ORIGINAL ARTICLE

Plasma Nitriding of CrMoV Steel for the Enhancement of Hardness and Corrosion Resistance

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Abstract In the plasma ionic environment of nitrogen and hydrogen at 4:1 ratio, nitriding had been realized in the plasma laboratory. Nitriding of steel samples was followed at the lower temperature of 450 °C and also at the higher temperature of 550 °C while the sample was biased at the fixed − 250 V. Steel nitrided at 550 °C had shown a significantly enhanced resistance to corrosion in comparison to that of steel nitrided at 450 °C. X-ray diffraction studies of nitrided steels had shown the presence of nitrides of iron (FexN). Scanning electron microscopic and the electron dispersive spectroscopic analyses (SEM + EDS) of the cross section of the nitrided steels had shown the nitrided layer and the elemental distribution from top to the core. Following structural analysis, microhardness and the potentiodynamic polarization tests were performed. A significant improvement in hardness ($\sim$ 1180 Hv) and the case depth $\sim$ 150 μm was obtained after nitriding at the higher temperature. Corrosion resistance was also found to be significantly improved. These achievements might be attributed to the presence of FexN, CrN phases and also to the nitrogen solid solution.

Keywords Corrosion · Polarization · Surface hardness · Microstructure · Steel · X-ray diffraction

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1 Introduction

High nitrogen alloys as the new class of materials had been the interest of the researchers and industrial sectors for its novel properties [1–10]. Like carbon in Fe–C alloys, nitrogen is also a good candidate for achieving the similar properties as shown by carbon. This is how it can cutoff the carbon content in the Fe–C alloy and give rise to Fe–N alloys and thus satisfy the present day's need of human survival in the less carbon environment [11]. N is the next to C in the periodic table with atomic number 7 and 6, respectively. Its atomic radii are also very near to carbon atom and both are forming interstitial solid solutions. The phase diagrams of Fe–N and Fe–C show the similar characteristics at eutectoid transformation point and show the stability of some phases viz. ferrite, pearlite, austenite and martensite [11]. It has been realized that the Fe–N alloys have significant improvement in corrosion resistance and mechanical properties. As compared to carbon inclusion, the nitrogen inclusion in the solid solution is found to be more advantageous, i.e., the interstitial solubility of N in ferrite is $\sim$ 0.1 wt% and $\sim$ 2.8 wt% in austenite leading to the greater effects on solid solution strengthening of ferrite and the austenite stability. On the other hand, a lower eutectoid temperature of 592 °C significantly saves the cost of the heat treatment [12–15].

Nitrogen as alloying element has the significant role in improving the corrosion resistance of steels such as austenitic stainless steel, duplex stainless steels [16–20]. Nitrogen in stainless steel enhances the resistance to pitting corrosion for which the following established equation is well known in terms of Pitting Resistance Equivalent Number – PREN given as follows: PREN = %Cr + 3.3 × % Mo + 16 × % N.

From mechanistic point of view N improves corrosion resistance by the formation of ammonia, anodic segregation, promoting Cr enrichment in the corrosion resisting passive film, synergistically affecting with the Cr and Mo, formation of iron nitrides with inherent property to resist corrosion and chloride repulsion theory and decreasing the point defects density [19, 21–26]. Nitrogen had been successfully incorporated in various steels by following nitriding process with the view to improve the mechanical and corrosion resistance properties. However, less is known about the effect on corrosion resistance of N incorporated martensitic stainless steel. The nitrogen solubility at atmospheric condition is too low to improve the resistance to corrosion. It may be expected that incorporation of nitrogen by ion nitriding process increases the N content in the solid solution. In this regard, plasma-assisted nitriding had been recognized as a successful method for including nitrogen in the metallic materials like steel, titanium etc. [27–36]. Though, plasma nitriding has been successfully applied for the various steels but a fewer studies have so far been made on the plasma nitriding of wood machining medium carbon martenstic stainless steel [27, 29, 33]. The surface of the tool made of this steel encounters commonly the frictional forces, and frequent jerks from the obstacles like knots inside the wood which exert high impact load, electrochemical wood juice oozing out during the wood machining from the body of the wood, and also other chemical agencies when exposed to the environment. To combat these problems causing mechanical and electrochemical degradation, surface modification of the materials is necessitated.

Hard coatings following physical or chemical vapor deposition is commonly practiced to solve the problem but the delamination of the deposited layer limits its widespread applications and reduces the longevity of the service life of the tool. Nitriding can overcome these problems by improving the surface hardness and the bringing the microstructural changes viz. dispersion of corrosion resistant and hard phases of nitrides. By inducing the compressive stress on the surface after nitriding the fatigue property can also be enhanced. The conventional nitriding offers only limited process control and is neither cost-effective nor eco-friendly. Long duration of nitriding to achieve the desirable thickness of the nitrided layer is not cost effective. In this regard, plasma nitriding had been recognized as more effective with several advantages viz. the cost-effectiveness, variable process control to achieve the desirable phases and the modified layer thickness within the short duration of the treatment time.

Nouveau et al. [27] improved the hardness of this steel and later Rao et al. [29, 33] studied the effects on corrosion resistance after plasma nitriding. The present study is concerned with the effects of high temperature nitriding on this steel. The corrosion resistance after nitriding has been the focus of this study.

2 Experimental Procedure

Medium carbon steel coupons (present steel) of $15 \times 10 \times 5$ mm^3 dimensions were cut from a bigger sheet of the steel after performing the heat treatment. The compositional analyses of the steel are summarized in Table 1 as shown below:

These sample coupons after metallographic polishing were cleaned ultrasonically in acetone to degrease and remove the deposited dirt or contaminants. The sample coupons so prepared were kept in the vacuum vessel of the plasma nitriding reactor and then evacuated by using the rotary and the diffusion pump coupling to a pressure 0.06×10^{-2} mbar. Sample coupons through the sample holder were connected to the power supply. The power supply was used to bias the sample negatively at 250 V which was required to accelerate the positively charged ions of nitrogen and hydrogen present in the plasma toward the surface of the sample. The nitriding parameters are summarized in Table 2 as below:

Ar gas was then fed into the vacuum chamber until the working pressure of ~ 0.5 mbar achieved.

Following this, the plasma was triggered and bombarded on the steel surface until the desired temperature for nitriding was achieved. Ar + ions sputterred cleaned the native oxide/dirt on the surface of the steel samples. Once the desired temperature was achieved, the ion bombardment stopped and nitriding cycle initiated after feeding the nitrogen and hydrogen gas mixture (at 4:1 ratio).

Nitriding was performed at a lower temperature of 450 °C and also at the higher temperature of 550 °C with the variation in the duration of the process. Temperature was monitored carefully to maintain the fluctuation within the range of ± 5.0 °C. After the nitriding cycle, the process was stopped and the sample coupons were allowed to cool in the chamber environment. It was cooled in the nitrogen and hydrogen gas environment to avoid the risk of oxidation. After cooling, gas feeding was stopped and the vacuum pumps were switched off and finally sample coupons were taken out of the vacuum chamber.

The visual inspection of the nitrided samples by unaided eyes has shown the difference in the reflection of surface. The surface of the bare steel (A) in Fig. 1 appears bright but after nitriding turns grayish as shown in Fig. 1b which is the typical color of the nitrided steel.

Both the bare and the nitrided steel coupons were the exposed to X-ray diffraction (XRD- XRD INEL CPS 120 diffractometer θ/2θ configuration) and scanning electron microscopic analyses (SEM) to reveal the microstructure of

Table 1 Compositional analyses of the various constituents of the steel in the present studies

Elements	Cr	C	Mn	V	Si	Mo	Fe
wt%	8.0	0.5	0.5	0.5	1	1.5	Bal

Table 2 Nitriding parameters

Steel	Temp. (°C)	Time (hrs.)	Initial pr. (mbar)	Working pr. (mbar)	Bias voltage (V)	N$_2$:H$_2$
CrMoV	450;550	10	0.06×10^{-2}	~ 0.5	$- 250$	4:1

