

Structure and properties of Cr_xN coating

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Abstract

In the present study, an attempt has been made to produce a coating of mixed nitride (CrN and Cr₂N) of ultrafine size on a low alloy high carbon steel by a two-stage hybrid process comprising electro-deposition of Cr (45-85 μm) followed by gas nitriding in controlled atmosphere (using a gas mixture of NH₃ : Ar = 1:3) in the temperature range 750–950 °C for 2–6 h. The nitrided surface records extremely high hardness (≈ 19 GPa), enhanced wear resistance and residual compressive stress. Potentiodynamic polarization test in a 3.56 wt.% NaCl solution shows an improvement in corrosion resistance due to formation of noble nitride. However, presence of brittle nitride phases and related surface roughness seems to deteriorate both tribological and corrosion properties.

Keywords: Plating, nitriding, wear, corrosion, steel

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INTRODUCTION

Ultrafine nitride coating with very high hardness and elastic/shear modulus may be ideal for tribological (wear resistant or low friction) and similar load bearing applications.¹ Formation of surface nitrides on surface may be achieved by advanced techniques (example: microwave plasma coating, magnetron sputtering, laser nitriding, ion implantation, *etc.*²⁻⁴). On the other hand, conventional surface engineering techniques like gas and plasma nitriding are effective to develop thick nitride coating on steel and significantly enhance hardness and wear resistance.⁵ Hard chromium coating by electro-deposition is another common surface engineering approach widely practiced in many engineering industries due to the high hardness and excellent corrosion resistance associated with this Cr-coating at room temperature.⁶ All metals are not amenable to nitriding. However, such metals can be subjected to a hybrid coating by first electro-depositing a suitable metal prone to forming nitrides (e.g. Fe, Cr, W) followed by nitriding to develop a monolithic or dispersed nitride layer. The resultant surface can induce high wear resistance and low friction to a softer substrate independent of the composition and mechanical properties of the latter. Though chromium coating can itself be hard, nitriding of electrodeposited chromium can improve the hardness and tribological property of the surface further.

In the present study, an attempt has been made to develop ultrafine hard chromium nitride layer on a low-alloy high-carbon steel substrate by conventional electrodeposition of 45–85 μm thick chromium layer on steel followed by gas nitriding. Subsequently, the nitrided samples were subjected to a detailed characterization of surface microstructure (phase identity, morphology and distribution), composition, topography, mechanical and electrochemical properties. The main objective of the study is to develop a new and easy to work out type of hybrid coating that will ensure improvement in both wear and corrosion resistance of the underlying steel substrate.

EXPERIMENTAL

Specimens with approximate dimensions of 10 mm x 10 mm x 4 mm were cut from annealed AISI 52100 steel bar with nominal composition of 1.05% C; 0.15% Si; 0.3% Mn; 1.51 % Cr; and balance

Fe (in wt.%). This low alloy high carbon steel used for various structural applications (other than bearing) is used here as a model system. The samples were metallographically polished and electroplated with chromium layer to a thickness between 45 to 60 μm using a plating bath consisting of chromic acid (250 g l⁻¹) and sulfuric acid (2.5 g l⁻¹). Electroplating was carried out at a current density of 7 mA mm⁻², plating time of 100 min and temperature of 45 °C.

The electroplated steel samples were gas nitrided in an indigenously developed controlled atmosphere furnace fitted with a set of mass flow controllers to maintain a steady flow of NH₃ + Ar. The system was evacuated to 1 x 10⁻³ mbar pressure before nitriding and purged with high purity and dehumidified argon three times to minimise the oxygen partial pressure in the chamber. NH₃:Ar (in a volume ratio of 1:3) was circulated at a constant rate of 60 ml min⁻¹ at a pressure of 1000 mbar. Gas nitriding was carried out at the isothermal temperatures of 750, 850 and 950 °C (using a heating rate of 10 °C min⁻¹) for three different time periods (2, 4 and 6 hours).

