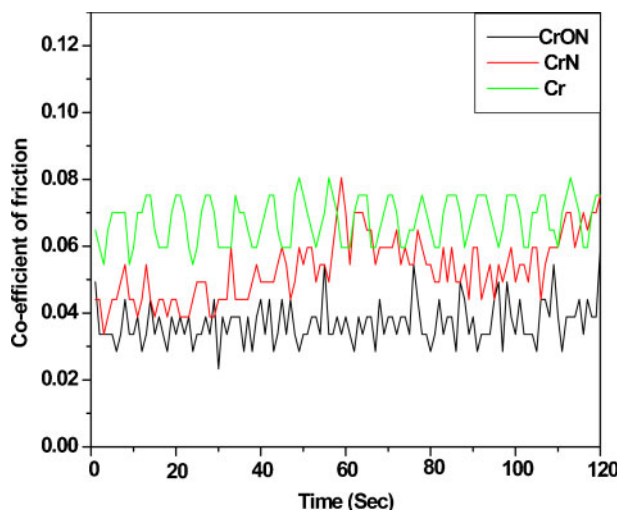
The results of scratch tests, which were carried out to determine the adhesion of the hard coating to the substrates, are shown in Fig. 5. A change in the traction force curve was observed for CrN/MS (Fig. 5b) specimen at 2.30 mm stroke length, which may be due to mild plastic deformation in the coatings. The cohesive failure, i.e. failure within the coating, occurs at 7 N critical load. An appreciable change in the traction curve at 3.5 mm stroke length occurs at 11 N critical load and the corresponding changes in the coefficient curve were observed. In addition, acoustic emission curve also significantly changes with respect to the coefficient of friction, which may be due to adhesive failure between the coating/substrate interfaces. The coated layer was found to peel off at stroke length 3.75 mm for CrON, and the cohesive failure was observed at 10 N as shown in Fig. 5c. An appreciable change in the traction force curve was observed at 5 mm stroke length and the adhesive failure also occurs. The CrON/MS stack layer was found to peel off only at the critical load of 15 N. A sufficiently high hardness of the coated layer and the substrate and the superior adhesion of the layer to the

substrate are prerequisite to the excellent wear properties of a coated material. The tribological characteristics of these films were measured using block on ring test. The ring material used for this test is high chromium high carbon tool steel (850 HV). Low and smooth friction behaviour typified by a steady trace at an average value of 0.035 friction coefficient was observed for CrON/MS stack, whereas a higher value of 0.045 was observed for the CrN/MS specimen and 0.06 for Cr/MS. The lower friction coefficient and wear rate observed in Figs. 6 and 7 for the CrN and CrON respectively indicate that the stack has better wear resistance.

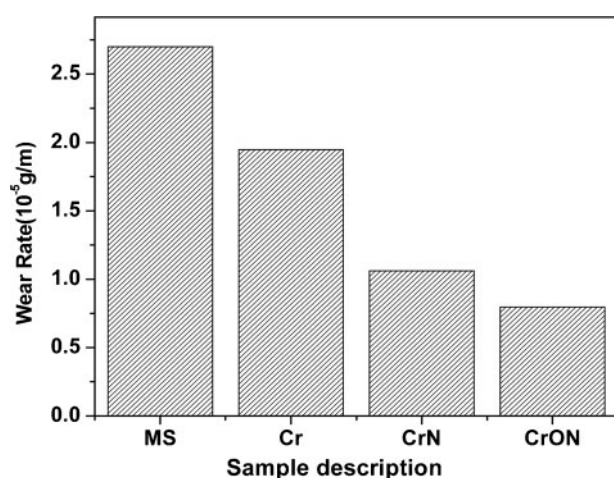
Corrosion studies

Tafel polarisation

Figure 8 shows the polarisation curves of MS, Cr/MS, CrN/MS and CrON/MS in 3.5%NaCl solution. The electrochemical parameters determined from these curves are displayed in Table 2. The corrosion potential of the Cr on MS substrate is about -0.551 V. The coated samples of CrON/MS show higher positive corrosion potential, when compared to the Cr/MS,

