



Science Arts & Métiers (SAM)

is an open access repository that collects the work of Arts et Métiers Institute of Technology researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <https://sam.ensam.eu>
Handle ID: <http://hdl.handle.net/10985/20098>

To cite this version :

Kalimi TRINADH, K. Ram Mohan RAO, Corinne NOUVEAU - Effects of plasma nitriding on low alloy Cr-Mo-V steel - Materials Today: Proceedings - Vol. 40, n°supplement 1, p.S79-S82 - 2021

Any correspondence concerning this service should be sent to the repository

Administrator : scienceouverte@ensam.eu





Effects of plasma nitriding on low alloy Cr-Mo-V steel

K. Trinadh^a, C. Nouveau^b, K. Ram Mohan Rao^{a,*}

^a Department of Chemistry, GITAM Institute of Science, Gandhi Institute of Technology & Management, Rushikonda, Visakhapatnam 530045, Andhra Pradesh, India

^b Laboratoire Bourguignon des Matériaux et Procédés (LaboMaP), Arts et Métiers Paris Tech de Cluny, Rue Porte de Paris, F-71250 Cluny, France

ARTICLE INFO

Article history:

Received 9 February 2020

Received in revised form 22 March 2020

Accepted 25 March 2020

Available online 4 May 2020

Keywords:

Corrosion

Plasma

Polarization

Steel

X-ray diffraction

ABSTRACT

In this study the effects on resistance to corrosion of a low alloy steel after plasma nitriding has been reported. Nitriding was performed at a low temperature of 450 °C and also at 520 °C for the same duration of 10 h in the plasma of nitrogen and hydrogen (80:20) gas mixture. Sample holder was biased at –250 V and the working pressure was kept at around 500 Pa.

After nitriding the steel samples along with the bare steel were exposed to X-ray diffraction (XRD) to understand the phase formation. For the assessment of corrosion resistance properties potentiodynamic polarization tests of the bare and plasma nitrided steels in 3.5% NaCl electrolyte were performed. Nitriding at 520 °C had shown the best corrosion resistance. However, broad passivation region had been shown after nitriding at 450 °C.

© 2020 The Authors. Published by Elsevier Ltd.

This is an open access article under the CC BY-NC-ND license (<https://creativecommons.org/licenses/by-nc-nd/4.0>). Selection and Peer-review under responsibility of the scientific committee of the 4th International Conference on Recent Advances in Material Chemistry.

1. Introduction

Corrosion is the environmental degradation of metal caused by chemical agencies commonly found in the environment. The process of corrosion continues until the materials fails and also it is difficult to be completely eliminated. However, the minimization of corrosion is more practical which can enable the materials to sustain for longer duration in the service life. Deposition of corrosion resistant layer though minimizes the corrosion, the disruption of the same speeds up the corrosion reaction due to the exposure of the materials surface along with the protective layer and hence the development of galvanic cells i.e. due to the change in electrochemical potential. Some other factors like oxide formation, diffusion of metal ions into the coated layer, change in local pH etc. affect the resistance to corrosion. However, surface alloying may overcome the problems caused by the delamination of corrosion protective deposition layer [1–4].

Evaluation of corrosion resistant layer by deposition or alloying for steels is important for prolonging the life of industrial components like tools, gears etc. Chromium-molybdenum-vanadium steel is low alloy steel which has good mechanical properties used as cutting/machining tools require attention for the improvement of

corrosion resistance. In the service conditions and also in the atmosphere the chloride ions are very commonly found corrosives which may attack these tools and ultimately cause the deterioration of the tools. Surface alloying is one of the important methods to enhance the resistance to the corrosive attack for prolonging the life of the tools.

The present studies relate the effects of plasma nitriding of chromium-molybdenum-vanadium steel on corrosion resistance in 3.5% NaCl electrolyte. Plasma nitriding is a cost effective, efficient and eco friendly method for surface modification of metallic materials to enable the surface more resistive to corrosion with improved fatigue and wear resistance [5–25]. Fernandes et al. [24] worked on plasma nitriding and nitrocarburizing of solution treated supermartensitic stainless steel and shown that surface hardness increases with temperature. Corrosion resistance was found to be better after plasma nitriding at low temperature of 400 °C than at 450 and 500 °C.