Fig. 1 Surface appearance of the bare steel A and the nitrided steel B
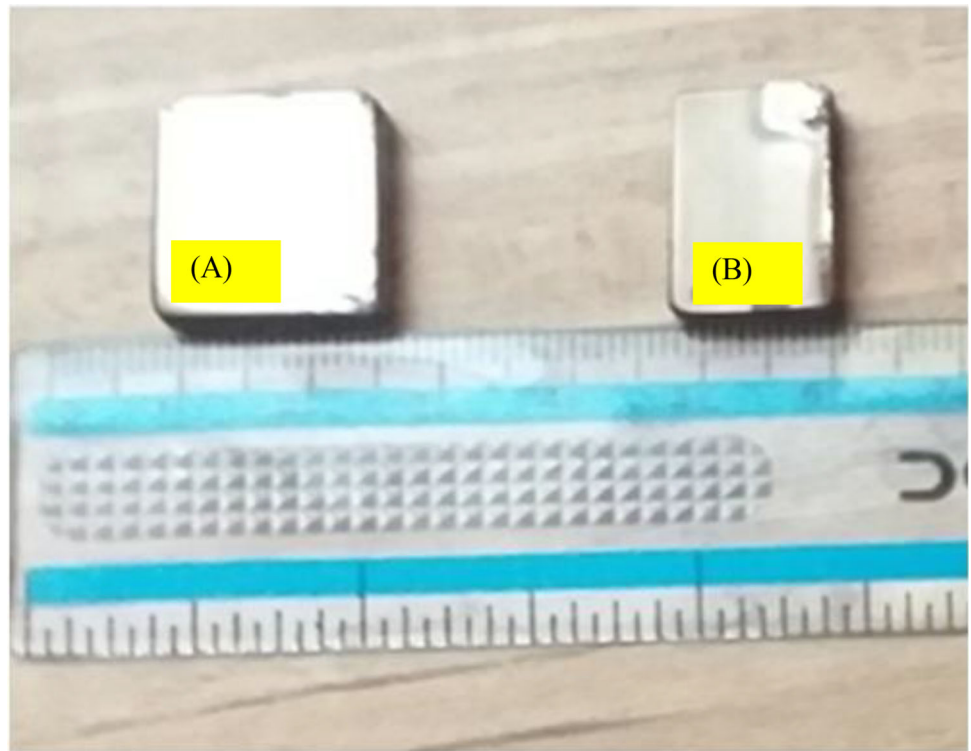
the nitrided steels. XRD was utilized for the phase evolution by using Co-$k\alpha$ radiation source (0.17902 nm). The cross-sectional analyses after metallographic polishing and etching with the Villela's reagent had been carried out under scanning electron microscope coupled with the energy dispersive spectroscopic analyses (SEM-Jeol, JSM5900).

To understand the mechanical properties bare and the nitrided steels were exposed to hardness measurements. Hardness was measured in terms of Vicker's microhardness by using LECO MST 210 microhardness tester at 50 g. applied load. The hardness was measured five times with the accuracy of ± 25 H$_v$ and average values were finally taken and plotted the hardness depth profile.

After the structural characterization, sample coupons were exposed to the corrosion tests in 3.5 wt% NaCl environment. Linear sweep polarization tests were conducted by utilizing the corrosion testing instrument (Electrochemical Interface: Solatron Analytical, U.K. → Model S1 1287) interfaced to a personal computer with software to data acquisition and analyses. A three electrode cell was utilized for this purpose. The cell consisted of → (a) saturated calomel electrode through the Luggin probe used as the reference electrode for all the potential measurements; (b) steel coupons connected as the working electrode and; (c) a counter electrode → Pt. electrode. Before the tests, the electrolyte was purged with the nitrogen gas to create the inert environment. Polarization tests were carried out by following ASTM G59-97 (2914) standard test method.

The scanning rate of the polarization was fixed at 1 mV/s. Finally, the polarization diagrams were analyzed after Tafel's extrapolation and the corrosion parameters were calculated.

3 Results and Discussion

3.1 X-ray Diffraction (XRD) and Scanning Electron Microscopic (SEM) Analysis

All the nitrided and bare steels were exposed to detailed X-ray diffraction studies (using Co-k_a radiation source) for understanding the phase formation on the surface layer (shown in Fig. 2). XRD revealed α-Fe (110), (200) and (211) peaks in the bare steel. After nitriding Fe$_x$N nitrides (x = 2–3, 4) peaks appeared in CM45-10 and CM55-10 steels (Fig. 2b, c). Both these steels were nitrided for the same duration of 10 h but at the two different temperatures 450 °C and 550 °C respectively.

It is clear from the XRD patterns that peaks of ε-nitride (ε-Fe$_{2-3}$N) along with the γ'-nitride (Fe$_4$N) and CrN appear after nitriding. The presence of ε-nitride is known to improve the resistance to corrosion. From Fig. 2d, it is clearly indicated that there is major peak α-Fe shifting toward left side after nitriding of the steel at higher temperature of 550 °C. This may be attributed to the lattice strain. Careful observation shows that same is true for the nitriding at 450 °C. Broad view of these peaks and its position can be further represented by Fig. 3 as given below. A careful observation shows the lower angle shifting and peak broadening after nitriding of the steel.

By considering the full width at half maximum (FWHM) of α- Fe peaks of CM0 and CM55-10 steels, the peak broadening has been calculated to be ∼ 75%. This indicates that the lattice strain is developed as a result of nitrogen atom
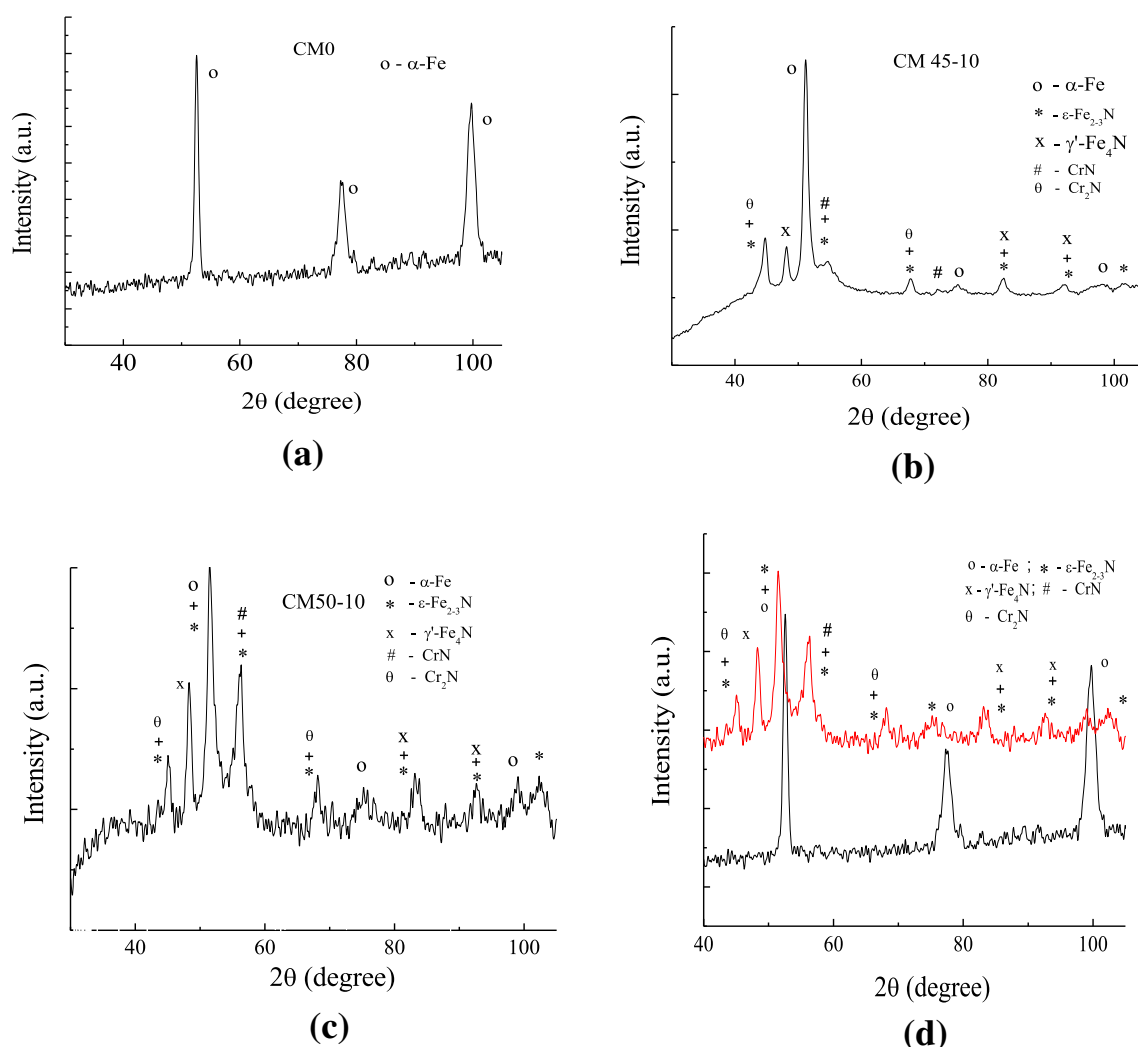