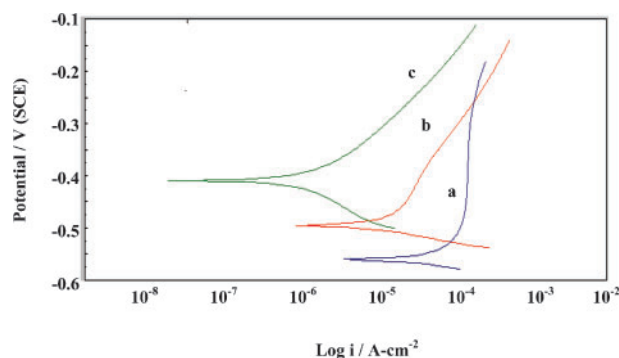


6 Variation of coefficient of friction with time for Cr/MS, CrN/MS and CrON/MS

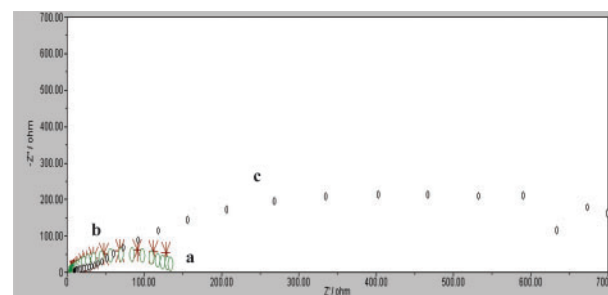


7 Wear rate of steel ring after sliding against MS, Cr/MS, CrN/MS and CrON/MS

CrN/MS. E_{corr} and I_{corr} values improve (a less negative value of E_{corr} and a lower value of I_{corr} signify an improvement in corrosion) for CrON on MS substrate. The positive shift of E_{corr} (from -0.551 to -0.407 V) indicates better corrosion resistance of all the coated samples. The corrosion rate is normally proportional to the corrosion current density. For the Cr/MS steel substrate, the corrosion current is about $0.0391 \mu\text{A cm}^{-2}$, which decreases to $0.0074 \mu\text{A cm}^{-2}$ for CrON/MS coating. Therefore, there is an appreciable increase in corrosion resistance for the CrON on MS substrate compared to CrN/MS and Cr/MS. The corrosion current is higher for the CrN/MS system in which the rapid corrosion of iron takes place at the cavities of the CrN coating owing to the combined effect of the rather noble steady state potential of the CrN



8 The potentiodynamic polarisation curves in 3.5%NaCl solution for a Cr, b CrN and c CrON



9 Nyquist plots of a Cr, b CrN and c CrON films deposited on mild steel

coating and the relatively active iron species. Consequently, the corrosion of MS is accelerated in spite of the CrN coating. However, in the CrON/MS stack, the oxide layer tends to act as a barrier which effectively retards the corrosion of iron.

