



Effect of Pulse Repetition Time on Pulsed Plasma Nitriding of AISI 4340 Steel

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Abstract

In this work, Pulsed Plasma Nitriding (PPN) is carried out on AISI 4340 steel by varying the pulse repetition (PR) time from 100 to 500 μ s while keeping the pulse duration, nitriding temperature, time and gas ratio constant. The effect of pulse repetition time on surface hardness, compound layer and diffusion layer formation, crystalline phase composition and corrosion rate has been studied. Scanning electron microscopy investigation shows that thick compound layers are formed during continuous plasma nitriding while thin and heterogeneous layers are formed at 500 μ s PR. X-ray diffraction analysis shows that the samples treated with continuous plasma contain predominantly γ -Fe₄N and ϵ -Fe₃N and small quantity of Cr₂N. However, the samples treated at 300 μ s PR contain predominantly ϵ -Fe₃N with Cr₂N and trace of γ -Fe₄N. The base material exhibited a high corrosion rate, while the corrosion rate is minimum for the PPN samples treated at 300 μ s PR.

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Introduction

The AISI 4340 steel is widely used in automobile industry because of its excellent forgeability and hardening characteristics. The parts such as crankshafts, camshafts and valves are produced from this steel. These parts undergo wear and fatigue during service and the as-produced material cannot be used till the life cycle of these parts. Numerous surface engineering techniques are available for improving the surface properties and enhance the fatigue life of this material [1-3]. Pulsed Direct Current (D.C) glow discharge is one of the modern surface hardening techniques, which uses plasma (ion) for the nitriding of steel parts [4]. As the kinetic energy of plasma is higher than gas, nitriding can take place in a shorter duration [5]. Typical pulsing system patented by ELTROPULS, GmbH has been used widely [6]. The nitriding reaction takes place at the surface and subsurface of the substrate through the diffusion of nitrogen atoms. The surface layer, also called as compound layer, is a thin layer made of a mixture of iron nitrides (γ -Fe₄N and/or ϵ -Fe₃N). This compound layer is considerably hard and possesses very good wear and corrosion resistance than untreated base material. It has been reported that, there is a preference of monophasic layers over biphasic layers due to difference in lattice structure and its associated stress components [7]. The diffusion zone, which is softer than compound layer, consists of very fine nitride particles dispersed in the subsurface of the substrate [8].

Some researchers have reported the effect of pulsed plasma nitriding variables such as temperature, time, duty cycle (10-80% t_{ON}), frequency, component geometry and gas ratio (50% N₂-50% H₂) on surface properties of AISI 4340 steel [9-12]. There is limited information on the effect of duty cycle by varying the pulse repetition and maintaining the gas ratio of 75% N₂-25% H₂ on the properties of AISI 4340 steel. The increase of nitrogen gas percentage is associated with the increase of nitrogen potential and that can promote the formation of ϵ -Fe₃N phase, which is

responsible for high wear and corrosion resistance than the γ -Fe₄N [4,20]. The pulse repetition time is related to the ionisation potential and the diffusion of nitrogen would be more when pulse repetition time is less.

It has been reported that the effect of duty cycle by varying the pulse duration from 10% to 80% resulted in a null effect on crystalline phase composition of AISI 4340 steel plasma nitrided at 540°C, 4 h using gas ratio of 50% N₂- 50% H₂ [9]. Similar plasma nitriding experiment was carried out at 500°C with a gas mixture of 25% N₂- 75% H₂ on AISI 4340 steel and found that the gas mixture ratio plays a vital role in formation of γ -Fe₄N and ϵ -Fe₃N nitrides [10]. It has also been reported that the single γ -Fe₄N phase is formed only when the gas mixture ratio resembles that of ammonia (NH₃) and the plasma is free of any carbon contamination. If the plasma contains traces of carbon, the ϵ -Fe₃₋₂N is formed (this could be possibly Fe₃₋₂N_xC_y). Formation of homogeneous ϵ layer is difficult to obtain due to the variation in substrate carbon level, which changes with the gas mixture. The other work published on AISI 4140 steel pulsed plasma nitrided at 500°C with a gas mixture of 25% N₂- 75% H₂ with the pulse on/off time of 70-200 μ s for a duration of 1, 2, 4, 15, 20 and 28 h reported that the increase of nitriding time changed the microstructure from dual phase (γ -Fe₄N and ϵ -Fe₃N) to monophasic (γ -Fe₄N) and the compound layer thickness did not follow a parabolic law with the treatment time [13].