Fig. 2 Representation of X-ray diffraction patterns of: **a** CM0 (bare steel) **b** CM45-10; and **c** CM 55-10; **d** stacked (**a** and **c**; XRD patterns representing the peaks shifting after nitriding)
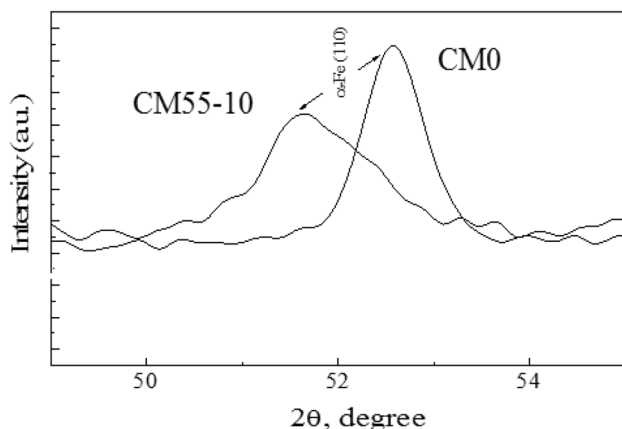
Fig. 3 α-Fe (110) peaks of the CM0 and the CM55-10 steels representing the lower angle peak shifting

dissolution and super saturation thus expanding and generating the compressive stress in the crystal lattice of the nitrided steel. Rise in hardness value and resistance to fatigue of the nitrided steel could be attributed to the supersaturation of nitrogen in the crystal interstices. The nitrogen incorporated will be released at the interface of surface and the electrolyte generating the NH_4^+ ions which in aqueous environment as NH_4OH make the electrolyte alkaline. The increased alkalinity of the electrolyte could be one of the reasons to disfavor the corrosion of steel.

On the other hand, the γ'- and ε- nitrides as revealed by XRD patterns are partially responsible for the improvement of corrosion resistance of the nitrided steel. When compared the peak intensities of these nitrides, the steel nitrided at the higher temperature of 550 °C (CM55-10) shows higher intensities. It can be speculated here that the CM55-10 steel has larger concentration of these nitrides. ε nitride as the predominating phase with higher concentration in this steel contributes more toward the resistance to corrosion.

Following XRD studies, both the nitrided steels CM45-10 and the CM55-10 were exposed to SEM/EDS analysis after metallographic polishing and etching with the Villela's reagent. The microstructure of the nitrided layer and the elemental availability across the cross section are revealed in this analysis. Point analysis was made from the top toward the bulk of the steel at 4 successive locations. Figure 4a, b as shown below represents the cross sectional microstructure along with the elemental analysis as captured by the SEM/EDS point analysis near the surface region. It is clear that the concentration of nitrogen at the surface is maximum and gradually decreases toward the core. A thin compound layer appeared at the top of the samples. Although, this layer is good from corrosion resistance point of view, but owing to its brittle nature, it may cause mechanical degradation.

Following the compound layer, a diffusion layer is formed which consists of Fe-nitrides, CrN and the nitrogen solid solution as clear from XRD analysis. Small precipitates may be the Fe-carbides. But further analysis is required for the confirmation. This layer contributes to the corrosion resistance of the steel. In Fig. 4c, the cross-sectional elemental analysis from top to the bulk of the steel reveals the presence of the alloying elements with variable concentration. Nitrogen availability is obvious from Fig. 4c. It clearly indicates that the nitrogen concentration at the top is maximum and gradually decreases toward the bulk of the steel.

3.2 Hardness Measurements

Hardness measurements of all the bare and the nitrided steel samples were carried out in terms of Vickr's microhardness tests. The tests were performed to understand the modification in mechanical properties of nitrided steels. The hardness *vs.* depth profiles are represented in the following Figs. 4a, b and 5. Figure 4a, b represent the SEM micrographs of the nitrided steels. The layers overlaid with the hardness vs. depth profile show the hardened layer's thickness/case depth. It is obvious from the curves as shown in this figure that the surface hardness attains a significantly high hardness value of around 1180 ± 30 H$_v$. The hardness of the bare steel is around 650 H$_v$. The hardness improvement is around two fold. These depth profiles explain the higher concentration of nitrogen and the nitride of Fe/Cr at the surface level and gradually decrease toward the core of the steel. For the steel nitrided at the lower temperature of 450 °C, the case depth is found to be ∼ 86 μm. and ∼ 153 μm for the steel nitrided at the higher temperature of 550 °C. A significantly wide case depth is obtained at the higher temperature nitriding. A wider case depth may prolong the longevity of the component in the harsh service conditions where the surface faces frequent frictional forces. Plasma nitriding thus proves to be beneficial for the wood machining steel by producing the protective layer and thus improving the service life of the tools.

3.3 Electrochemical Characterization

Potential Versus Time Analyses Both the bare and the nitrided steel samples were immersed into the cell containing the electrolyte 3.5 wt% NaCl and left for 1 h. until the voltage fluctuations subsided. Voltage vs. time plots for the three steels → (a) CM 0 (bare steel); (b) CM 45–10 (nitrided at 450 °C for 10 h); (c) CM 55–10 (nitrided at 550 °C for 10 h) were recorded and presented in the following Fig. 6a → c.
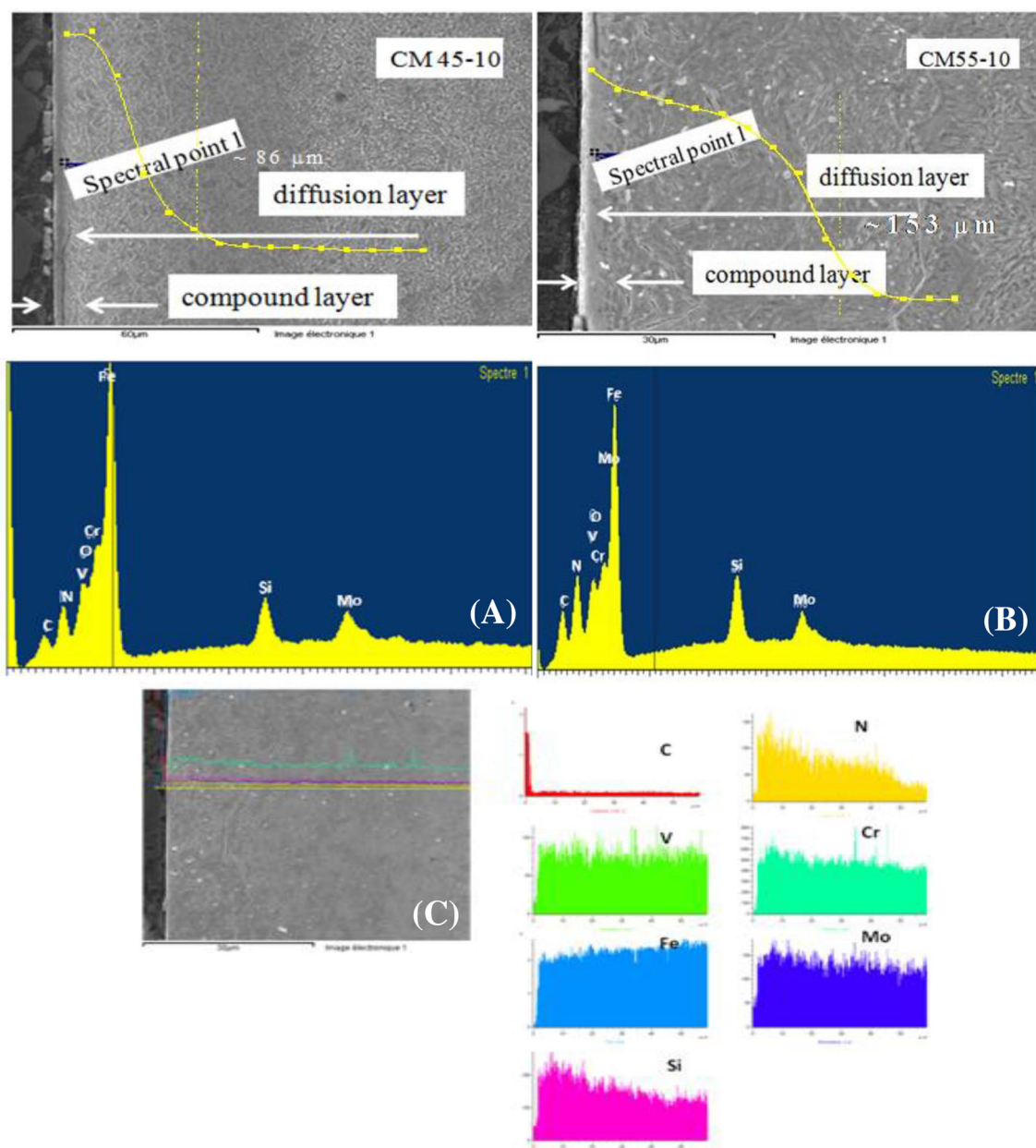
Fig. 4 SEM coupled with EDS across the cross section of the **a** CM45-10 steel; **b** CM55-10 after etching with Villela's reagent (×1000) and **c** elemental analysis across the cross section of CM55-10

The above diagrams reveal the three stages → (a) initial stage from where the potential rises sharply; (b) maximum potential region; (c) the final and the stable potential region indicating the gain of stability. Table 3 summarizes the potential variations in the three stages of bare and nitrided steels.