After nitriding, the phase aggregate at the near surface region was analyzed by Bragg-Brentano (θ -2 θ) X-ray diffraction (XRD) and glancing incidence XRD (GIXRD) configuration using Cu K α (λ = 0.15406 nm) radiation in a Philips PW 1710 diffractometer. Quantitative analysis of different phases formed were calculated from integrated intensity of x-ray peaks using normalized relative (integrated) intensity ratio (RIR) method or matrix flushing model.⁷ If X_α is the concentration of α phase, $I_{(hkl)\alpha}$ is the integrated intensity of (hkl) plane of α phase (obtained from XRD or GIXRD profile), RIR_α is the relative intensity ratio compared to corundum of α phase mentioned in JCPDS database, $I_{(hkl)a}^{rel}$ is the relative intensity of α phase mentioned in JCPDS database. Then the concentration or wt. % of the α phase is:

$$X_\alpha = \frac{I_{(hkl)\alpha}}{RIR_\alpha I_{(hkl)\alpha}^{rel}} \left[\frac{1}{\sum_{j=1}^n (I_{(hkl)j} / RIR_j I_{(hkl)j}^{rel})} \right]$$

Surface residual stress was measured by $\sin^2\psi$ method using a stress Goniometer attached to the XRD unit.^{8,9}

Microstructures of nitrided surface and along the cross section were examined using optical microscope, scanning electron microscope (SEM) (JEOL JSM-5800 with Oxford EDS Detector) and field emission gun assisted scanning electron microscope (FESEM) (ZEISS: SUPRA 40). While microstructural investigation of the nitrided surfaces was carried out in as-nitrided condition (without etching), the cross sectional plane (perpendicular to the nitrided surface) was polished and etched with aqua-regia ($\text{HNO}_3\text{:HCl} = 1\text{:}3$) before investigation. Surface topography of selected samples was studied using atomic force microscope (AFM) in the tapping mode of scanning to evaluate the surface roughness and topography.

Microhardness readings were taken on the surface as well as along the cross sectional plane using a Vickers hardness indenter with 50 g load (0.49 N) in a LECO LM700 system. Each hardness value reported is an average of 4-5 measurements at equivalent locations.

Tribological property including sliding wear resistance of the as received and nitrided samples was evaluated using a ball on disc type wear testing instrument (DUCOM TR-208-M1) having a diamond cone indenter as per Rockwell C geometry. Tests were carried out with an applied load of 4 kg and 1.6 mm s^{-1} linear sliding speed (sliding track diameter 2 mm with 15 rpm speed). Surface damage caused by wear testing was subsequently studied by SEM.

The electrochemical characterization was carried out by potentiodynamic polarization test using a Potentiostat/Galvanostat connected to a standard three electrode cell comprising the sample as the working electrode, a saturated calomel reference electrode and a platinum counter electrode. The electrolyte used was 3.56 wt. % NaCl solution. The post corroded samples were subjected to microstructural evolution by SEM to reveal the severity of corrosion damage.

RESULTS AND DISCUSSION

XRD analysis

Phase evolution by nitriding was characterised by XRD analysis. Fig. 1(a) shows the XRD profiles of the electrodeposited surface and that of deposition followed by gas nitriding at 850°C for 6 h. Cr

coating shows BCC Cr peaks, whereas the treated sample exhibits a number of peaks due to different nitrides of Cr (both CrN and Cr₂N). A detailed GIXRD results shows change in relative intensity of the CrN and Cr₂N peaks from the surface towards the substrate. Further elaborate XRD study on phase identification and analysis was reported in one of our earlier work with the same material subjected to identical surface engineering routine.¹⁰

