Indian Journal of Chemical Technology
Vol. 32, March 2025, pp. 223-229
DOI: 10.56042/ijct.v32i2.13129

Corrosion resistance of plasma nitrided tool steel at variable temperature and time

P. Janardhana Kiran[1], K. Ram Mohan Rao[2]*, V. Srinivas[1] & Anurag Gautam[3]

[1]Department of Mechanical Engineering, GITAM Institute of Technology, Rushikonda, Visakhapatnam-530045, Andhra Pradesh, India

[2]Department of Chemistry, GITAM School of Science, Gandhi Institute of Technology & Management, Rushikonda, Visakhapatnam-530045, Andhra Pradesh, India

[3]Department of Physics, School of Sciences, Malla Reddy University, Dulapally, Hyderabad 500100, Telangana, India

*E-mail: rammohanrao.k@gmail.com

Received 13 August 2024; accepted 11 January 2025

Wood machining steel has been nitrided with the view to enhance the corrosion resistance properties. Nitriding is performed by varying the time and temperature in the nitrogen and hydrogen plasma. Steel samples after polishing are kept inside the nitriding reactor and biased at -250 V to attract the nitrogen and hydrogen ions. Nitrided and bare steels were then subjected to X-ray diffraction (XRD) for the phase analysis. The presence of Fe_xN (where x = 2-3, 4) is observed after XRD analysis.Corrosion resistance of the bare and nitrided steels is assessed by following potentiodynamic polarization tests at room temperature in 3.5 wt% NaCl solution. Field emission electron microscopic analysis of the corroded surface revealed pittings more on the surface of the bare steel than that on the nitrided steels. Finally, it has been concluded that corrosion resistance of nitrided steels was significantly improved when compared to that of the bare steel due to the formation of Fe-nitrides after nitriding.

Keywords: Corrosion, Iron nitrides, Nitrided steel, Plasma, Polarization

Introduction

Surface initiative degradation caused by wear and corrosion severely affects the longevity of the metallic materials. Recently, tool manufacturing industries realized the premature failure of Cr-Mo-V tools due to harsh service conditions causing wear and corrosion. In the working environment where the tools interfaced with corrosive electrolytes, encounter frequently with the frictional forces. In these circumstances the tools undergo mechanical and electrochemical degradation synergistically, thus, early replacement of the tools will be necessitated to avoid the disruption of the industrial processes**.** The solution to overcome this problem is possible by deposition of hard and corrosion resistant layers by following physical and chemical vapour deposition. However, the delamination of these layers may limit its widespread applications. It has also been realized that these processes require the high temperature and longer treatment time, use of corrosives, explosives, and toxic precursors which could be challenging to the safety of the workers and the environment. In this regard, nitriding had been recognized as a better solution to overcome these problems.

Nitriding is a thermochemical diffusion of nitrogen into the near surface region of metallic materials and widely practiced for the steel processing. There are no layer deposition in this process and hence eliminating the risk of delamination. Plasma nitriding have received much more attention due to more controllability of the process and cost effectiveness[1-9]. The enhancement of hardness and resistance to fatigue, wear and corrosion may be achieved by tuning the process parameters like working pressure, current density, treatment time and temperature[10- 16].

In the past, researches have also used plasma nitriding for the improvement of hardness, wear and corrosion resistance properties[17-25]. Though the nitriding of various steels had been studied but poorly known about the nitriding of $90CrMoV_8$ steel and its effects on wear, corrosion and fatigue resistance. Only a few studies on nitriding of $90CrMoV_8$ steel had been reported in the literature[10,12,16]. The present study is focused on the plasma nitriding of Cr-Mo-V steel by varying the process duration and the temperature. The nitrided steels were then exposed to NaCl environment to assess the resistance to corrosion.