It has also been reported that, in special circumstances the steel specimens are electroplated with nitride forming elements such as chromium, molybdenum and then plasma nitrided to enhance the corrosion resistance by forming alloy nitrides on the surface which suppresses the corrosion rate in a higher order [18,22]. Other researchers have also reported that the oxidized samples were having higher corrosion resistance than nitrided samples [23,33]. The specialty of this research work is to optimize the compound layer properties by varying the pulse repetition duration. In pulsed

plasma Nitriding, pulse duration and pulse repetition duration plays vital roles and in general, the pulse duration is varied while keeping the pulse repetition as constant, and the nitriding properties were studied whereas, this research work focuses on pulse repetition duration and study the Nitrided compound layer properties. The selection of pulse repetition duration is to understand its maximum effect on Nitriding. This pulse repetition duration can be varied from 50 millisecond to 500 millisecond. Hence, an attempt has been made to optimize the pulse repetition duration by studying its effect on AISI 4340 steel. The hardness, compound layer properties and corrosion resistance of this steel have been investigated after pulsed plasma nitriding.

Experimental

Medium carbon low alloy steel (AISI 4340) with a typical chemical composition (wt-%) of Fe-0.38C-0.017S-0.63Mn-0.008P-0.19Si-1.18Cr-1.64Ni-0.2Mo was selected (base material-BM), and the steel has the microstructure of tempered martensitic and upper bainitic (Figure 1) with an average hardness of 250 ± 20 HV1 [4,16,17]. Samples of dimensions 25 mm diameter and 20 mm height were machined, ground and polished to a surface roughness (R_a) of $0.1 \mu\text{m}$ (maximum). The samples were then ultrasonically cleaned to remove fine residues. The samples were pulsed plasma nitrided in ELTROPULS chamber. The process parameter details are given in Table.1. Prior to nitriding process, a sputter cleaning process was carried out using hydrogen gas to remove the passive layers on the surface. During sputtering a small amount of material is removed from the surface [6]. The samples nitrided with continuous plasma are designated as PR-0 and the pulsed plasma nitrided samples for PR times of 100, 200, 300, 400 and 500 μs are designated as PR-100, PR-200, PR-300, PR-400 and PR-500, respectively.

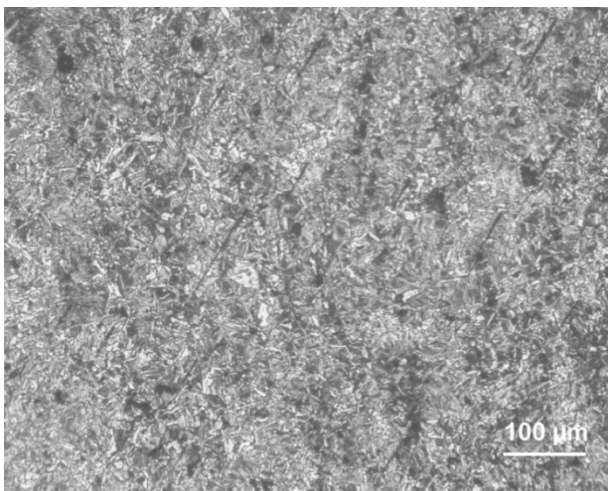


Figure 1: Microstructure of AISI 4340 steel showing tempered martensitic structure.

Table 1: Pulsed plasma nitriding process parameters.