Fig. 1(b) shows the variation of the amount (wt.%) of chromium nitrides (both CrN and Cr₂N) phases obtained from GIXRD analysis as a function of nitriding temperature at different depth of the samples treated for 4 hours. For quantitative analysis of CrN and Cr₂N phases JCPDS files used are 76-2494 and 79-2159 respectively. It may be noted that the amount (wt.%) of CrN phase decreases with increase in nitriding temperature in general at a given glancing angle or depth of the sample. CrN content in the coated region was found to decrease with increase in depth. On the other hand, the amount (wt.%) of Cr₂N phase increases with increase in temperature of nitriding at a given depth and increase in depth for a particular nitriding temperature. Samples nitrided for 6 hours also showed the same trend. The presence of a large mass fraction of chromium nitride (CrN) at the surface is attributed to availability of more nitrogen at the near surface region. On the other hand, the greater amount of Cr₂N (than CrN) below the top surface is due to reduced level of nitrogen in the interior below the surface than the nitrogen-potential in contact with the free surface. Similarly, increased amount of Cr₂N with increasing temperature is due to the increased stability of such nitrides at higher temperature.^{5,11}

Microstructure

Fig. 2 shows the FESEM image of the top surface of the Cr coated steel sample obtained after nitriding at 850 °C for 4 hours. After nitriding the luster of Cr coating turns dark grey and surface develops noticeable roughness. The surface microstructure consists of ultrafine nitrides and it may be pointed out that along with inherent hard nature of the nitrides the ultrafine morphology of the nitrides may have contributed to high toughness value due to Hall-Petch effect.¹²

Fig. 3 shows the SEM image of the cross-sectional surface of chromium deposited steel substrate. The coating thickness was, however, found uniform all throughout. A careful observation of the cross section reveals the presence of very fine micro-cracks originating from the interface towards the surface (Fig. 3(a)) in some samples. The presence of micro-cracks at the surface may be due to residual stress or due to entrapment of hydrogen during electro-deposition, as reported earlier.¹³ Fig. 3(b) shows the SEM image of the cross section of the sample nitrided at 850 °C for 4 hours. It shows that the cracks get closed during nitriding due to the new phase or layer preferentially forming at the crevice/crack. Similar features were also noted in samples nitrided at other temperatures. It clearly shows closure of cracks after nitriding and the presence of such nitride at the crack tip is beneficial for closer of the cracks in the as-deposited Cr layer. Mixed nitrided layer followed by unreacted Cr coated layer are clear visible in the cross sectional view from surface towards substrate, though CrN and Cr₂N cannot be distinguished as it was a graded mixture of CrN and Cr₂N as observed by XRD study.

Microhardness and wear study

Microhardness of the surface and cross section of the coating was evaluated in details and the average of five maximum values obtained from each treated sample was recorded. The maximum hardness thus observed in the nitride layer was around 19 GPa (950 °C, 6 hours). Table 1 summarises the maximum microhardness achieved in as-received, chromium deposited and nitrided surface after chromium deposition. From Table 1 it is apparent that hardness of nitrided surface increases with increase in nitriding temperature and this may be due to the formation of harder type of nitride (Cr₂N) in greater volume fraction and thickness at higher temperature.

Fig. 4 shows the variation of cumulative wear loss (in terms of vertical penetration of the indenter or depth of wear) as a function of sliding distance at an applied load of 4 kg and 1.6 mm s⁻¹ sliding speed after nitriding at 750, 850 and 950 °C for 6 h along with that of untreated steel, Cr-coating and stress relieved Cr-coating (to judge the stress relieved coating 1 h heating was done at

700°C). It can be observed that both deposition and nitriding followed by deposition leads to improved wear resistance as compared to as-received substrate. From Fig. 4, it is also observed that wear resistance deteriorates after gas nitriding as compared to that in the Cr-coated sample. After nitriding of the Cr-coated steel, both the trend in wear behavior and hardness was reversed. Hence, it may be concluded that though Cr-nitrides were superior to Cr-coating in terms of hardness, due to the presence of brittle nitrides, wear resistance property was deteriorated. For a similar reason, wear resistance was found to decrease with increase in nitriding temperature, which is possibly due to increased volume fraction of brittle phase (Cr_2N). Similar fact was reported by Bertrand *et al.* during formation of Cr-nitrides by magnetron sputtering.¹⁴ Deterioration in wear resistance can be caused by another reason as mentioned below.