Experimental Section

Steel samples with dimension 10 x 10 x 5 cm^3 were cut from a bigger sheet after hardening and tempering heat treatment processes. The composition of the steel is given as 8.0%Cr, 1%Si, 1.5% Mo, 0.5%Mn, 0.5%C, 0.5%V, balance Fe. After mirror polishing these samples were placed on a sample holder inside the nitriding chamber. Schematic of nitriding involving sample temperature and time profile is shown in the Fig. 1.

Fig. 2 shows the schematic of plasma nitriding system revealing the basic components on the sample holder was biased at -250 V. Using the combination of rotary and diffusion pump systems the nitriding chamber was evacuated to the pressure to 0.5 Pa. Ar gas was fed into the chamber and triggered Ar+ plasma. These ions were bombarded on the surface of the steel samples for the removal of native oxide and dirt/greasy materials. Ion bombardment and external heating raised the temperature of the steel samples. After achieving the desirable temperature Ar+ bombardment was stopped and a gas mixture of nitrogen and hydrogen (4:1) was fed into the nitriding chamber to a pressure of 550 Pa. Plasma was then triggered for initiating the nitriding cycle. Nitriding was performed at 500℃ and 550℃ by varying the process time between 6 and 10 h. Steel samples nitrided at 550℃ for 6 and 10 h were named as CM556 and CM5510, respectively. Steels nitrided at 500℃ for 10 h were named as CM5010.

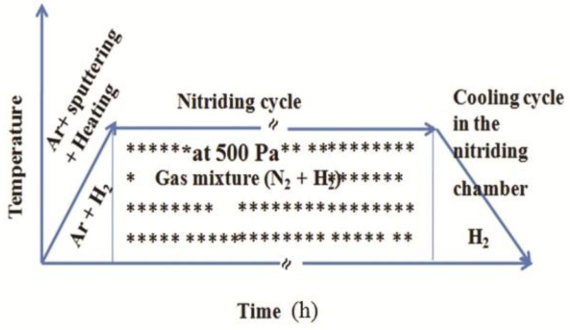

Fig. 1 — Schematic of plasma nitriding cycle

The structural characterization of the post nitrided steels were done using XRD-INELCPS120 X-ray diffractometer with Co-*kα* (λ = 0.17902 nm) as the radiation source. Corrosion resistance property was assessed by following linear sweep polarization tests in 3.5 wt% NaCl electrolyte at room temperature by utilizing the instrument – Electrochemical Interface: Solatron Analytical, U.K., Model S1 1287. The surface of the corroded steels were analyzed under High Resolution Scanning Electron Microscope (HR FESEM) (Model: TESCAN, MIRA, Made in U.S.A.).

Results and Discussion

X-ray Diffraction Studies

All the bare and nitrided steel samples were subjected to detailed X-ray diffraction studies. The diffraction patterns of the bare steel revealed the Fe (110), Fe (200) and Fe (211) peaks as shown in Fig. 3a. Steel nitride at 500°C for 10 h (CM5010) had shown the peaks of Fe-nitrides→Fe_4N (γ’) and $Fe_{2\text{-}3}N$