From Fig. 6a, it is revealed that the bare steel CM0 initially has most active potential – 0.64 V ($E_{initial}$) and the maximum potential of − 0.31 V which is more positive potential/noble potential. Then, the potential falls to − 0.51 V stable potential. This may be attributed to the

surface flaw/defects causing the dissolution of the steel in the initial stages. XRD shows the formation of CrN and Fe_xN which may lead to the surface heterogeneity. It may also be speculated that the lower temperature nitriding may provide the scope to grow these precipitates as the nitrogen diffusion is slower in this case. These precipitates may form the microgalvanic cells on the surface which causes the faster dissolution.

The retention time at this maximum potential (− 0.31 V) is of few moments only and then fall down to − 0.51 V and subsequently attains stability at this
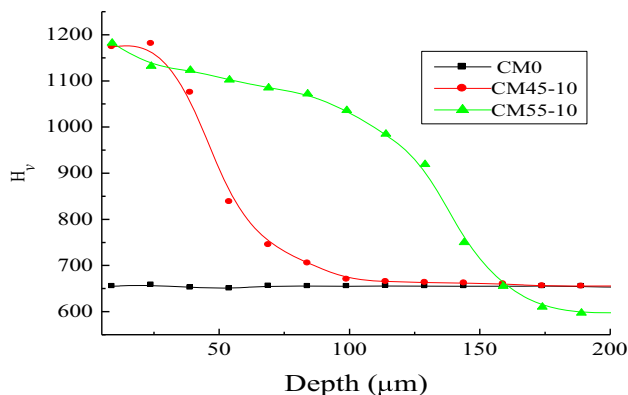
Fig. 5 Hardness vs. depth profiles of steels after plasma nitriding at low and high temperatures

potential. More positive value in comparison to the initial value may be due to the formation of passive film.

After nitriding of steel at low temperature of 450 °C, the initial potential—0.56 V is reached, which is more noble than that shown by the steel CM0 (Fig. 6b). Then the peak potential of − 0.38 V is attained which immediately falls to − 0.49 V stable potential. However, the difference of this potential is marginal when compared to that of the bare steel CM0.

CM 55–10 steel (Fig. 6c) has shown the lesser propensities toward the corrosion as compared to the bare and the CM 45–10 nitrided steels. Initial potential and also the maximum potential is − 0.58 V, which is lesser than that shown by the bare steel (− 0.64 V) and almost similar to that of the value shown by the C45-10 steel. However, the stability gained is at the higher potential of − 0.40 V, which is more positive than the other steels. It could be due to the fact that release of nitrogen is more in the nitrided steels, which makes the environment more alkaline and thus favor the resistance to corrosion. After achieving the
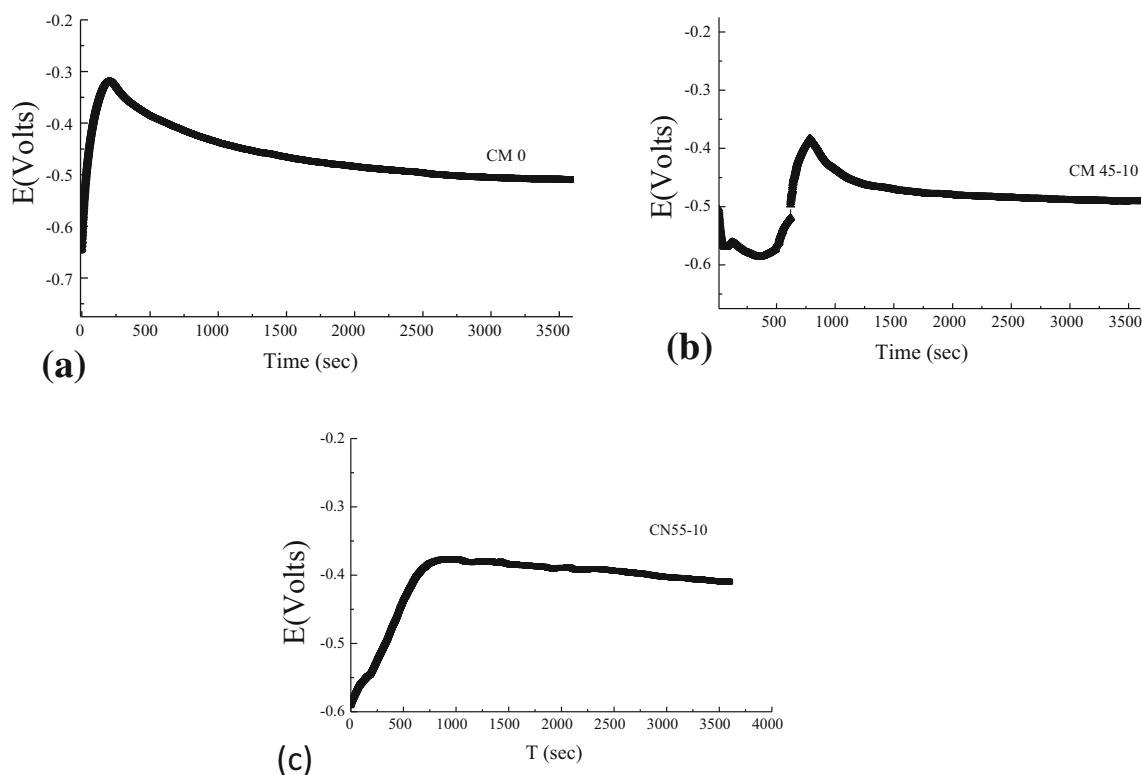

Fig. 6 Potential versus time curves of → **a** bare steel and the nitrided **b** CM45-10 and **c** CM55-10 steels

Table 3 Variation of potential with time of immersion of steels before and after nitriding in the 3.5 wt% NaCl electrolyte

Sample code	$E_{maximum}$ (V)	E_{stable} (V)	$E_{initial}$ (V)
CN0	− 0.31	− 0.51	− 0.64
CN45-10	− 0.38	− 0.49	− 0.56
CM 55-10	− 0.37	− 0.40	− 0.58

stability, these steels are exposed to the potentiodynamic polarization.

Potentiodynamic Polarization Tests All the bare and nitrided steels were exposed to the potentiodynamic polarization tests. After purging with the nitrogen, polarization was carried out in 3.5 wt% NaCl in the scan range ± 1.0 V and rate 1.0 mV/s. The bare steel CN0 shows the E_{corr} value -0.4958 V, whereas the nitrided steel CN45-10 shows -0.663 V. However, the E_{corr} for the CM55-10 steel has shown this value to be equal to -0.562 V which is nobler than that of CM45-10 showing -0.663 V. This is slightly less noble than the bare steel. Thus, the CM55-10 steel has shown the corrosion propensity less than shown by the CM45-10 steel. The polarization curves are represented in Fig. 7 a, b.

After Tafel extrapolation on the polarization curves, the corrosion parameters have been calculated and summarized in Table 4.

It seems that the bare steel had lesser flaws/defects on the surface as compared to that of the nitrided steels which may be the reason of its nobler potential. The possibility that the nitrided steels may have the Fe-nitrided precipitates which may have created the surface heterogeneity.

On the other hand, comparison of the i_{corr} values for these steels, shows the order: I_{corr} (Amp/cm^2) values observed for these steels can be represented in the increasing order as $2.646 \times 10^{-6} < 8.678 \times 10^{-6} < 1.816 \times 10^{-5}$, respectively, for the steels as CM55-10 < CM0 < CM45-10. Thus, the dissolution kinetics of CM55-10 steel has been found to be lesser than the other steels. Similar is the case with the rate of corrosion where the order of rate of corrosion (MPY) can be given as: $1.085 < 3.659 < 7.660$ and accordingly the order of the steels in terms of rate of corrosion can be given as CM55-10 < CM0 < CM45-10. Therefore, it may be concluded that the corrosion resistance of CM55-10 steel is more than other steels. The resistance to corrosion for this steel is significantly higher than the CM45-10 steel. It may be suggested here that nitriding at the higher temperature is more effective to incorporate more nitrogen into the steel which makes the solution more alkaline in the electrolyte and thus causing more resistance to the corrosion.