A detailed study of surface roughness shows that the roughness of the nitrided surface increases with increase in nitriding temperature (Table 1). Increase in roughness results in higher friction coefficient and consequently greater wear loss after nitriding at higher nitriding temperature as it is known that surface topology or roughness influences the type and rate of wear.¹⁵ However, such increase in surface roughness may prove benign as nitride phases having higher hardness and elastic modulus than that of substrate may reduce friction coefficient or wear unless the hard nitrides suffer ploughing (or dislodging from the matrix). But, here the wear mechanism might have changed from adhesive to abrasive regime with increase in nitriding temperature. Formation of increased volume fraction of nitrides at higher temperature thus proves detrimental to wear resistance. Fig. 5 shows the scanning electron micrograph of the worn tracks on Cr layer before and after nitriding (at 950 °C for 6 h) formed by ball on disc wear tests with 4 kg load. It can be observed that wear tracks on Cr coated surface was smaller in width (Fig. 5(a)) compared to that after nitriding (Fig. 5(b)). As a result, the amount of wear debris produced by wear tests is also more in case of nitride samples. Thus, higher roughness and brittleness of nitrides are responsible for deterioration of wear property in nitrided samples in this study.

Residual stress measurement

Fig. 6 shows the variation of residual stress developed on the nitrided surface with nitriding time and temperature. It was observed that for a particular nitriding time, the residual stress value decreases with increase in nitriding temperature. It was also observed that for a particular nitriding temperature the residual stress value decreases with increase in nitriding time. Compressive residual stress at the surface was noticed when the samples were nitrided at a higher nitriding temperatures or for a prolonged time. It was mentioned earlier that the surface contains primarily CrN phase. Formation of CrN from Cr₂N brings change in the surface residual stress level due to change in crystal structure. Residual stress is governed by coating growth process and thermal expansion/contraction mismatch. Here the last one plays big role as stress level change is more at higher temperature of processing. It is also worth mentioning that as lattice parameter of nitrides are always higher than that of the parent metal, nitride formation on outer surface produces compressive type of stress. It was also observed that the stress condition caused by the formation of CrN at a higher temperature is more compressive in nature which was earlier observed by Budna *et al.*¹⁶

Corrosion study

The nitrided samples and as deposited samples along with the substrate were subjected to potentiodynamic polarization tests in a 3.56 wt. % NaCl solution to study the mechanism and rate of anodic dissolution. The corresponding polarization diagrams for the as-received vis-à-vis coated surface (both chromium deposited and nitrided followed by chromium deposition at different parameters) are presented in Fig. 7. Table 1 summarises the corrosion parameters of the as-received and coated surface. From Table 1 it may be pointed out that in as-electro-deposited surface, the corrosion resistance increases in terms of increase in corrosion potential (E_{cor}) and decrease in corrosion rate (Table 1). As Cr is nobler than ferritic steel, Cr coating is widely adopted for corrosion resistance application. Furthermore, it is also observed that after nitriding, corrosion

resistance increases further and the sample nitrided at lower temperature, offers a superior corrosion resistance property. It is observed that with decrease in nitriding temperature, the corrosion potential (E_{cor}) increases whereas the corrosion rate decreases (Table 1), which means that nitriding at lower temperature is more likely to increase the corrosion resistance.