Process parameters	Experimental levels
Plasma nitriding temperature	550°C
Nitriding duration	5 hours
Pulse duration	50 μs (fixed)
Pulse Repetition (PR) time	100 μs to 500 μs
Gas ratio ($\text{H}_2:\text{N}_2$)	1:3
Pressure (mbar)	260
Voltage	500 V

After plasma nitriding, the samples were carefully sectioned, polished with a series of emery papers from coarse to fine type followed by cloth polishing with an application of 1 to 3 μm diamond suspensions to obtain a mirror finish for metallographic studies. The surface hardness was measured using Shimadzu Vickers hardness tester with 1 kg load and dwell time of 10 seconds. Case depth was found out by the depth up to which the hardness is 50 HV higher than the core hardness [14,15]. The microstructure was revealed by etching the specimen using 2% Nital (2 mL HNO_3 in 100 mL ethanol) and the compound layer thickness was determined by FEI Quanta 200 Scanning Electron Microscope (SEM).

The formation of iron-nitride phases, and other alloy nitrides plays significant role on overall properties [8-9,16-18]. Hence, in order to identify the crystalline phases of PPN samples, X-ray diffraction (XRD) analysis was done using $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation within a 2θ range from 30° to 90° .

The corrosion resistance of nitrided samples was assessed by potentiodynamic polarization tests in a 3.5 wt% NaCl saline solution. The polarization curves were recorded from -1200 mV to +200 mV with the scan rate of 1.0 mV/s. The test specimen is made in contact with the prepared saline solution and the graphite electrode and standard calomel electrode are being used as an auxiliary and reference electrode. The corrosion rate was calculated by using Tafel extrapolation method. After polarisation test, the samples were examined under SEM to study the corroded surface.

Results and Discussion

Microstructure and hardness

The surface properties of PPN samples such as surface hardness, case depth and compound layer thickness are shown in Figure 2. The formation of iron nitrides (precipitate particles) is responsible for the increase of surface hardness. The variations in surface hardness at different pulse repetition durations could be due to the different types of nitrides formation [19]. The kinetics of the formation of compound layer was influenced by the sputtering rate (SR) and the amount of carbon in the steel [7]. This sputtering rate is influenced by different gas compositions and it increases with nitrogen gas percentage [4,6]. The increase in compound layer and diffusion layer thickness during the increase of pulse duration or decrease of pulse repetition could be related to the concept of ion fluence (F), which is defined as the quantity of ions impinging on the surface of the samples during a single pulse of length t_p (pulse duration). According to Lopez-Callejas et al., based on Child-Langmuir law and after some considerations, the ion fluence is denoted by F which is given in equation 1.

$$F = n(s(t) + t_p \left(\frac{kT_e}{M} \right)^{1/2}) \quad (1)$$

where n is the electron plasma density, $s(t)$ is maximum sheath width, k is Boltzmann constant, T_e is electron temperature, M is the ion mass and t_p the pulse length. Since the discharge parameters were kept constant during processing, and it is expected that the electron plasma density and electron temperature were constant in all experiments, and the main effect on fluence is given by the pulse length. Thereby, the increase in the pulse duration will directly increase the quantity of ions impinging on the surface of samples leading to a higher availability of nitrogen to be introduced on the surface of the samples. Hence, nitrogen diffusion process towards substrate will occur at a higher rate and thicker nitrided layers will be obtained [20]. The formation of precipitate particles can hinder dislocation motion and therefore, slip band penetration through the nitrided layer. A diffusion layer, which is

formed during ion nitriding process, causes compressive residual stresses on or near the surface of machined parts, as well as low tensile residual stresses in the core [21,30].