From the XRD, it is clear that the ε-Fe$_{(2-3)}$ N peaks obtained after 550 °C nitriding have higher intensity than that obtained after 450 °C nitriding. If we look for the peaks from left to right direction, the peaks representing ε-Fe$_{(2-3)}$ N in steel nitrided at higher temperature have higher intensity. It is also known that ε-Fe$_{(2-3)}$ N formation increases with the rise in temperature. It is known that ε-Fe$_{(2-3)}$ N possess good corrosion resistance. CrN precipitation is common in both the nitrided steels, in fact formation of CrN is favored at 450 °C and with the rise in temperature, the precipitation of this phase is more. It may be suggested here that the overall concentration of ε-Fe$_{(2-3)}$ N and nitrogen in the solid solution is more than that found after nitriding of the steel at the lower temperature of 450 °C. Hence, the corrosion resistance is better in the steel nitrided at the higher temperature of 550 °C.

The bare steel may be showing better corrosion resistance initially, but later the corrosion kinetics is faster than that of the 450 °C nitrided steel. Maybe because of the FexN phase formation and its dispersion affects the surface homogeneity. Presence of CrN phase after nitriding, as evidenced by the XRD analysis obviously will cause the deterioration of the corrosion resistance because of the Cr depletion from the solid solution. In the bare steel, there is no Cr depletion and CrN phase formation which could be the reason of better corrosion resistance than the nitrided steel at this lower temperature. However, further studies will be focused on the concentration of various nitrides and CrN phase dispersed on the surface layer. It seems that after the dissolution of the first few surface layers, the lower layer get exposed which consists of the nitrogen
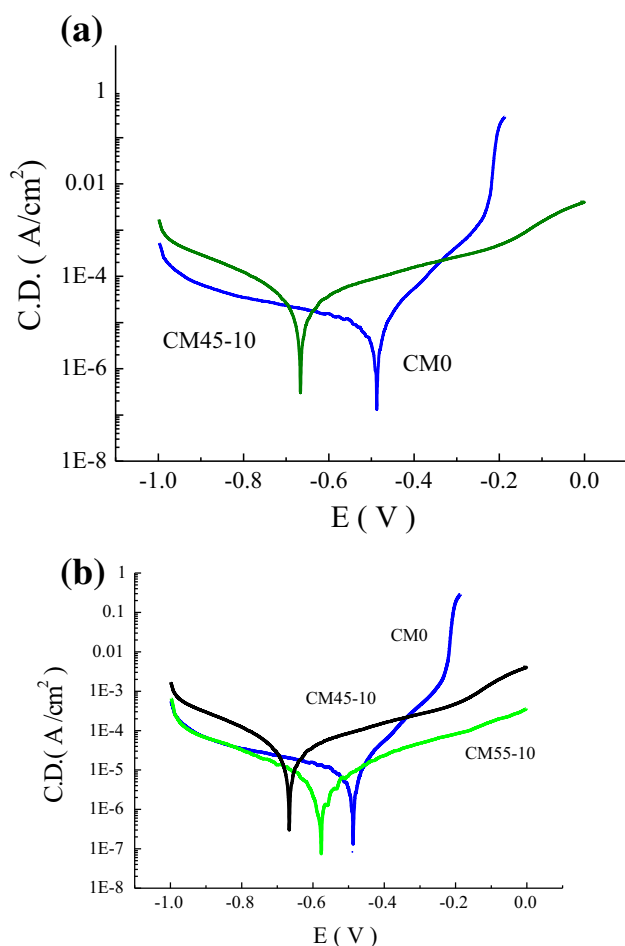

Fig. 7 Potentiodynamic polarization diagrams of steels **a** CM0 and CM45-10; **b** CM0, CM45-10 and CM55-10 steels; showing a distinct passivity and lower current density for the nitrided steels.

Table 4 Corrosion parameters obtained after Tafel extrapolation on polarization curves

Steel code	Corrosion rate (MPY)	Corrosion current (i_{corr} in Amp/cm^2)	Corrosion potential (E_{corr} in Volts)
CM0	3.660	8.678×10^{-6}	-0.496
CM45-10	7.660	1.816×10^{-5}	-0.663
CM55-10	1.085	2.646×10^{-6}	-0.575

incorporated and the FexN (where, $x = 2$–3, 4) layer with less CrN or less Cr depleted layer. So, a better passivation range and lower dissolution kinetics is shown by the nitrided steel in comparison to that of the bare steel (Fig. 3a).

Feng et al. [37] worked on the role of nitrogen on microstructure, passivity and corrosion resistance of martensitic stainless steel. It has been suggested in this study that the inclusion of nitrogen in the martensitic stainless steel reduces the concentration of $M_{23}C_6$ content and converts to the precipitates of M_2N which improves the resistance to corrosion. However, high concentration of M_2N phase is detrimental form the corrosion resistance point of view. The change in microstructure first increases and then deteriorates the corrosion resistance with the increase of nitrogen.

Nitrogen incorporation which increases the Cr concentration as Cr_2O_3 and CrN in the passive layer and also the formation NH_4^+ ions improves the protective ability. It has also been suggested that the increase in nitrogen concentration in the solid solution increases the repassivation ability [37]. These reasons could be attributed to the improvement of corrosion resistance with the increase of process temperature and hence increase in nitrogen inclusions.

From the above results it can be concluded that plasma nitriding at the higher temperature of 550 °C has shown a significant improvement in hardness and corrosion resistance the CrMoV steel. These improvement may be attributed to the presence of FexN (where $x = 2$–3, 4) and CrN phases along with the nitrogen solid solution.

4 Conclusions

In the present work, it has been shown that the nitrogen inclusion by following plasma nitriding at a higher temperature of 550 °C for 10 h is effective for the improvement of hardness and corrosion resistance. Improvement in corrosion resistance after nitriding at the lower temperature of 450 °C is not so effective as in the case of higher temperature nitriding. It could be due to the nitrogen ingress in the solid solution at the higher temperature is greater owing to its greater rate of diffusion and also due to

the presence of ε-$Fe_{2–3}N$ phase. It may also be suggested here that the higher nitrogen concentration renders the environment more alkaline and thus disfavor the corrosion of the steel.

Chromium–molybdenum–vanadium based alloy steel may be nitrided at the higher temperature of 550 °C for the improvement of both hardness and corrosion resistance. Nitriding at this temperature prolong the longevity of wood machining CrMoV tool steel in the harsh service conditions. Hence, the early replacement of the tools can be avoided and thus the cost of materials and manufacturing can be minimized.

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Enhancement of hardness of low alloy steel after low temperature plasma nitriding

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ABSTRACT

The present work is focused on the plasma assisted nitriding of martensitic stainless steel at low temperature. Sample coupons of dimensions $8 \times 8 \times 6$ mm^3 were cut from the hardened and tempered steel sheet. Following grinding and mirror polishing samples were placed inside the chamber. At a low temperature of 460 °C (±10) nitriding was performed in the plasma generated by nitrogen and hydrogen gas mixture, Nitrided samples were then subjected to hardness measurements. The structural characterization was followed by X-ray diffraction (XRD) studies for the phase analysis. It was shown that even at a low temperature the surface modifies to high hardness for the improved tribological properties.
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1. Introduction

Plasma niriding is known as a thermochemical treatment which involves nitrogen diffusion at a given temperature. Based on the temperature applied the content of the nitrogen is expected to be incorporated in the materials. A host of literature exists on the nitrogen incorporation in steel surface and near surface regions to make it high nitrogen steel. Incorporation of nitrogen into the crystal lattice plays the role in enhancing the surface initiative properties like wear and corrosion resistance [1-10].

However, less effort has so far been made for nitriding of CrMoV tool steel which requires wear and corrosion resistant surface layer to prolong the service life in harsh erosive/corrosive environment.

Nouveau et al. [11] proved the enhanced hardness of this steel after plasma nitriding. Rao et al. worked for the improvement of hardness and resistance to corrosion by following plasma nitriding route [12-17]. The work has been continuing to understand the optimized process conditions so that the wear and corrosion resistant layer can be obtained. High temperature nitriding at 500 and 550 °C had shown the enhanced hardness and corrosion resistance properties [11,12].

Temperature of the nitriding was fixed to low value of 460 °C in the present work. Low temperature nitriding has now become most promising method for the inclusion of nitrogen to supersaturation and also energy saving to make the process comparatively less expensive. The idea behind the improvement of surface hardness is related to several occurring in the nitrided steel.