So far, plasma nitriding of 90CrMoV8 grade of steel has less been studied. Earlier Corinne et al. [5] studied the effects of plasma nitriding of the same steel to improve the mechanical and corrosion resistance properties. But the propensity towards the corrosion in wood juice was shown to be more. Rao et al. [6,7] has further extended the studies for achieving the improvement of hardness and corrosion resistance. This study had shown the significant enhancement of hardness after low temperature nitriding

* Corresponding author.

E-mail address: rammohanrao.k@gmail.com (K. Ram Mohan Rao).

at 450 °C for 6 h. Hence, in this study the nitriding temperature was chosen to be 450 °C but the time increased from 6 h to 10 h. The increase in nitriding time is known to increase the case depth which is evident from the previous study by Corinne et al. [5]. Nitriding at the higher temperature of 550 °C though increases the surface hardness but at the loss of core hardness, hence to avoid this risk the temperature was kept at 520 °C for the higher temperature nitriding and compared the corrosion resistance with the lower temperature nitrided steel sample.

2. Experimental

Steel samples of $8 \times 8 \times 5 \text{ mm}^3$ were cut from hardened and tempered steel sheet. The composition of the steel is given as: C-0.5%; Si-1.0%; Mn-0.5%; Cr-0.8%; Mo-1.5%; V-0.5% and Fe-balance. These samples were then mirror polished and cleaned in acetone ultrasonically. In the vacuum chamber of nitriding reactor samples were placed on the sample holder and evacuated to around 0.5 Pa. Sample holder was kept at around -250.0 V then fed the Ar gas raising the pressure inside the chamber to around 500.0 Pa as working pressure. Then the Ar + plasma was triggered by using the power supply. Ar + from the plasma was accelerated on to the surface which sputter cleaned the native oxide and dirt, if any. Thus the sputtering continued till the nitriding temperature

attained. The samples were heated to the temperatures of 450 and 520 °C maintained during the nitriding process. The nitrogen and hydrogen gas mixture (80:20) was fed into the vacuum chamber and triggered the plasma. Nitrogen ions were attracted towards the sample surface which on heating diffused into the bulk of the steel.

Nitrided and the bare steel samples were then subjected to X-ray diffraction (XRD) studies by using the Co $k\alpha$ radiation source (0.1790 nm). Corrosion resistance was assessed by following potentiodynamic polarization of nitrided and bare steels in 3.5% NaCl electrolyte by using Electrochemical Interface-Solatron Analytical, Model SI 1287, U.K. Cl^- ions are commonly found corrosive agent in the atmosphere and particularly in coastal areas hence NaCl environment was chosen for the corrosion tests. The calomel reference electrode, an auxiliary Pt. electrode and the steel/nitrided steel sample as working electrode constituted the electrochemical cell.

3. Results and discussions

3.1. X-ray diffraction (XRD) analyses

All the nitrided and bare steel samples were exposed to detailed XRD analyses. Fig. 1 SN (A) and SN (B) reveal the XRD patterns of