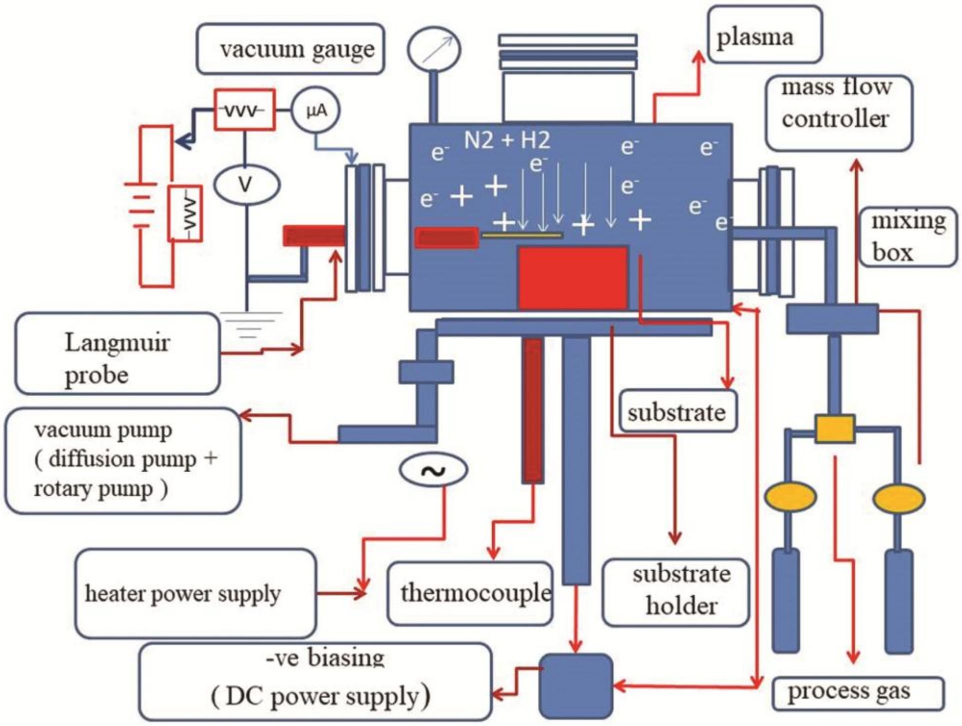

Fig. 2 — Schematic representation of plasma nitriding system

(εN). Presence of εN-phase is the good indication of improvement of corrosion resistance. Cr-nitride peaks are also visible after nitriding at the higher temperature 550°C. At the process temperature of 550°C the presence of CrN is expected as the Cr content of the steel is 8% which is enough to produce CrN. The presence of these nitrides is also attributable to the improvement of hardness of the steel.

It has also been found that the increase in nitriding time from 6 to 10 h increased the εN-peak intensity indicating an increase in the concentration of εN-phase. Hence, it is expected that the longer duration of nitriding may be more beneficial for enhancing the corrosion resistance.

It is evidenced from the XRD patterns of the bare and nitride steels (Fig. 3) that there is a shifting of Fe peaks to a lower angle. This observation is clear when Fe(100) peak has been analyzed. Fe (100) peak shows a shifting from its initial state at 52.6^o to a lower angle at 51.5^o in CM5010 steel nitrided for 10 h. Similarly, this shifting has been marked for the steel CM556 and CM5010 nitrided at 550°C and 500°C, respectively, for 6 h and also for a longer duration of 10 h. In the latter case, the peak has been shifted to 51.7°. The peak shifting suggests that there is the stress generation due to the nitrogen inclusion in the crystal lattice developing a compressive strain. Shorter duration of nitriding leads to more strain than that of steel nitrided for longer duration. This could be due to the longer time nitriding allowing more diffusion of nitrogen hence less accumulation at the surface. The stress generation in the crystal lattice can improve the hardness and fatigue resistance of the steel. Nitrogen dissolution in the solid solution is one of the reasons that disfavour the corrosion of steel. The dissolved nitrogen released at the steel/electrolyte interface renders the electrolyte alkaline by forming NH_4OH and thus suppresses the corrosive attack. It is expected that more the nitrogen concentration more will be the Fe-nitride formation. This may have greater corrosion resistance than that of the steel with low nitrogen concentration.

Potentiodynamic Polarization Tests

All the nitrided and bare steels were immersed in 3.5 wt% NaCl electrolyte before initiating potentiodynamic polarization tests. Samples were kept immersed in the electrolyte until the equilibrium attained. Corrosion tests were carried out by fixing the electrodes in a cell. These electrodes were: saturated calomel electrode as reference electrode; a counter Pt electrode; and the working electrode. Polarization was scanned at the fixed rate of 1 mV/sec. After polarization corrosion parameters were calculated after Tafel's extrapolation on the polarization diagrams.