Nitrogen supersaturation, expansion of crystal lattice, phase transformation, development of strains, the refinement of microstructure and diffusion of nitrogen all are interrelated in the development of the surface microstructure and the finally the properties. These occurring sustained, for example in the austenitic steel there is a possibility of fine grained microstructure. If not so, may be the homogeneous structure converts to the heterogeneous microstructure. The plastic strain caused in the coarse grains like austenite may be effective in refining them.

The present work has been focused on the application of low temperature 460 °C for nitriding the CrMoV steel with the view to improve surface hardness. The aim of the work is to achieve a high hardness without applying high temperature and thus avoiding the risk of deterioration caused by the depletion of chromium from the solid solution. The purpose of this work is to increase the longevity of the tools made up of this steel. This process involves heating of the samples in the plasma of nitrogen and hydrogen at the certain temperature to achieve the desired microstructure to enhance the hardness and wear and corrosion resistance [13,14]. The samples after metallogrheaphic polishing placed at certain distance on the conducting sample holder. The nitriding chamber was first evacuated to around 0.5 Pa and then raised the pressure with

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the working gas nitrogen and plasma to around 500 Pa. Samples were biased negatively to attract the nitrogen and hydrogen ions towards the sample surface.

2. Experimental

2.1. Materials and methods

Samples of dimensions $8 \times 8 \times 6$ mm³ were cut from the steel sheet after hardening and tempering heat treatment processes. The composition of the steel samples taken in wt. % was: 0.5C, 1.0Si, 0.5Mn, 8.0Cr, 1.5Mo, 0.5V, balance Fe. These steel samples were mirror polished and then cleaned ultrasonically.

2.2. Plasma nitriding procedure

Samples were then kept inside the vacuum chamber on a conducting sample holder and evacuated the chamber to approximately 0.5 Pa. Samples through the sample holder was biased negatively. Then raised the chamber pr The present work has been focused on the application of low temperature 460 °C for nitriding the CrMoV steel with the view to improve surface hardness. The samples after metallogrheaphic polishing placed at certain distance on the conducting sample holder. The nitriding chamber was first evacuated to around 0.5 Pa and then raised the pressure first with the Ar gas and then the working gas nitrogen and plasma to around 500 Pa. Samples were biased negatively to attract the nitrogen and hydrogen ions towards the sample surface. First the Ar + plasma was triggered and accelerated towards the surface to sputter clean the native oxide/any dirt. The sputtering was continued uptil the desired temperature reached. Then switched off this cycle and initiated the nitriding cycle. A low temperature of 460 °C was fixed and nitrided by varying the exposure time through 1 h to 8 h.

2.3. Characterization of the nitrided steel

Nitrided steel samples along with the bare steel sample were exposed to the hardness measurement by utilizing the Vicker's microhardness tester.

X-ray diffraction studies (X-ray diffraction (XRD: INELCPS 120 diffractometer- in Bragg Brantano mode) analysis with Co-$k\alpha$ (0.17932 nm) radiation source)) were performed for the phase evaluation and/or the microstructural modifications on the surface.

3. Results and analyses

3.1. Microhardness measurements and case depth

The nitrided steel samples were tested by utilizing Vicker's micro hardness tester (LECO MHY-210 microhardness tester) at an applied load of 50.0 g. The tests were repeated five times for the reproducibility and the reliability. Fig. 1 shows hardness with ± 5. H_v variation from the surface towards the bulk of the nitrided steel samples. Fig. 2

The microhardness measurements as a function of depth inside the bulk of the materials are one of the methods to measure the case depth of the hardened/nitrided steels. The case depth affects the mechanical properties of the steel like surface hardness, fatigue resistance, toughness etc. Thus, the surface hardness becomes important to understand these properties [18-20]. Cr, V, W, Al, Mo shown to high affinity towards nitrogen and forms their nitrides and thus improves the hardness [21,22]. In the present steel sample the presence of Cr, Mo, V are the elements which are prone to react with nitrogen and known as nitride formers.
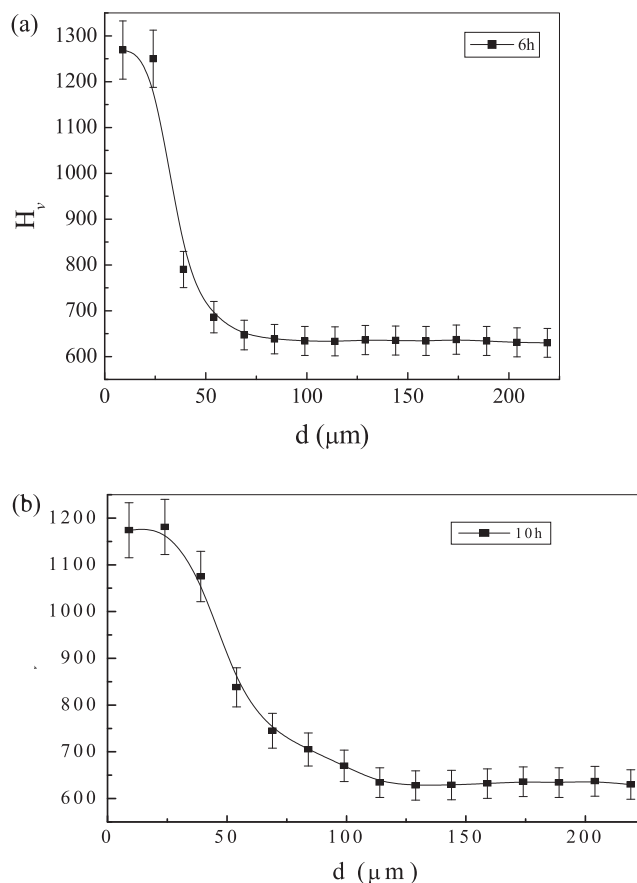

Fig. 1. Representation of Vicker's microhardness *vs.* depth in the bulk of the nitrided steel at 450 °C for (a) 6 h and (b) 10 h duration.
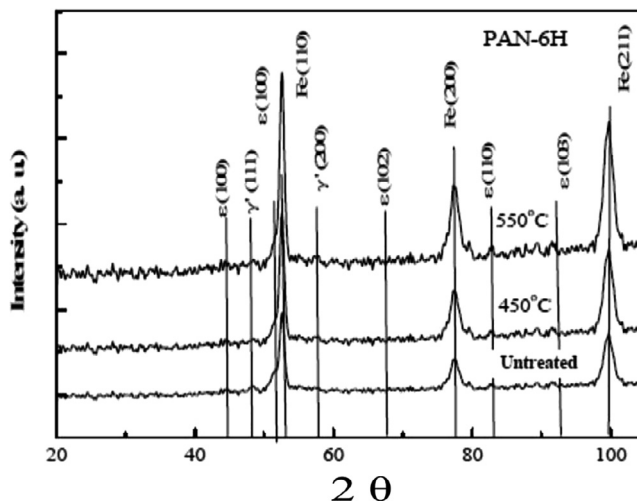

Fig. 2. Representation of XRD patterns of steel nitrided for 6 h at temperatures (a) 450 °C and (b) 550 °C [24].

These nitrides are responsible to improve the hardness of the steel. Some hardness values were achieved by other workers and summarized with the present observations in Table 1.

The above summary represents the hardness and case depth achieved by other workers [23] and in the present study. It can be seen that in the present study the hardness achieved by nitriding at 460 °C and for the duration of 6 h is 1272 H_v and for 10 h it is 1177.40 H_v which is stated here that for 6 h nitriding the hardness

Table 1

Plasma nitriding parameters		Case depth (μm)	Surface hardness (H$_v$)	Reference
Time (h)	Temperature °C			
10	450	150	1044.60 ± 8.46	2.3–2.7 CrMoV steel (2015) [23]
30	450	310	1150.53 ± 4.87	[23]
8	500	190	1167.73 ± 73	[23]
6	550	310	985.10 ± 23.98	[23]
6	450	56.68	1272 ± 5.0	8.0 CrMoV steel Present study (2020)
10	450	93.24	1177.40 ± 5.0	Present study (2020)
6	550	120	1270.0	[24] (2019)

achieved is maximum. For 10 h nitriding also the hardness is around 1177 H$_v$ which is the achievement over other treatments. The case depth obtained is also 93.24 μm for 10 h nitriding. In some other studies by Rao et al. [24] the case depth obtained was around 120 μm but at a significantly higher temperature of 550 °C for 6 h. The microhardness was also almost the same as that of 1270.0 μm. These finding conclude that even at the lower temperature nitriding similar hardness and case depth can achieved and thus process time and energy and cost can be saved.