In any diffusion controlled process, the thickness of the compound layer increases when duration of the nitriding increases [8,19,30]. Similarly, the effect of nitriding potential increases the sputtering and re-deposition activity and thus compound layer

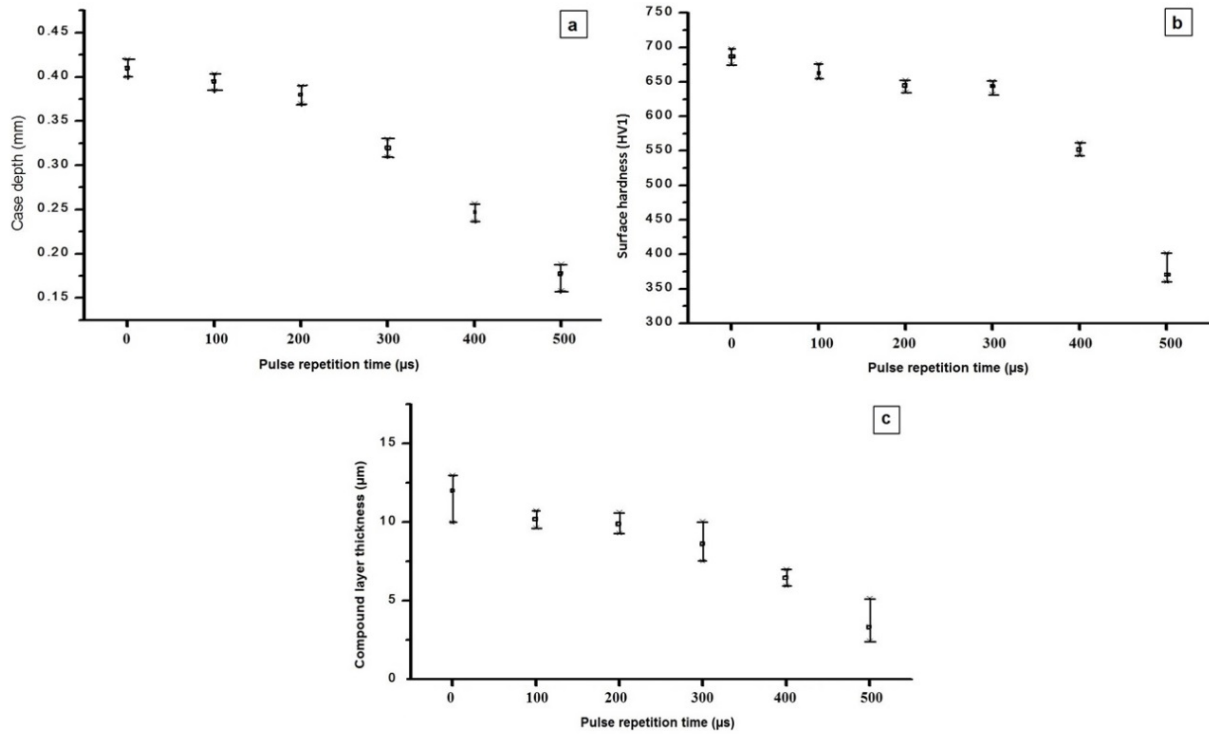


Figure 2: Surface properties of PPN samples at different pulse repetition times; (a) Case depth, (b) Surface hardness, and (c) compound layer thickness.

The ionisation potential/Ion fluence is inversely proportional to pulse repetition time. As shown in Figure 2(b), the surface hardness decreases when pulse repetition time increases. The high surface hardness, case depth and compound layer thickness are achieved after continuous plasma nitriding and the observed values are approximately 700 HV1, 420 µm, and 12.7 µm, respectively. Similar hardness values (666 HV1) are obtained for PR-300 sample. The steep decrease in surface hardness in PR-500 sample is due to negligible ion fluence/ionisation potential. Increasing the pulse repetition time beyond 300 µs will not be effective for the effective diffusion layer formation. The nitrogen transfers across the sample surface would increase when the ion fluency is more that can increase the diffusion layer (case depth) significantly. When the ion fluence/ionisation potential is not enough for the diffusion of nitrogen, the case formation and compound layer formation are affected. The reason for steep reduction in surface hardness at PR time of 500 µs is due to very low ionisation (glow discharge) potential conditions established at the sample surface during nitriding. The formation of iron nitrides is reduced due to limited amount of nitrogen diffusion into the subsurface; however, the observed hardness values are marginally higher than the core hardness values. This result can be explained by the time (glow) dependence of nitride precipitates dispersion within the matrix. Precipitates of certain size will be the more effective in obstructing the movement of dislocations, resulting in maximum strengthening and hardening [7-9]. In order to obtain the effective precipitate particle size and higher precipitate density, optimum pulse repetition time is needed for a given nitriding duration. The error bars in Figure 2 show the mean absolute deviation of 10 measurements in random regions of the sample. The hardness variations within the sample readings are due to synergy effect of compound layer, diffusion zone and substrate hardness.