Fig. 4 represents the polarization diagrams of the nitrided and bare steels. It is obvious that the initial

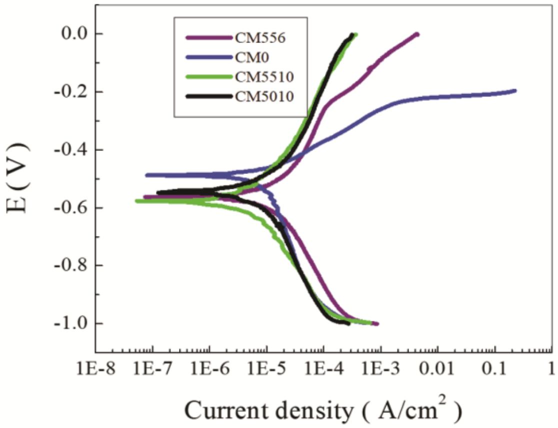

Fig. 4 — Potentiodynamic polarization of (a) as-received steel CM0, (b) CM556, (c) CM5510 and (d) CM 5010 in 3.5 wt% NaCl solution

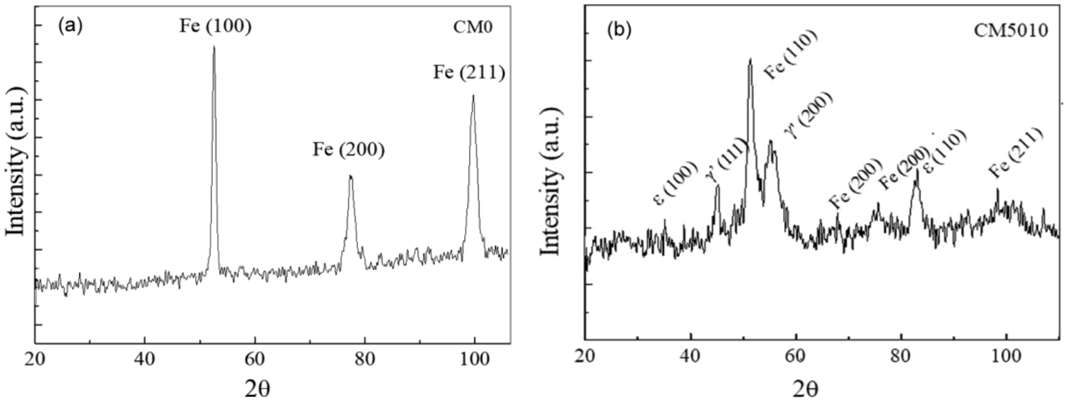

Fig. 3 — X-ray diffraction using *Co kα radiation* source unfolds the peaks representing (a) CM0 (bare steel) and (b) CM5010 steel

potential is more positive in the bare steel when compared to the nitride steel; however the dissolution kinetics is faster in the bare steel. This indicates that the bare steel undergoes corrosion at a faster rate than that of the nitrided steel. In the initial stages, nitrided steels the corrosion initiated earlier than the bare steel due to the surface heterogeneity. After some time exposure of the Fe-nitrides and also possibly due to the presence of Cr in the passive layer might have decreased the rate of corrosion.

Fig. 5 represents the trends of variation of corrosion potential E/V*vs.*SCE and corrosion current with respect to (a) nitriding time 6 and 10 h at a fixed temperature of 550°C and (b) with respect to temperature 500 and 550°C for a fixed time of 10 h. These curves are obtained after Tafel extrapolation and plotted to obtain an idea about the variation of corrosion potential and current with respect to time and temperature.

Corrosion parameters calculated after Tafel extrapolation on the polarization curves is summarized in the Table 1. From this table, it is obvious that the bare steel CM0 has corrosion rate 3.660MPY where as the CM5510 steel nitride at 550°C/10 h (CM5510) had shown the corrosion rate 1.0853 MPY shown by CM5510. Bare steel CM0 had shown the i_{corr} value 8.678 E-6 amp/cm^2 whereas the nitrided steel CM5510 had shown 2.646E-6 amp/cm^2. CM556 steel had shown a better kinetics than CM0. For CM556 the i_{corr} value was 6.6645E-6 amp/cm^2 which is lower than 8.678 E-6 as shown by the steel CM0.