Though Cr plating increases corrosion resistance, nitriding increases the corrosion resistance further due to its chemical inertness. Furthermore, it is relevant to mention that Cr_2N is nobler than CrN in NaCl solution.¹⁷ In this study it was observed that samples nitrided at lower temperature show a marginal superior corrosion resistance property as compared to the same nitrided at high temperature, which is attributed to the formation of CrN- Cr_2N galvanic cell due to the presence of Cr_2N on the surface along with CrN as compared to only CrN when nitrided at low temperature. Samples nitride at 750 °C shows only CrN at surface (Fig. 1(b)) resulting in the best corrosion resistance compared to mixed nitride formation at higher temperature resulting in galvanic cell formation.

Fig. 8(a) shows post corrosion SEM image of gas nitrided chromium coated steel, nitrided at 850 °C for 4 hours. It can be observed that there no such specific attack on crack position is evident, which may be due to the presence of residual compressive stress developed during nitriding (Fig. 6). Fig. 8(b) shows post corrosion cross sectional SEM image of the same sample and it reveals that there is no crack opening due to corrosion attack. Hence, these evidences strongly suggest that that such gas nitrided and Cr coated layer can be used for applications where corrosion resistance, apart from wear resistance is of interest for specific application or environment.

CONCLUSION

In the present study, an attempt has been made to develop a hybrid layer comprising mixed chromium nitrides dispersed in prior deposited chromium layer on a low alloy high carbon steel by electro-deposition of Cr followed by gas nitriding using a NH_3+Ar (1:3) gas mixture in temperature range 750 – 950 °C. The following conclusions may be drawn from the present investigation:

- (i) The microstructure at the near-surface region primarily consists of a mixture of CrN and Cr₂N and the volume fraction of CrN decreases with depth from surface.
- (ii) Though hardness was significantly improved after nitriding, wear resistance of as-deposited chromium coating is better than that of both the steel substrate before and after gas nitriding. In particular, wear resistance decreases with increase in nitriding temperature due to increased surface roughness and brittle nitride (Cr₂N) formation.
- (iii) With increase in nitriding time and temperature the residual tensile stress at nitrided surface decreases and ultimately enters the compressive regime.
- (iv) Though Cr plating itself increases corrosion resistance, nitriding further increases the corrosion resistance due to the chemical inertness of nitride phases.

Thus, the present routine of electrodeposition followed by gas nitriding appears a suitable approach for developing a hybrid coating that can ensure improvement in hardness and in resistance to corrosion and can be used for application like boiling acid storage.

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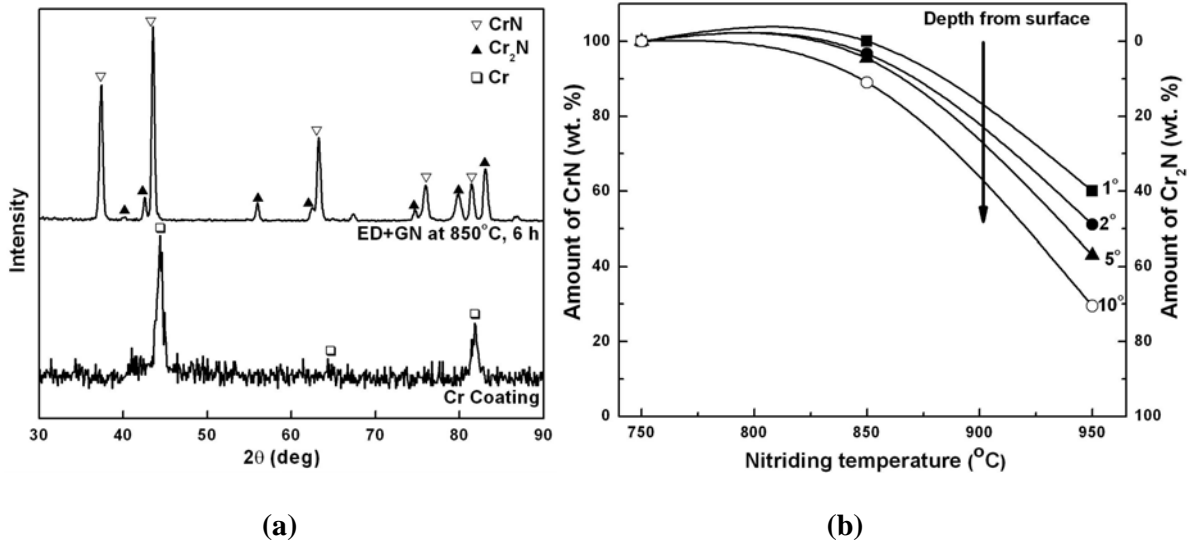
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Table