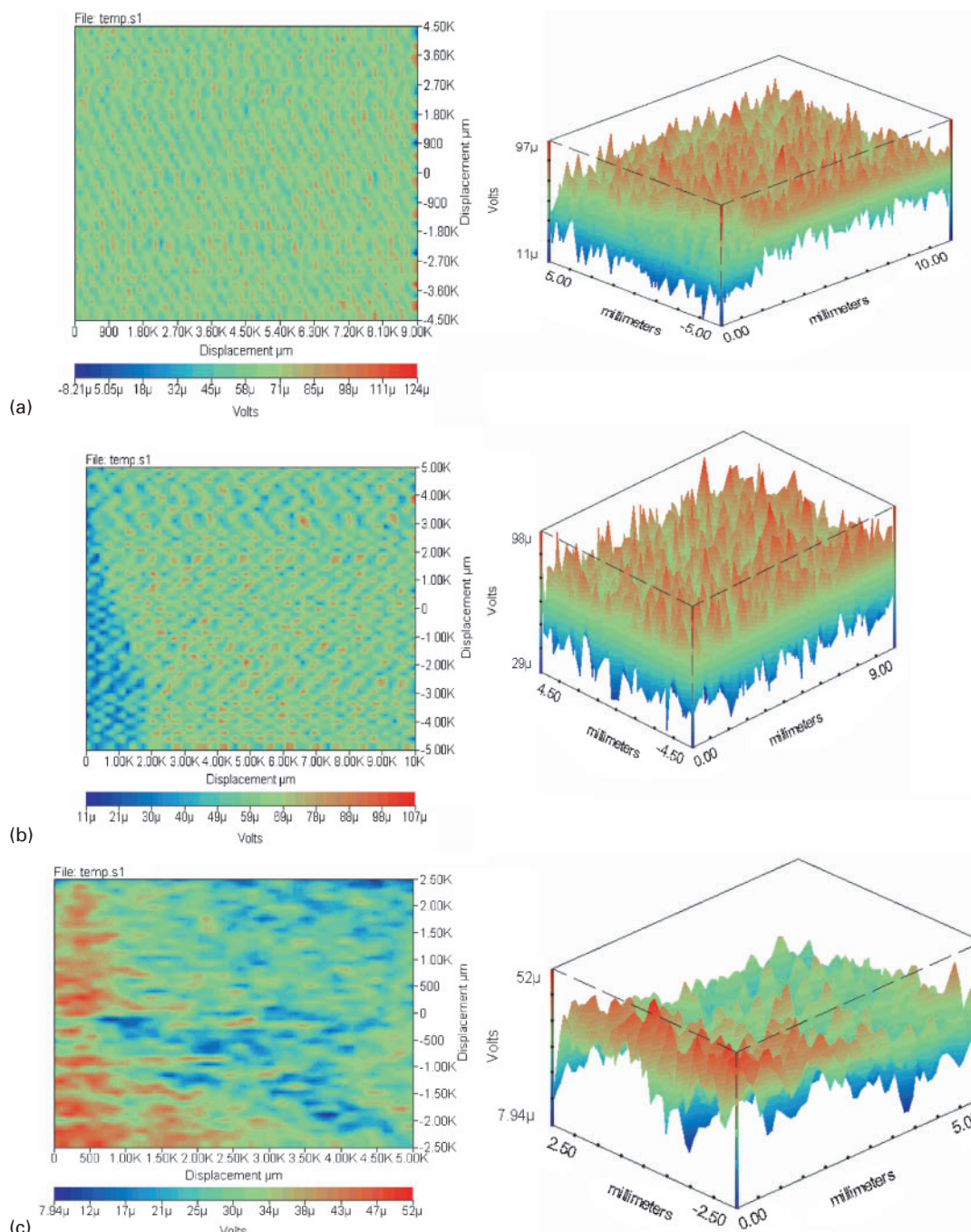
Alternating current impedance analysis

The same three-electrode cell stack, as used for the potentiodynamic polarisation experiments, was employed for the alternating current (ac) impedance investigations. Impedance measurements were made at OCP applying an ac signal 10 mV in the frequency range from 10 mHz to 1 MHz. The Nyquist plots for the samples used for corrosion tests in 3.5%NaCl solution are shown in Fig. 9. When the sample is immersed in the electrolyte, the defects in the coating provide the direct diffusion path for the corrosive media. In this process, the galvanic corrosion cells are formed and the localized corrosion dominates the corrosion process. Cr/MS < CrN/MS < CrON/MS, which shows that CrON coating on steel substrate has higher corrosion resistance.

CrON/MS stack confirms the better corrosion resistance of these systems compared to CrN/MS and Cr/MS substrates. A more semicircular region in the case of the CrON/MS stack indicates that this system has maximum corrosion resistance, as observed from the high frequency region of the impedance spectra.

Table 2 Potentiodynamic polarisation and EIS data

Sample	$E_{\text{corr}}(\text{SCE}), \text{V}$	$b_a, \times 10^{-3} \text{ V dec}^{-1}$	$b_c, \times 10^{-3} \text{ V dec}^{-1}$	$I_{\text{corr}}, \times 10^{-6} \text{ A cm}^{-2}$	$R_{\text{ct}}, \Omega \text{ cm}^2$	$C_{\text{dl}}, \times 10^{-6} \text{ F cm}^{-2}$	Corrosion rate, $\times 10^{-9} \text{ m/year}$
Cr/MS	-0.551	22	148	0.0391	175	0.219	17.87
CrN/MS	-0.491	30	194	0.0129	235	0.163	5.89
CrON/MS	-0.407	86	103	7.475	780	0.090	3.41



10 Two- and three-dimensional potential gradient maps for *a* MS, *b* CrN/MS and *c* CrON/MS obtained from SVET

Analysis using scanning vibrating electrode technique

Minute variations in dc current scanning vibrating electrode technique (SVET) have been developed to allow high spatial resolution investigation or voltage associated with localized corrosion activity which is detected and used to map both anodic and cathodic corrosion activities in a localized area. The difference in initial corrosion activity under various films can be correlated to the performance life of the films. In the current study, the SVET was used to discriminate the corrosion protection performance of selected coated systems. The potential gradients E caused by current flowing between the local anode and local cathode on coated steel samples were mapped and measured at 64 points within an area of $5000 \mu\text{m}^2$. The E is developed around the corroded metal surface due to the ionic current between the local anodic

and cathodic areas. The distribution of E leads to an evaluation of the corrosion behaviour of the metal in terms of current density. The degree of growth of the corrosion can be evaluated by the difference of potential gradient ΔE : $\Delta E = E_a - E_c$, where E_a is the mean value of the three highest E values at cut part and E_c is the mean value of E values at the local cathode part.

The two- and three-dimensional maps of potential gradients E by SVET of MS and CrN/MS and CrON/MS specimen in aqueous solution of 3.5% NaCl after immersion for 1 h are shown in Fig. 10. Scanning vibrating electrode technique was able to discretely map relative cathodic (blue in colour) and relative anodic sites (red in colour) as seen from Fig. 10 at a macroscopic defect and to record the changes of local electrode activities in a real time. The E is developed

around the corroded metal surface due to the ionic current between the local anodic and cathodic areas. The distribution of E leads to an evaluation of the corrosion behaviour of the metal in terms of current density. By summing the anodic and cathodic potentials measured using SVET for each scan, a quantitative comparison was made and shown in Fig. 10. The E increased in the following order: CrON/MS < CrN/MS < MS. The results exhibit that CrON has good corrosion resistance.

Conclusion

Chromium nitride thin film was successfully grown by reactive dc magnetron sputtering onto MS substrates. The coating was found to be polycrystalline in nature from XRD studies, with face centred cubic structure. The observed d values from the XRD pattern were found to be in good agreement with the standard d values. A dense rectangular cellular structure was observed from AFM analysis. The corrosion current is high for the CrN/MS system in which the rapid corrosion of iron takes place at the cavities of the CrN coating owing to the combined effect of the rather noble steady state potential of the CrN coating and the relatively active iron species. Lower E value was observed for CrON/MS than for CrN/MS and bare substrate. The results exhibit that CrON has better corrosion resistance.

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