Finally, the Rp values for CM0 and CM5510 are significantly different which are 3006.1 and 9858.9 ohm/cm^2, respectively, exhibiting the better corrosion resistance by CN5510 steel. Steel CM 556 has shown E_{corr} value -0.56239 V which is more active than that of CM0 which has the E_{corr} value -0.4957 V. This means that the initial tendency towards the corrosion for as-received CM0 is lesser than that of the nitride steel CM556 and same is true for the nitride steel CM5510 which had shown the E_{corr} value - 0.57483 V.

Further to the above studies, an attempt had been made to understand the effect of temperature on corrosion resistance. Hence, the steel CM5010 nitrided at 500°C for 10 h exposed to the polarization tests in the similar experimental conditions. Corrosion current density i_{corr} and corrosion rate was found to be 3.8302E-6 amp/cm^2 and 1.6153 MPY, respectively.

On comparison, it can be concluded that these are marginally different than that of C5510 steel. Fig. 5 is the graphical representation of the trends in the variation of corrosion potential and corrosion current of CM556 and CM5510 steel where nitriding

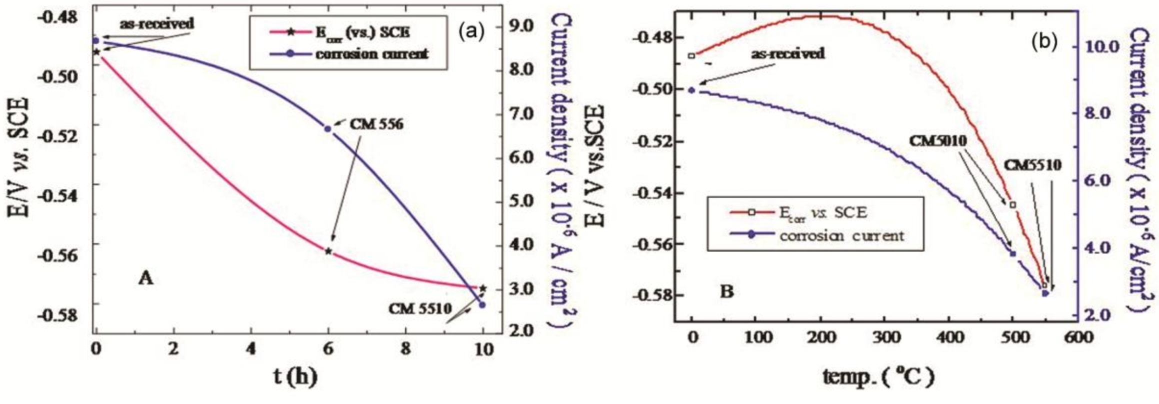

Fig. 5 — Graphs for variation of E/V vs. SCE and corrosion current density: (a) with respect to nitriding time 6 and 10 h for CM556 and CM5510, respectively, at a fixed temperature of 550°C and (b) with respect to nitriding temperature 500°C and 550°C for a fixed time of 10 h

Table 1 — Corrosion parameters obtained after Tafel extrapolation on polarization

Steel code	Corrosion rate (MPY)	Corrosion current i_{corr} (amp/cm^2)	Corrosion potential E_{corr}/ V*vs.* SCE	Rp (ohm/ cm^2)
CM0	3.660	8.678E-6	-0.4957	3006.1
CM556	2.8106	6.6645E-6	-0.56239	3914.3
CM5510 (Ref. 12)	1.0853	2.646E-6	-0.57483	9858.9
CM5010	1.6153	3.8302E-6	-0.5450	6810.9

performed at a fixed temperature of 550°C at the variable time of 6 and 10 h, respectively. Fig. 5b represents the similar trends for the CM5010 and CM5510 steels. It is obvious from these figures that the CM556 has higher corrosion current than CM5510 steel, similarly CM5010 and CM5510 had shown the marginal difference corrosion current and potential. Hence, it may be concluded that nitriding at 500°C as well as 550°C are the suitable temperatures for the improvement of corrosion resistance.