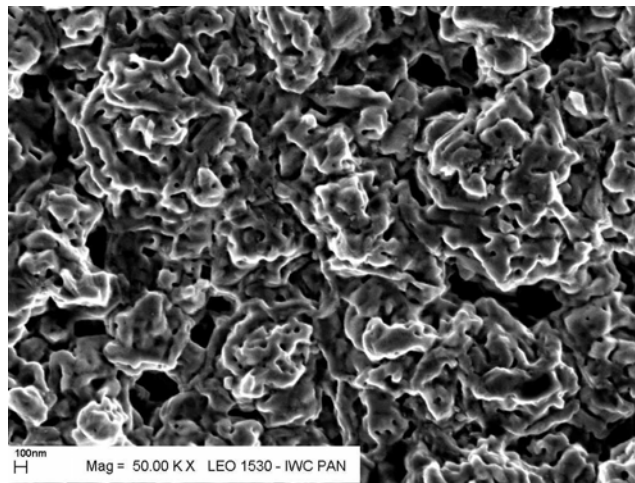
Table 1. Surface mechanical and electro-chemical properties of nitrided samples

Samples (temperature and time)	Hardness (GPa)	Roughness R_a (nm)	E_{cor} (mV)	Corrosion rate (mm year ⁻¹)($\times 10^{-3}$)
Substrate	2.6	30 (polished)	-765	550.2
Untreated Cr	3.9	40	-255	1.569
Nitrided at 950 °C for 4 h	19.4	148	-26	1.536
Nitrided at 850 °C for 4 h	18.7	111	52	0.663
Nitrided at 750 °C for 4 h	12.3	41	126	0.612

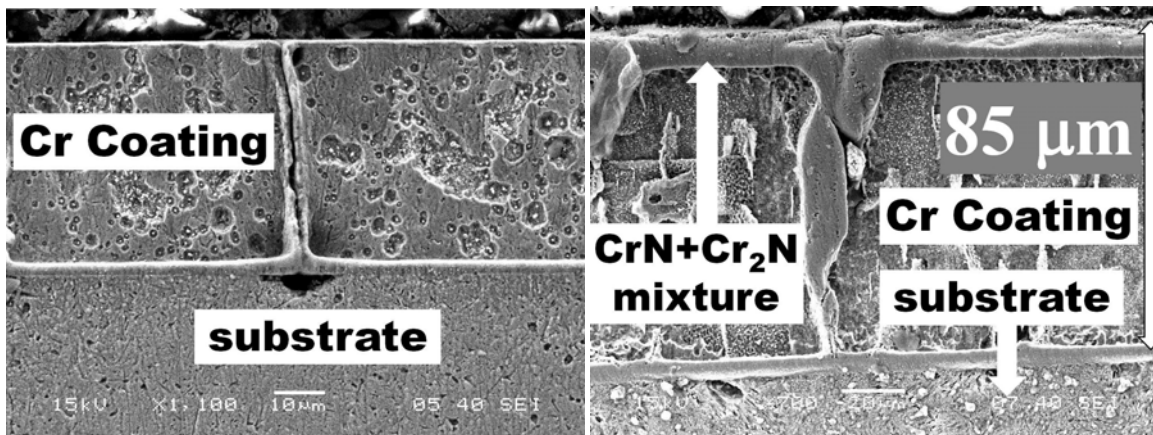
Figures



- (a) XRD profiles of chromium coating and the same after gas nitriding at 850 °C for 6 h.
- (b) Variation of volume fraction of CrN and Cr₂N at different depths of the samples with nitriding time of 4 hours at different temperatures (at 1, 2, 5 and 10° glancing angle).