formation [8]. The SEM micrographs (Figure 3) show compound layer thickness of samples at different PR times.

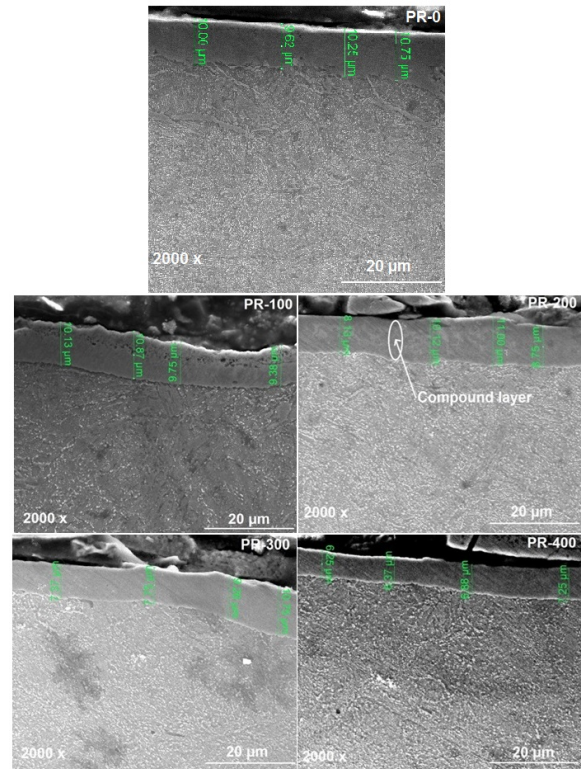


Figure 3: Typical SEM images of PPN samples treated at different PR time.

The higher compound layer thickness of 12.7 μm was observed in PR-0 sample (100% duty cycles). When PR time increases, the compound layer thickness decreases. The reason for thickness reduction on the surface of the specimen is due to low nitrogen activity (ionisation potential) in the treatment atmosphere especially at the surface of the specimen [19,20]. Researchers have also reported that on increasing the nitride forming alloying elements, such as chromium, the growth rate of compound layer is decreased due to the higher demand for nitrogen [4,17]. This is evidenced at PR-300 sample, where strong Cr_2N formation is observed, which could have hindered further diffusion layer formation. However, the surface hardness is significantly higher (666 HV1) than PR-200 sample (655 HV1). The PR-0 samples have a high surface hardness (689 HV1), compound layer (12.7 μm) and diffusion layer thickness. The reduction of both case depth and compound layer is more significant when PR times are 400 μs and 500 μs . The average compound layer thicknesses observed are 6.7 μm for PR-400 samples and 3 μm for PR-500 samples.