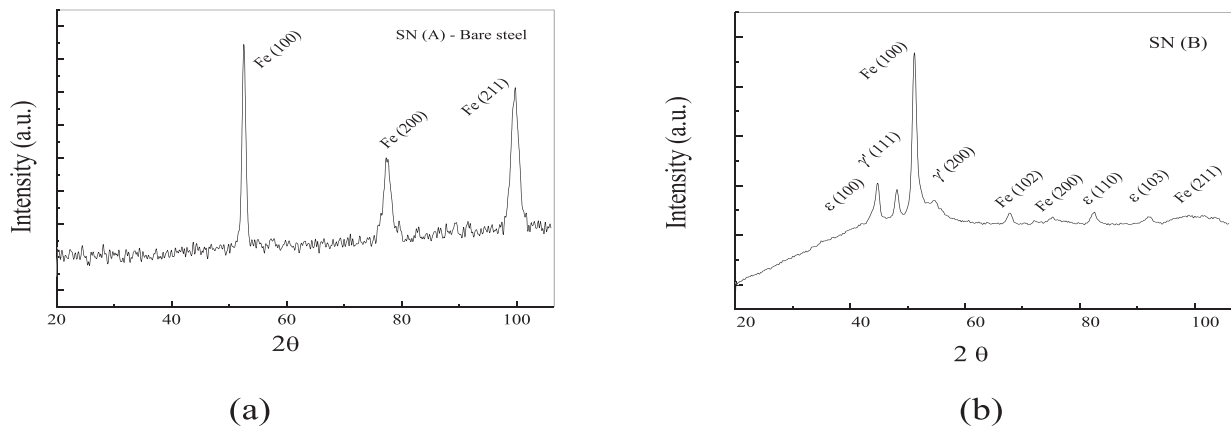


Fig. 1. X-ray diffraction patterns of bare steel (A); and plasma nitrided steel at 450 °C for 10 h (B).

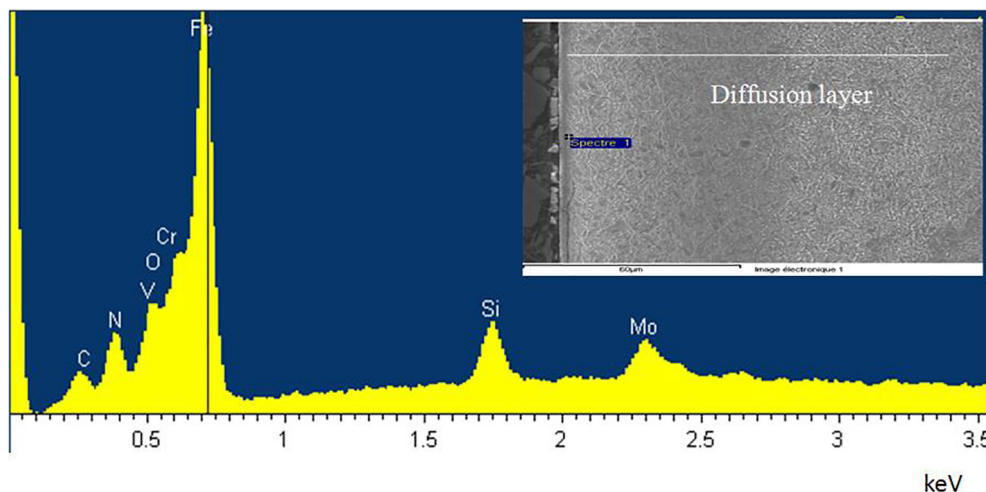


Fig. 2. Representation of the microstructure coupled with EDX elemental analysis of steel nitrided at 450 °C for 10 h as-revealed by scanning electron microscope (etched with Vilella's reagent).

the bare and nitrided steels respectively. The XRD patterns of bare sample reveal only the Fe (1 1 0), Fe (2 0 0) and Fe (2 1 1) phases (Fig. 1). XRD patterns of steel samples nitrided at 450 °C show the presence of Fe-nitrides Fe_xN ($x = 2, 3$) (Fig. B.). The iron nitride peaks are mainly γ' (Fe_4N) and the ϵN . Surface microstructure thus contains these two nitrides causing heterogeneity. This may lead to corrosion because of the different electrode potentials for these phases. However, when observed the entire surface as the iron matrix with the continuous dispersion of small precipitates of its nitrides the corrosion resistance may be enhanced. The assessment of corrosion resistance property is given in the following section.

3.2. Scanning electron microscopic (SEM) analyses

The nitrided steel was cut across the cross section and mirror polished. The cross sectional surface was then etched with the Vilela's reagent and then exposed to SEM to understand the microstructure of the modified surface. Fig. 2 shows the microstructure of the nitrided steel which reveals a very thin white layer. The presence of very thin layer on the surface is the indicative of mechanical integrity as the thick white layer is so brittle that causes the deterioration of the surface and/or degrading the steel by causing wear. The thin layer followed by the diffusion which consists of the iron nitride precipitates and the nitrogen

solid solution. These in turn attribute to the enhanced hardness and corrosion resistance. Similar is the case with the sample nitrided at 520 °C for the same duration of 10 h.