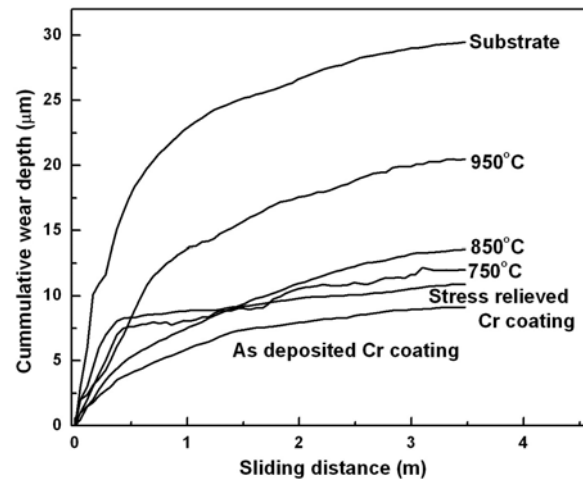
2 FESEM micrograph of gas nitrided sample surface, treated at 850 °C for 4 h



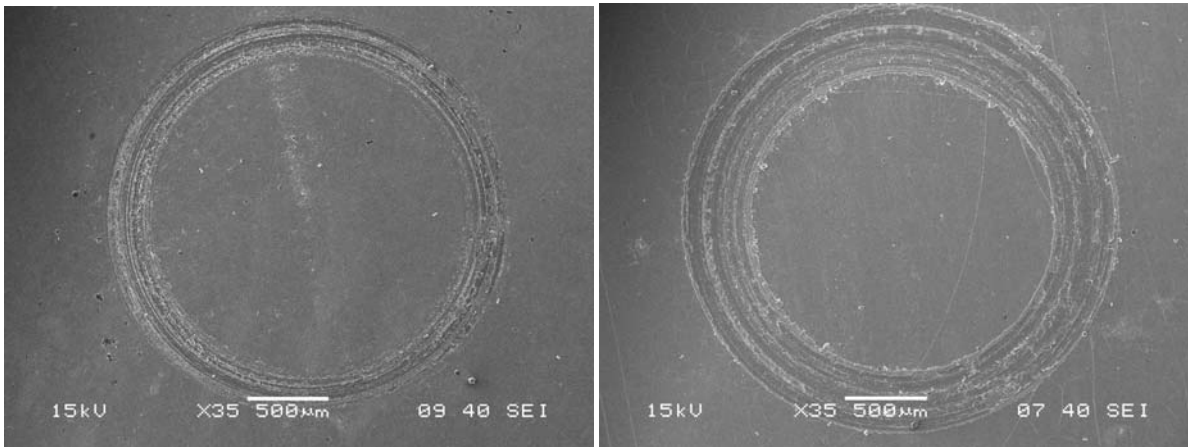
(a)

(b)

3 SEM micrograph of cross-sectional surface after (a) chromium coating, (b) after chromium coating and gas nitriding at 850 °C for 4 h.



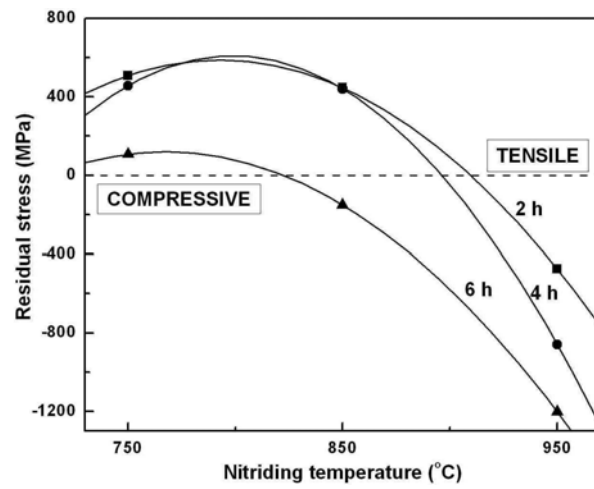
- 4 Wear test results of gas nitrided samples nitrided for 6 h at different nitriding temperatures and compared with electrodeposited Chromium and stress relieved Cr coating.