Phase Analysis through X-Ray Diffraction

The XRD patterns of base material and PPN samples are shown in Figure 4. The XRD pattern of base material (BM) reveals the presence of $\alpha\text{-Fe}$. The PPN samples (PR-0, 100, 200 and 300) have mixed phases containing gamma nitride ($\gamma\text{-Fe}_4\text{N}$; JCPDF Number: 83-0875) and epsilon nitride ($\epsilon\text{-Fe}_3\text{N}$; JCPDF Number: 83-0878). The PR-400 and PR-500 samples have epsilon nitrides of Fe_3N (JCPDF Number: 76-0091) and $\text{Fe}_{2.3}\text{N}$ (JCPDF Number: 73-2102) [19,20]. In the case of PR-300 samples, there is also a strong diffraction line of chromium nitride (Cr_2N ; JCPDF Number: 79-2159) due to the presence of chromium in the base material, which is one of the major nitride forming alloying elements [17,21-22]. The formation of $(\text{CrFe})_2\text{N}_{1-x}$ nitride in the PR-300 sample is due to the replacement of Fe atoms by Cr atoms in the nitrides, forming mixed nitrides, which have been reported by other authors also [28,29].

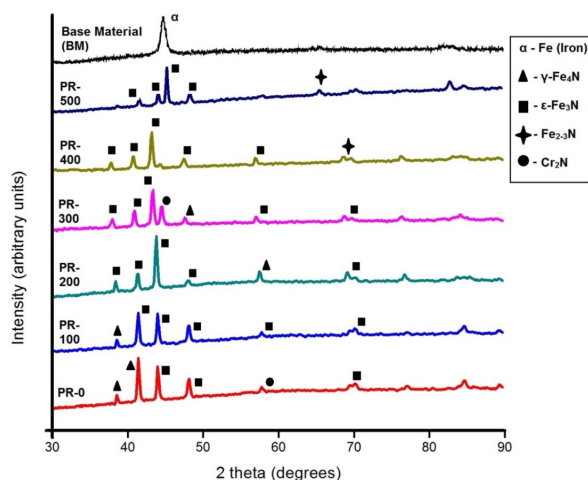


Figure 4: XRD patterns of pulsed plasma nitrided samples at different pulse repetition times.

It is said that, upon diffusion of nitrogen into the specimen and formation of compound layer, chromium carbides normally present in the compound layer tend to convert to chromium nitrides or carbo-nitrides. The same has been observed in PR-300 sample. Consequently, (some) carbon will be liberated which can diffuse to either side of the compound layer and enrich those regions with carbon. The formation of randomly distributed chromium nitride particles and the introduction of large internal stresses are responsible for high hardness. This implies that the formation of

homogeneously nitrided matrix is mainly responsible for the surface hardening, rather than simply a precipitated iron nitride phase [17,34]. For a duty cycle of 100% (PR-0), the compound layer constitutes mixed phases of predominantly $\gamma\text{-Fe}_4\text{N}$ and then $\epsilon\text{-Fe}_3\text{N}$ with small quantity of Cr_2N (JCPDF Number: 79-2159) phase. At 50% duty cycle (PR-100), the compound layer consists of a mono-phase ($\epsilon\text{-Fe}_3\text{N}$) structure with minor quantity of $\gamma\text{-Fe}_4\text{N}$. This can be explained by the diffusion of carbon outward from the steel during nitriding, leading to decarburization of the steel surface and the destabilization of $\epsilon\text{-Fe}_3\text{N}$ phase [4,7,18]. In contrast to the expected formation of $\epsilon\text{-Fe}_3\text{N}$ at high nitrogen gas atmosphere (75% N_2 -25% H_2), the formation of $\gamma\text{-Fe}_4\text{N}$ is associated with the sputtering effect which increases with duty cycle and shift the formation of $\epsilon\text{-Fe}_3\text{N}$ to $\gamma\text{-Fe}_4\text{N}$. This has been confirmed with other research works, i.e., nitriding in atmospheres with higher nitrogen concentrations such as 50%, 75%, and even 100%, did not result in production of an ϵ monophase layer but a dual phase ($\epsilon+\gamma$) compound layer. Low proportions of nitrogen and carbon in these layers is believed to be the main reason for the tendency for γ phase formation [17,35]. When the duty cycle is reduced to 25% (PR-200), the formation of monophasic $\epsilon\text{-Fe}_3\text{N}$ is observed with the trace of $\gamma\text{-Fe}_4\text{N}$. It has been reported that the pulse repetition duration could be varied from 0 to 300 μs for better nitriding properties for the intended service applications [5]. When the duty cycle was reduced further to 17% (PR-300), the results are similar to the duty cycle of 25% with the strong intensity of Cr_2N . PPN samples with duty cycle of 13% (PR-400) and 10% (PR-500) show weak intensities of Fe_3N and $\epsilon\text{-Fe}_{2.3}\text{N}$ due to the reduced glow discharge as discussed earlier. Hence, the duty cycle has to be optimized for the required compound layer composition. The pulse repetition study suggests that, it is possible to obtain monophasic layers of either $\gamma\text{-Fe}_4\text{N}$ or $\epsilon\text{-Fe}_3\text{N}$ through the manipulation of nitriding pulse repetition time.