3.3. Potentiodynamic polarization

The bare and nitrided steels were exposed to 3.5% NaCl electrolyte and potentiodynamic polarization tests were conducted at room temperature. In Fig. 3 SN (A), (B) and (C) represent the polarization diagrams of the bare and nitrided steels at 450 and 520 °C respectively. Nitrided steels show more active potential than the bare steel. This means the propensity towards corrosion after nitriding is more. This could be due to the flaws on surface microstructure. Different nitrides on the surface γ' (Fe_4N) and ϵ -nitrides (Fe_{2-3}N) as evidenced by XRD analyses might have different electrode potential and/or may be the non uniform distribution of these phases on the surface might have caused the development of micro galvanic cells resulting in the corrosion of the steel. But after some time the rate of corrosion of bare steel is found to be faster than that of the nitrided steel as evidenced by the Fig. 3 SN (B and C). The wider passivation zone in the nitrided steel might be due to the the release of nitrogen from the solid solution in the electrolyte causing it to be more alkaline and thus minimizing the corrosion.

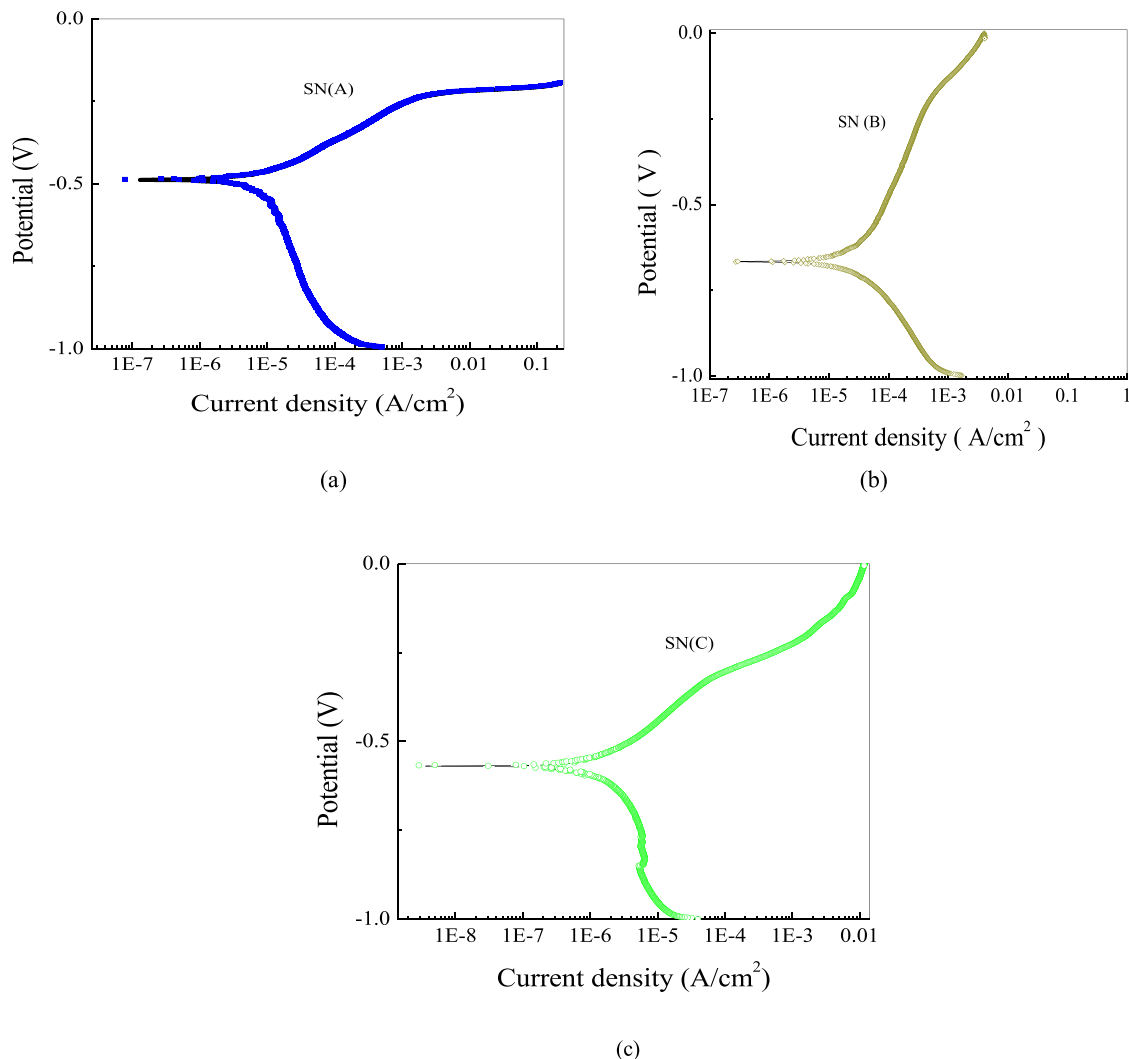


Fig. 3. Potentiodynamic polarization curves of (a) SN (A) (bare steel), and steel nitrided for 10 h at: (b) 450 °C (SN(B)) and (c) 520 °C (SN(C)) in an electrolyte of 3.5% NaCl.

When compared to the bare and the nitrided steel (at 450 °C) the rate of corrosion of the steel nitrided at 520 °C for the same duration of 10 h has shown the best corrosion resistance.

4. Conclusions

Low temperature plasma nitriding of chromium-molybdenum-vanadium tool steel at 450 °C for 10 h has successfully modified the surface by producing iron nitrides γ' (Fe_4N) and ϵ -nitrides (Fe_{2-3}N). The presence of these nitrides and nitrogen in the solid solution are found to be the reason to enhance the hardness and corrosion resistance. The steel nitrided at high temperature of 520 °C for the same duration the corrosion resistance was found to be much better than low temperature nitriding. Nitriding at 450 °C causes the corrosion initiation earlier than the bare steel may be because of the surface heterogeneity due to the dispersion of nitride precipitates. Moreover, a wider passivation zone in this nitriding condition is the indication of resistance to dissolution is better than that shown by the bare steel which is desirable. This could be due to the release of nitrogen from solid solution which increases the alkalinity of the electrolyte hence not favouring the dissolution kinetics. The improvement of both hardness and corrosion resistance would be the subject of further studies with the view to extend the application of this steel.

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.

Acknowledgements

The authors thankfully acknowledge GITAM (Deemed to be University), Visakhapatnam, Andhra Pradesh for the encouragements to perform this research and granting the permission for the presentation of the work.