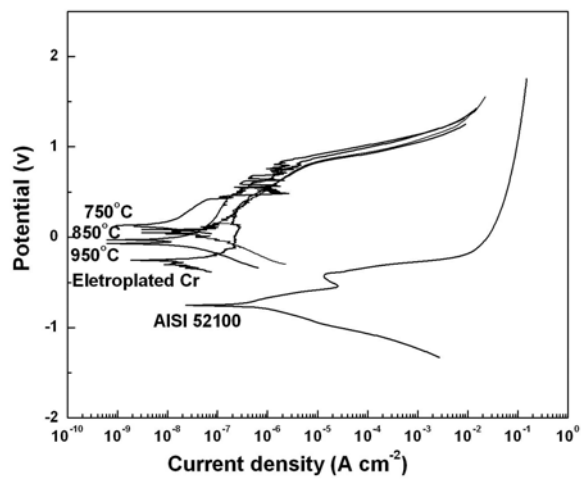
(a)

(b)

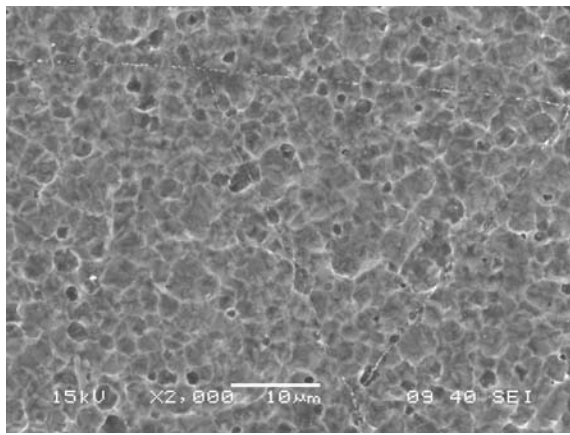
- 5 Scanning electron micrograph of the wear track of (a) Cr coating, (b) Cr layer nitrided at 950 °C for 6 h.



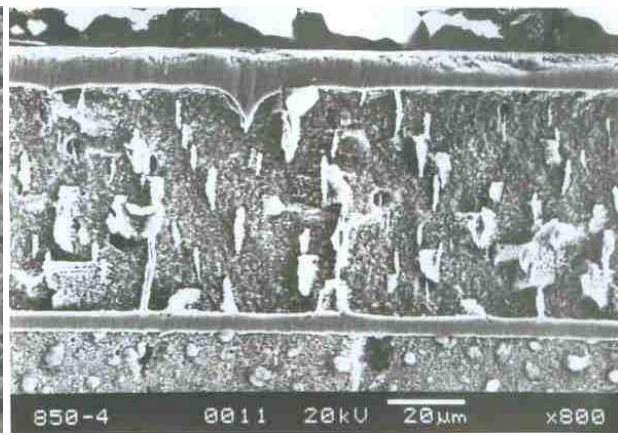
6 Variation of stress level at nitrided surface of chromium coated steel with nitriding time and temperatures.



7 Potentiodynamic polarization behavior after gas nitriding of chromium coated steel, nitrided for 4 h at different nitriding temperatures and compared with electrodeposited chromium and bare substrate.



(a)



(b)

- 8 (a) Post corrosion SEM micrograph of gas nitrided chromium coated steel, nitrided at 850 °C for 4 h. (b) Post corrosion cross sectional SEM micrograph of the same sample.