Steel CM556 had shown the corrosion rate 2.8106 MPY which is approximately double to that of the other nitrided steels. Moreover, it is worth noticing that the corrosion tendency found to be more in the initial stages in the nitrided steels than the bare steel CM0 steel, however in the later stages it has been found that the passivation is more pronounced in the nitrided steels. Thus, the passive layer formation on the surface slowed down the dissolution kinetics. Passivation might be due to the formation of Cr-oxide layer on the surface. Thus, it may be concluded that the corrosion resistance is better in steels after nitriding at 550 °C/10 h.

Surface Morphology by HR FESEM

One of the nitrided steels CM5010 with the best corrosion resistance had been selected for the understanding of surface damage. The bare and CM5010 steel had been exposed to HR FESEM analyses and represented in Fig. 6. It is obvious from Fig. 6a for the bare steel that the surface has undergone numerous pittings when compared to pitting of CM5010 steel (Fig. 6b). CM5010 shows almost uniform dissolution. This could be due to the presence of $Fe_{2\text{-}3}N$ (εN).

This observation is in accordance with the findings in corrosion tests. From XRD, it is revealed that the εN is dominating in steel nitrided at 550°C for 6 and 10 h. When compared to 6 h nitriding, steel nitride for 10 h had shown better resistance to corrosion, it may be because of the increased concentration of εN with increase in the duration of nitriding. εN found in these steels is beneficial from corrosion resistance point of view. Apart from this, nitrogen supersaturation in the crystal lattice is also responsible for the resistance to corrosion as it releases at the steel/electrolyte interface. The released nitrogen in the aqueous environment form ammonium hydroxide to form the electrolyte alkaline.

From the above observations, it is suggested that the improvement of corrosion resistance is significant in nitrided steels when compared to bare steel. Improvement of corrosion resistance may be attributed to the nitrogen inclusion in the solid solution and iron nitride. The present study shows that with the increase in duration of nitriding from 6 to 10 h the corrosion resistance increases. It could be due to the presence of higher concentration of nitrogen and iron-nitrides (εN).

Nitrogen in the solid solution when comes in contact with the aqueous electrolyte react to produce the reaction product as represented in potential-pH diagram for the system N-H_2O[24, 25]. In the surrounding of the surface/electrolyte interface nitrogen released from the solid solution produces thermodynamically stable NH_4^+, NO_2^-, and NO_3^- as the reaction products.

Chiba et al. suggested the formation of NO_3^- attributed to the passivation[26]. Baba et al. suggested

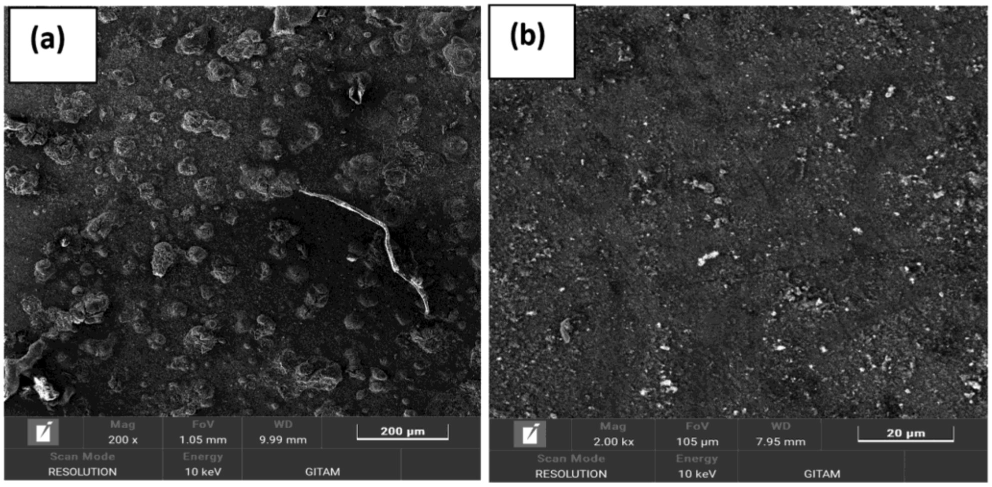

Fig. 6 — HR FESEM images of (a) CM0 (bare steel) and (b) CM5010 steel after potentiodynamic polarization in 3.5% NaCl