3.2. X-ray diffraction (XRD) and phase evaluation

The nitrided steel along with the as-received steel sample were exposed to XRD analysis to know the phase formation and microstructural modifications after nitriding. After nitriding γ' (1 1 1) and γ' (2 0 0) peaks appeared at 48.23° and 54.9°. Other nitrides ε (1 0 0) and ε (1 0 3) also appeared at 44.6 and 91.4° respectively.

4. Conclusions

Plasma nitriding improves the hardness of Cr-Mo-V steel significantly. At a low temperature of 450 °C for 6 and 10 h the hardness improves to around 1272 H$_v$ which is almost similar to that obtained at higher temperature of 550 °C. Moreover, at this higher temperature there is the risk of core softening which can be avoided at the lower temperature of 450 °C. On the other hand higher temperature nitriding may cause Cr depletion from the solid solution which may adversely affect the resistance to corrosion. On the other hand, a case depth of 56.68 to 93.24 μm can be achieved without sacrificing significantly the surface hardness by increasing the nitriding time from 6 to 10 h. It may be speculated at this point the increase in the process time may increase the case depth. To further increase the case depth an attempt may be made to further increase the nitriding duration. The improvement in the case depth and hardness may increase the several mechanical properties like toughness and resistance to wear and fatigue resistance, Thus, the life of the tool can be prolonged and save the replacement cost.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

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Further Reading

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Plasma based nitriding of tool steel for the enhancement of hardness

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ABSTRACT

The present work is concentrated on plasma assisted nitriding of steel at a higher temperature of 450 and 525 °C. Steel samples hardened and tempered after heat treatment were mirror polished. Samples are then cleaned ultrasonically and placed in the vacuum chamber of reactor and then evacuated. The gas mixture of nitrogen and hydrogen was fed into the chamber and when the pressure to a desirable level plasma was generated.

The hardness measurement of steel samples after nitriding had shown a significant improvement of hardness. Hardness and also the case depth was found to be increased to around 1200 H_v and 108 μm respectively, as the treatment temperature was raised from 450 to 525 °C. The X-ray diffraction studies revealed the presence Fe and Fe-nitride peaks and also a lower angle shifting of Fe peak indicating the stress generation in crystal lattice. The improvement of hardness may be attributed to the presence of these nitrides and the lattice expansion.

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Selection and peer-review under responsibility of the scientific committee of the 2nd International Conference on Manufacturing Material Science and Engineering.

1. Introduction

Nitriding is a thermochemical treatment process for the incorporation of nitrogen into the materials at a suitable temperature. For the surface hardening and corrosion resistance improvement of steels nitriding had long been practiced in industries. Improvement of these properties are the requirements for prolonging the longevity of the industrial components/tools. Physical or chemical vapour deposition for the improvement of these properties had also been used to improve these properties however; the coated layer delamination limits its widespread application [1–3]. Nitriding overcomes the delamination problem and thus prevents the premature failure of the parts/components [4–11]. Plasma based nitriding is one of the plasma based surface modification techniques known as the environmental friendly and efficient method eliminating these drawbacks.

Plasma nitriding is a plasma based thermochemical process in which the part/substrate to be nitrided acts as the cathode. The ion bombardments and also the auxiliary heating assist the diffusion of nitrogen into the substrate surface. At the suitable temperature the desired hard phases can be produced and thus in the near surface region the hardness can be improved. The hardness at the surface is found to be highest and decreases with the depth towards until the bulk hardness is achieved. The hardness and the case depth can be tailored which can improve the load bearing capacity of the components/parts.

Plasma nitriding can be employed on the materials for the modification of microstructure and desirable properties, the process involves nitrogen inclusion and stress generation, control of process parameters to achieve improved biocompatibility, mechanical and corrosion resistance properties of materials [12–20]. Though this process has already proved to enhance the mechanical and corrosion resistance properties however, for the martensitic stainless steel where the chromium content is not high the preservation of corrosion resistance is still not very clear. Chromium may be consumed in the formation of its carbide during the heat treatment for the improvement of bulk mechanical properties and its nitride during the nitriding process. The studies on the improvement of both hardness and corrosion resistance or the hardness improvement without degrading the corrosion resistance are desirable for prolonging the life of the tools/components. During nitridng for the surface hardening of this steel care must be taken to preserve the corrosion resistance. Chromium-molybdenum–vanadium is one of this kind of steels which requires the attention for the improvement of these properties. Plasma nitriding of Cr-MoV steel

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had been attempted by Nouveau et al. [13] and also extended by Rao et al. [17–22] for the improvement of surface hardness and resistance to corrosion. The present work is focused on the plasma based nitriding at variable temperature for the improvement of hardness of this steel.

2. Experimental

2.1. Materials and methods

After hardening and tempering of a big steel sheet the samples of dimensions $8 \times 8 \times 6$ mm^3 were cut and mirror polished.

The composition of the steel samples taken in wt. % was: 0.5C, 1.0Si, 0.5Mn, 8.0Cr, 1.5Mo, 0.5 V, balance Fe. These steel samples were mirror polished and then cleaned ultrasonically.

2.2. Plasma nitriding treatment

The mirror polished samples were kept on the sample holder inside the vacuum chamber. The vacuum chamber was first evacuated to around 0.5 Pa and then the pressure was raised first with the Ar gas and then the working gas mixture ofnitrogen hydrogen to around 500 Pa. Negative voltage was applied to the sample holder and thus to the samples. The negatively charged samples accelerate the positively charged ions from the plasma. Ar + plasma was first generated after feeding Ar gas to the chamber which were accelerated towards the sample and sputter cleaned the native oxide or dirt deposited on the surface. Ar ion bombardment had been continued until the desired temperature reaches and then the sputtering was stopped and the nitriding cycle initiated. Nitrogen and hydrogen gas mixture was fed into the chamber and then plasma was generated. After generating the plasma, nitriding cycle was initiated. The samples were nitrided at 515 °C and exposed for the different times.

2.3. Characterization

Nitrided and the bare steel samples were subjected to the hardness measurement by utilizing the Vicker's microhardness tester. X-ray diffraction studies (X-ray diffraction (XRD): INELCPS 120 diffractometer- in Bragg Brantano mode) analysis with Co-$k\alpha$ (0.17932 nm) radiation source) were performed for the phase evaluation and/or the micro structural modifications on the surface.

3. Results and analyses

3.1. Microhardness and case depth

To understand effect of nitriding on surface hardness the nitrided and the bare steel samples were subjected to hardness measurements using Vickers's micro hardness tester at 50.0 gm. load. Measurements were repeated at the nearby location for the reliability of the results. The hardness values are measured with a small fluctuation of ± 5–10 H$_v$. Samples nitrided for 8 and 10 h at 515 °C were taken for the hardness measurements and compared with the sample nitrided at 450 °C.

Fig. 1 represents the hardness vs. depth profiles for the samples treated at temperatures 450 °C (10 h) and 515 °C ± 5 °C (8 and 10 h). Fig. 1a shows the curve representing the microhardness with respect to the depth for the nitrided steel at 450 °C (10 h). From the curve it is obvious that the maximum surface hardness was found to be 1177.40 $\pm$ 5.0 H$_v$ [22]. This improvement of hardness is approximately two fold as compared to its initial hardness ∼ 630 H$_v$. The case depth was also found to be around 93.24 μm. Fig. 1b shows the hardness vs. depth profile for the sample nitrided at a

(a)

(b)

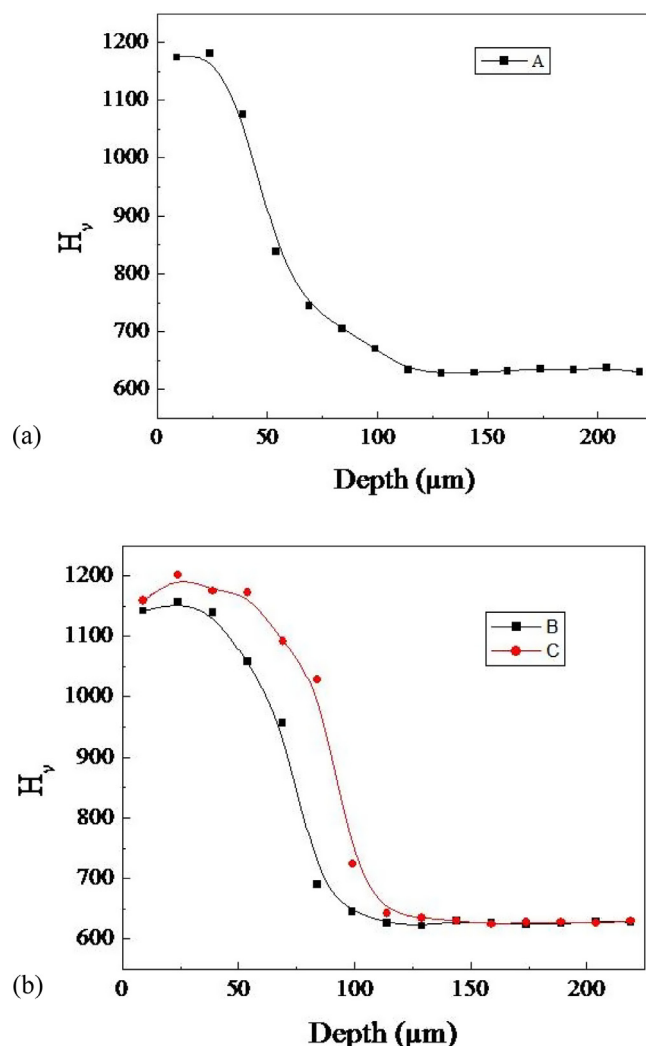**Fig. 1.** Microhardness vs. depth profile of the steel samples nitrided at (a) 450 °C for 10 h [22]; and (b) 515 °C for sample B (8 h) and C (10 h).