References

- [1] M. Van Stappen, M. Kerkhofs, L.M. Stals, C. Quaeys, *Surf Coat Tech.* 629 (1995) 74–75.
- [2] C. Nouveau, M.A. Djouadi, R. Marchal, M. Lambertin, *Applications of hard coatings (Cr_xN_y) obtained by PVD methods in wood machining*, *Méca. Indus.* 3 (2002) 333.
- [3] M. Bader, H.J. Spies, K. Höck, E. Broszeit, H.J. Schröder, *Properties of duplex treated (gas-nitriding and PVD-TiN,-Cr2N) low alloy steel*, *Surf Coat Technol.* 98 (1998) 891.
- [4] A. Chala, L. Chekour, C. Nouveau, C. Saied, M.-S. Aida, M.-A. Djouadi, *Study of the duplex treatment on 32CrMoV13 low alloy steel: application in wood machining* *Surf. Coat. Technol.* 200 (2005) 512.
- [5] C. Nouveau, P. Steyer, K. Ram Mohan Rao, D. Lagadrillere, *Plasma nitriding of 90CrMoV8 tool steel for the enhancement of hardness and corrosion resistance* *Surf. Coat. Technol.* 205 (2011) 4514–4520.
- [6] H. Forati Rad, A. Amadeh, H. Moradi, *Wear assessment of plasma nitrided AISI H11 steel*, *Mater. Des.* 32 (2011) 2635–2643.
- [7] A. Mashreghi, S. Soleimani, S. Saberifar, *The investigation of wear and corrosion behavior of plasma nitrided DIN 1.2210 cold work tool steel*, *Mater. Des.* 46 (2013) 532–538.
- [8] A. Maniee, F. Mahboubi, R. Soleimani, *The study of tribological and corrosion behavior of plasma nitrided 34CrNiMo6 steel under hot and cold wall conditions*, *Mater. Des.* 60 (2014) 599–604.
- [9] J. O'Brien, D. Mand Goodman, *Plasma (Ion) Nitriding*, *Metals Handbook*, 190 American Society for Metals, Metals Park, OH, 1991, pp. 420–424.
- [10] R.M. Muñoz Riofano, L.C. Castteleti, L.C.F. Canale, G.E. Totten, *Improved wear resistance of P/M tool steel alloy with different vanadium contents after ion nitriding*, *Wear*, 265(2008) 57–64.
- [11] D. Cherng Wen, *Microstructure and corrosion resistance of the layers formed on the surface of precipitation hardenable plastic mold steel by plasma nitriding*, *Appl. Surf. Sci.* 256 (2009) 797–804.
- [12] C.X. Li, T. Bell, *Corrosion properties of plasma nitrided AISI 410 martensitic stainless steel in 3.5% NaCl and 1% HCl aqueous solutions* *Corr. Sc.* 48 (2006) 2036–2049.
- [13] M.K. Lei, Z.L. Zhang, *Surf. Coat. Technol.* 91 (1997) 25–31.
- [14] L. Chekour, C. Nouveau, A. Chala, M.A. Djouadi, *Wear* 255 (2003) 1438.
- [15] K. Ram Mohan Rao, Kalimi Trinadh, Corinne Nouveau, *Glow discharge plasma nitriding of low alloy steel*, *Mat. Tod. Proc.* 19 (2019) 864–866.
- [16] K. Ram Mohan Rao, K. Trinadh, C. Nouveau, *Low temperature plasma nitriding of low alloy steel for the enhancement of hardness*, *Mat. Tod. Proc.* 17(2019) 26–33.
- [17] M.T. Umemura, L.B. Varela, C.E. Pinedo, R.C. Cozza, A.P. Tschiptschin, *Assessment of tribological properties of plasma nitrided 410S ferritic-martensitic stainless steels* *Wear* 426–427 (2019) 49–58.
- [18] K. Trinadh, A.S. Corinne Nouveau, Karanveer S. Khanna, K. Ram Aneja, Mohan Rao, *Electrochemical study on the corrosion resistance of surface modified Cr-Mo-V steel by elevated temperature plasma nitriding*, *Mat. Res. Express.* 6 (2019) 076507.
- [19] Abdelrahman FARGHALI and Tatsuhiko AIZAWA, *Nitrogen Supersaturation Process in the AISI420 Martensitic Stainless Steels by Low Temperature Plasma Nitriding*, *ISIJ International*, 58 (2018) 401–407.
- [20] K. Ram Mohan Rao, K. Trinadh, Corinne Nouveau, *Effects on Corrosion Resistance of Low Alloy Steel*.
- [21] J. Alphonsa, S. Mukherjee, V.S. Raja, *Study of plasma nitriding and nitrocarburising of AISI 430F stainless steel for high hardness and corrosion resistance* *Corrosion Engineering, Sci. Technol.* 53 (2018) 51–58.
- [22] C.J. Scheuer, F.I. Zanetti, R.P. Cardoso, S.F. Brunatto, *Ultra-low-to high-temperature plasma-assisted nitriding: revisiting and going further on the martensitic stainless steel treatment*, *Mater. Res. Express* 6 (2019) 026529.
- [23] K. Ram Mohan Rao, Kalimi Trinadh, Corinne Nouveau, *Elevated temperature plasma nitriding and effects on electrochemical properties of steel*, *Mat. Tod. Proc.* (in press).
- [24] Frederico Augusto Pires Fernandes, Carlos Alberto Picone, George Edward Totten, Luiz Carlos Casteletti, *Material Research* 21 (2018) 1–9.
- [25] Insup Lee, *Optimization of Processing parameters on Low Temperature Plasma Nitriding of AISI 420 Martensitic Stainless Steel* *International Journal of Mining, Mater., Metall. Eng.* 6 (2020) 18–26.