The development of $\gamma\text{-Fe}_4\text{N}$ or $\epsilon\text{-Fe}_3\text{N}$ monophasic layers can be related to both ion population and sputtering phenomenon. By reducing the pulse repetition duration, the plasma ion population can be increased allowing more nitrogen and consequently increasing the incorporation rate of nitrogen atoms on the steel surface. Thus, the $\epsilon\text{-Fe}_3\text{N}$ will be expected at reduced pulse repetition duration. However, the presence of $\epsilon\text{-Fe}_3\text{N}$ phase is inhibited by sputtering phenomenon which increases at reduced pulse repetition duration (or high duty cycle). This phenomenon promotes surface decarburization in nitrided steels, allowing the stabilization of $\gamma\text{-Fe}_4\text{N}$ phase instead of $\epsilon\text{-Fe}_3\text{N}$ phase even though the nitrogen potential is higher at the surface [4,7]. This phenomenon can be explained by during shorter nitriding or increased pulse repetition duration, the carbon atoms were diffused to the surface and by reacting with iron and nitrogen, helped in the formation of epsilon phase. In the case of long nitriding duration or reduced pulse repetition duration, the surface got decarburized which means that, the carbon was sputtered away and replaced by nitrogen. With the lack of carbon atoms, the nitriding potential of the plasma was shifted towards gamma prime, the lower nitrogen phase and the epsilon phase got disappeared completely. As we know that, the presence of carbon stabilizes the epsilon phase due to the very wide solubility range of both for nitrogen and carbon atoms. Steel contains more carbon develops more epsilon phase during nitriding and consequently the epsilon peak in difference is more intense. The rate of sputtering (SR) has been reported in the literature is 0.124 $\mu\text{m/h}$ to 0.427 $\mu\text{m/h}$ for nitriding temperatures ranging from 530 C to 570 C. Also, it has been reported that for a gas mixtures of 50% N_2 +50% H_2 , the sputtering rate of 0.425 $\mu\text{m/h}$ was observed with gamma and epsilon nitrides are being the primary constituents in the compound layer. In this case, the nitriding potential was higher. Similarly for a gas mixture of 15% N_2 +85% H_2 , SR=0.036 $\mu\text{m/h}$ was observed with gamma

nitrides alone are the predominant phases in the compound layer. When the gas mixtures of 75%N₂+55%H₂, the sputtering rate might be probably on the higher side which is well enough to remove the surface carbon and influences the crystalline phase composition [17,36].

Potentiodynamic studies

Potentiodynamic polarization diagrams of PPN samples are shown in Figure 5. It is observed from the Tafel plot that the increase of PR time increases the corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate ($A\text{ cm}^{-2}$). The corrosion improvement phenomena can be attributed to the presence of dense nitride layers formation on the surface. As nitride is a noble phase, the formation of more nitrides helps to cover the surface from the corrosion attack. The presence of mixed phases of iron nitrides (epsilon and gamma prime) is responsible for increase of corrosion resistance. This can be explained that, the denser the coverage, the lesser would be the corrosion rate and vice versa. The increase of corrosion rates are due to reduction of iron and alloy nitrides on the surface which makes the saline solution to penetrate into the voids of nitrides on the surface and attack the grain boundaries and increases the dissolution rate of the sample.