higher temperature of 515 °C $\pm$ 5 °C. The maximum hardness of 1156 $\pm$ 5.0 H$_v$ was obtained after 8 h exposure. This hardness is near to the hardness obtained after nitriding at 450 °C (10 h). This shows that the hardness was increased when the temperature was raised from 450 °C (10 h) to a higher temperature 515 °C $\pm$ 5 °C (8 h). This hardness improvement was obtained after nitriding at a higher temperature but for the shorter duration of 8 h unlike 10 h nitriding at the lower temperature. The maximum hardness obtained after nitriding at 515 °C for 10 h was found to be around ∼1200 H$_v$ and the case depth ∼108 μm. Thus, the higher temperature nitriding improved both the hardness and case depth. Increase in case depth may affect the mechanical properties e.g. fatigue resistance, toughness etc [23–25]. Cr, Mo. V elements have affinity to react with nitrogen to form their nitrides. These nitrides are hard phases responsible for the improvement of hardness. Nitrogen solid solution and its super saturation may also lead to the stress generation and thus improve the hardness.

3.2. Phase evaluation following X-ray diffraction (XRD) studies

Nitrided as well as the bare steel samples were subjected to the XRD studies to know about the phase formation (Fig. 2). Bare steel shows the major peaks Fe or α' (martensite peaks). XRD patterns revealed the presence of Fe$_4$N peaks i.e. γ' (1 1 1) and γ' (2 0 0) peaks
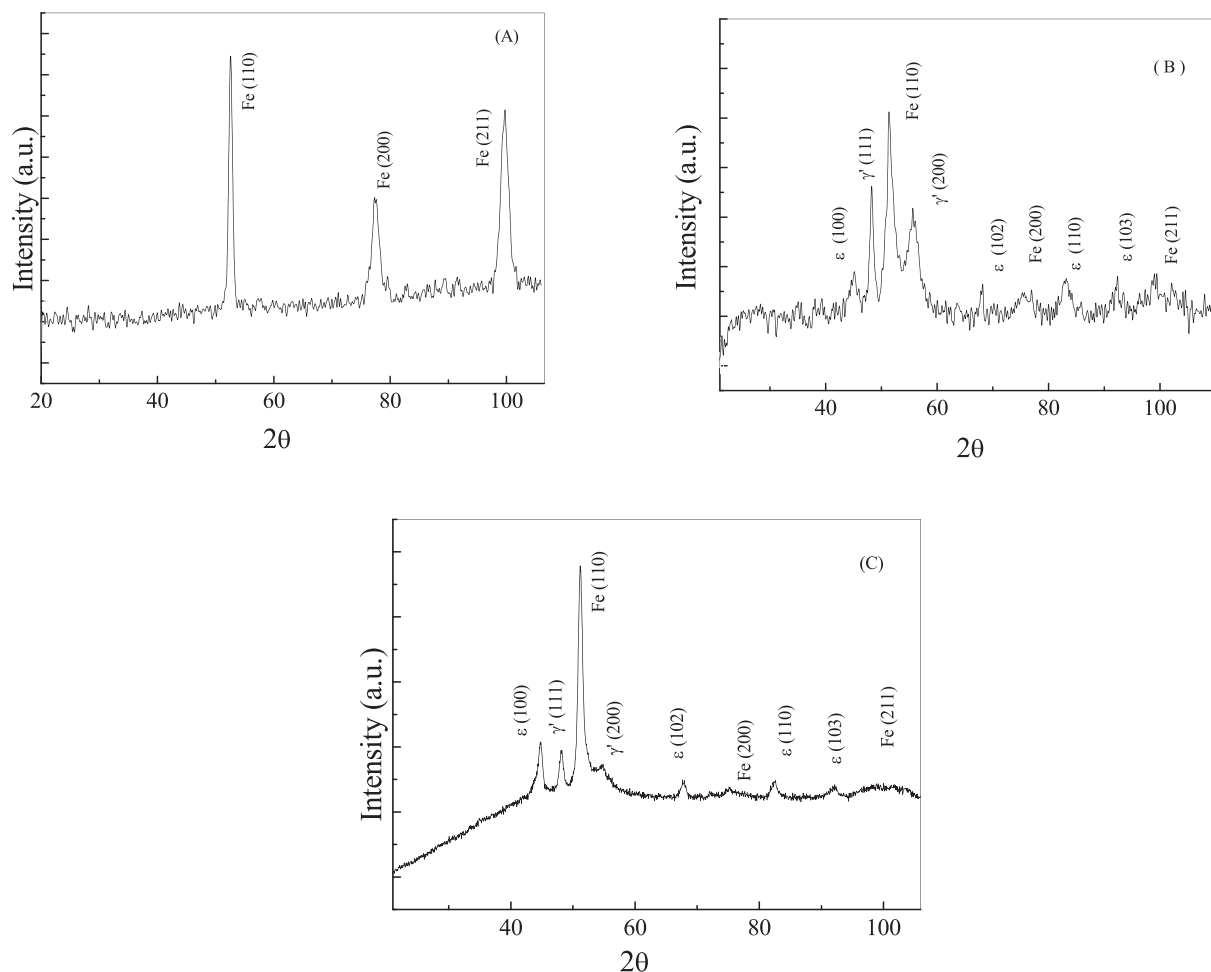
Fig. 2. X-ray diagrams of (A) bare steel revealing the Fe peaks; nitrided steel at (B) 515 °C revealing Fe and Fe-nitrides and (C) nitrided steel at 450 °C revealing Fe and Fe-nitrides.

at 48.23° and 54.9°. Apart from these nitrides ε (1 0 0) and ε (1 0 3) nitrides at 44.6 and 91.4° respectively also appeared. These nitrides are known to improve both the hardness and corrosion resistance properties. XRD patterns already had been shown in other studies of the similar steels by Corinne et al. [13] and also Rao et al. [17]. The present studies shown the higher intensity of Fe-nitrides at the higher temperature of 515 °C when compared to the sample nitrided at a lower temperature of 450 °C. A peak shift of Fe from its initial position at 52.85° to the lower angle position 50.91° indicates the lattice expansion. This phase is given the name expanded martensite and also the expanded ferrite [26]. This may cause the stresss generation due to nitrogen incorporation and thus cause an enhancement of hardness of steel after nitriding. Frandsen et al. [27] and other researchers Li et al. [28] worked on nitriding of Corrax nitriding and suggested that the nitrogen activities beyond a threshold limit causes transformation of b.c.t. (α'_N) to f.c.c. (γ_N) as the nitrogen is an austenite stabilizer.

Presence of ε-nitrides in the nitrided steel treated at both the lower and higher temperatures is the good indication from the corrosion resistance point of view. Higher temperature nitriding produces higher concentration of ε-nitride. This may improve both the corrosion resistance and the surface hardness of the steel more than the steel nitrided at the lower temperature. However, depending of the heterogeneity of the microstructure the corrosion resistance may be decided. Heterogeneous microstructure may

develop the microgalvanic cells which may cause the corrosion. This study is beyond the scope of this presentation.

4. Conclusions

Nitriding at a higher temperature of 515 °C ± 5 °C has shown the improvement of maximum surface hardness to around 1200 H_v after 10 h treatment time. The case depth achieved was around ~108 μm. The increase in case depth may increase the toughness and the fatigue resistance of the steel. The presence of iron nitrides is beneficial for the hardness and also the corrosion resistance improvement. Improvement of the mechanical and also the corrosion resistance may prolong the longevity of the tools made up of this steel which can save the replacement cost.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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