that the interstitial nitrogen with water forms NH^+ and OH^- ions [27]. Based on these ideas it may be concluded that the nitrogen solid solution is responsible for the wider passivation range or the kinetics of dissolution to be slow in the nitrided steels.

Conclusion

Plasma nitriding at the higher temperature of 550°C for 10 h improves the corrosion resistance of Cr-Mo-V tool steel. However, nitriding for shorter duration of 6 h had shown a wider passivation than the bare steel. In any case, the corrosion resistance for both the nitrided steels was found to be improved. Finally, it is concluded here that nitriding for 10 h is better than nitriding for 6 h for the better corrosion resistance. On the other hand, nitriding condition 500 °C/10 h proved to be better than 550 °C/6 h and almost similar to 550 °C/10 h from corrosion resistance point of view. Hence, longer duration of nitriding for 10 h at both the higher temperatures 500°C and 550°C may be recommended as suitable condition to enhance the corrosion resistance. The enhancement of corrosion resistance could be attributed to the presence of Fe_xN ($x \rightarrow 2$ to 3, 4) and nitrogen inclusion in the solid solution. But still it may be speculated here that the possibility of Cr-enrichment on the surface layer could be effective in improving the corrosion resistance and hence the passivation of the steel. Hence, further analysis of the surface layer is required to understand the presence of Cr/Cr_2O_3.

Acknowledgements

The authors thankfully acknowledge GITAM (Deemed to be University), Visakhapatnam, for the support and encouragements and granting the permission to present this work.

References

1 Sista V, Kahvecioglu O, Erylmaz O L, Erdemir A & Timur S, Electrochemical boridingand characterization of AISI D2 tool steel, *Thin Solid Films*, 520 (2011) 1582.

2 Steinmann P A & Hintermann H E, Adhesion of TiC and Ti(C,N) coatingson steel, *J Vac Sci Technol*, A3 (1985) 2394.

3 Staia M H, Perez-Delgado Y, Sanchez C, Castro A, Le-Bourhis E & Puchi-Cabrera E S, Hardness properties and high-temperature wear behavior of nitrided AISI D2 tool steel, prior and after PAPVD coating, *Wear*, 267 (2009) 1452.

4 Nouveau C, Djouadi M A, Marchal R & Lambertin M, Applications of hard coatings(Cr_XN_y) obtained by P.V.D. methods in wood machining, *Méca Indus*, 3 (2002) 333.

5 Van-Stappen M, Kerkhofs M, Stals L M & Quaeyhaegens C, State of the art for the industrial use of ceramic PVD coatings, *Surf Coat Technol*, 629 (1995) 629.

6 Ohring M, The material science of thin films, (San Diego: Academic) (1992).

7 Michler T, Influence of plasma nit riding on hydrogen environment embrittlement of 1.4301 austenitic stainless steel, *Surf Coat Technol*, 202 (2008) 1688.

8 Ramírez G, Mestra A, Casas B, Valls I, Martínez R, Bueno R, Goez A, Mateo A & Llanes L, Influence of substrate microstructure on the contact fatigue strength of coated cold work tool steels, *Surf Coat Technol*, 206 (2012) 3069.

9 Chen-Yi W, Fan-Shiong C, Characterization on multi-layer fabricated by TRD and plasma nitriding, *Mat Chem Phys*, 90 (2005) 178.

10 Nouveau C, Steyer P, Rao K R M & Lagadrillere D, Plasma nitriding of 90CrMoV 8 tool steel for the enhancement of hardness and corrosion resistance, *Surf Coat Technol*, 205 (2011) 4514

11 de Araújo L N M, de Araújo A G F, Ferreira M O G, de Sousa R R M, Cavalcante L S & Nunes L C C, Effect of plasma nitriding time on the structural and mechanical properties of AISI-O1 steel, *Eng Rep*, 2 (2020) e12279.

12 Bhadraiah D, Nouveau C & Rao K R M, Plasma nitriding of CrMoV steel for the enhancement of hardness and corrosion resistance trans, *Trans Indian Inst Met*, 75 (2021) 10.

13 Rao K R M, Trinadh K & Nouveau C, Low temperature plasma nitriding of martensitic stainless steel Trans, *Trans Indian Inst Metals*, 73 (6) (2020) 1695.

14 Bhadraiah D, Nouveau C & Rao K R M, Plasma based nitriding of tool steel for the enhancement of hardness, *Mater Today Proc*, 46 (2021) 940.

15 Godec M, Podgornik B, Kocijan A, Donik Č & Skobir-Balantič D A, Use of plasma Nitriding to improve the wear and corrosion resistance of 18Ni-300 maraging steel manufactured by selective laser melting, *Sci Rep*, 11 (2021) 3277.

16 Trinadh K, Nouveau C & Rao K R M, Effects of plasma nitriding on low alloy Cr-Mo-V steel, *Mater Today Proc*, 40 (2021) 579.

17 Wong-Ángel W D, Martínez-Trinidad J, Campos-Silva I, Hernandez-Hernandez V, Silva-Rivera U S & García-Leó R A, Wear corrosion synergy on Din-16MnCr5 steel under nitriding and post-oxidizing treatments, *J Bio Tribo Corros*, 7 (2021) 83.

18 Lee I, Optimization of processing parameters on low temperature plasma nitriding of AISI 420 Martensitic stainless steel, *Int J Min Mater Metall Eng*, 6 (2020) 18.

19 Rao K R M, Nouveau C, Lakshman S, Muralidhar P & Trinadh K, Effect of low and high temperature plasma nitriding on elctrochemical corrosion of steel, *Mater Today Proc*, 39 (2021) 1367.

20 Bhadraiah D, Nouveau C, Veeraswami B, Lakshman S & Rao K R M, Enhancement of hardness of low alloy steel after low temperature plasma nitriding, *Mater Today Proc*, 46 (2021) 689.

21 Najafizadeh M, Ghasempour-Mouziraji M, Sadeghi B & Cavaliere P, Characterization of tribological and mechanical properties of the Si_3N_4 coating fabricated by duplex surface treatment of pack siliconizing and plasma Nitriding on AISI D2 tool steel, *Metall Mater Trans A*, 52A (2021) 4753.

22 Naidu S S, Alphonsa J & Yadav N, Effect of nitrogen content in plasma nitriding of low carbon alloy steel, *AIP Conf Proc*, 2224 (2020) 040001.
23 Godec M, Podgornik B, Kocijan A, Donik Č & Skobir Balantič D A, Use of plasma nitriding to improve the wear and corrosion resistance of 18Ni-300 maraging steel manufactured by selective laser melting, *Sci Rep*, 11(2021) 3277.
24 You Y, Li R, Yan M, Yan J, Chen H, Wang C, Liu D, Hong L & Han T, Low-temperature plasma nitriding of 3Cr13 steel accelerated by rare-earth block, *Coatings*, 11 (2021) 1050.
25 Roine A, HSC chemistry thermo-chemical database, Version 9, Outotec Oy, Pori, Finland (2016).
26 Chiba A, Nagataki A & Nishimura T, Electrochemical aspects of interstitial nitrogen in carbon steel: Passivation in neutral environments, *J Electrochem Soc*, 164 (2017) C17.
27 Baba H, Kodama T & Katada Y, Role of nitrogen on the corrosion behavior of austenitic stainless steels, *Corros Sci*, 44 (2002) 2393.