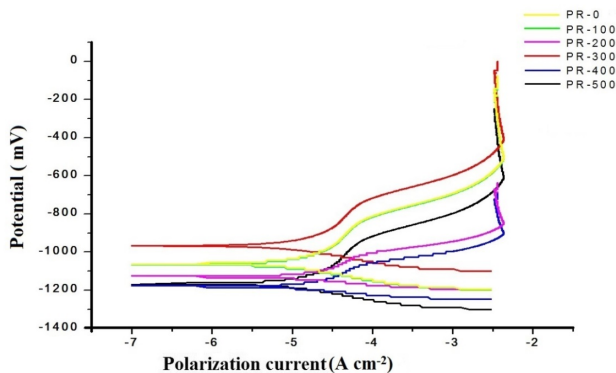


Figure 5: Tafel plots of PPN samples at different pulse repetition times.

The untreated sample (base material) shows a high corrosion rate of $4.2 \times 10^{-5} A\text{ cm}^{-2}$ than PPN samples. Among the PPN samples, a high corrosion rate of $1.8 \times 10^{-5} A\text{ cm}^{-2}$ is observed for PR-500 sample and the least corrosion rate of $3.7 \times 10^{-6} A\text{ cm}^{-2}$ is observed for PR-300 sample. The corrosion rate of PR- 0, 100, 200, and 400 samples are $5.8 \times 10^{-6} A\text{ cm}^{-2}$, $5.7 \times 10^{-6} A\text{ cm}^{-2}$, $6.6 \times 10^{-6} A\text{ cm}^{-2}$ and $1.4 \times 10^{-5} A\text{ cm}^{-2}$, respectively. All PPN samples show a passivation behavior by shifting the corrosion potential towards noble direction which is an indication of reduced corrosion rate. The higher corrosion potential and lower corrosion rate of PPN samples are due to the formation of dense and thick compound layer, which aids the passivation and prevents saline solution penetration.

It is clear from the Tafel plot that the increase of PR time increases the corrosion rate by increasing the corrosion current significantly. However, the least corrosion rate observed for PR 300 sample is due to the presence of strong chromium nitride formation as evidenced from XRD pattern (Figure 3). This chromium nitride(Cr_2N) is ductile and corrosion resistant than the other phases, which can enhance the corrosion resistance significantly. The presence of less dense nitrides and pores on the nitrides can affect the corrosion behavior of the treated steels. The increase of corrosion resistance in the presence of Cr_2N is due to the fact that nitrogen ions in the nitrided layer first dissolve into the solution, and then could repel the chloride ions (Cl^-) away from the sample surface [13,24-26]. The nitrogen anion (N^-) then combines with hydrogen ion (H^+) in the solution to form the ammonium ion (NH_4^+) resulting in an increase of solution pH, which can decrease

the corrosion attack from the solution [33]. The finding shows that, the increase of PR time beyond 300 μs will be of no use, since there is a steep increase of corrosion rate due to reduction in compound layer thickness. In the case of PR-100 sample, mixture of gamma and epsilon nitrides with traces of chromium nitride is noticed.

The polarization tested samples surface were examined under SEM to see the corroded surface since the reaction takes place only with the surface (Figure 6) which is in par with the other research works. The surface of the corrosion tested samples reveals mixed morphologies due to the difference in nitriding conditions. The formation of dense nitrides (PR-300) suppresses the oxidation reaction with the compound layer by maintaining the solution hydrogen potential on the positive side. The effect of pores formation during nitriding and its effect on corrosion are not much studied. However, these pores will have a significant effect on the corrosion resistance. Typically, these pore sizes are ranging between 5 μm and 10 μm . Sometimes, these pores are helpful by retaining the lubricants for lubrication purpose. The increase of pulse repetition duration increases the pores formation and the surface is not formed with dense nitrides and thick compound layers [23].

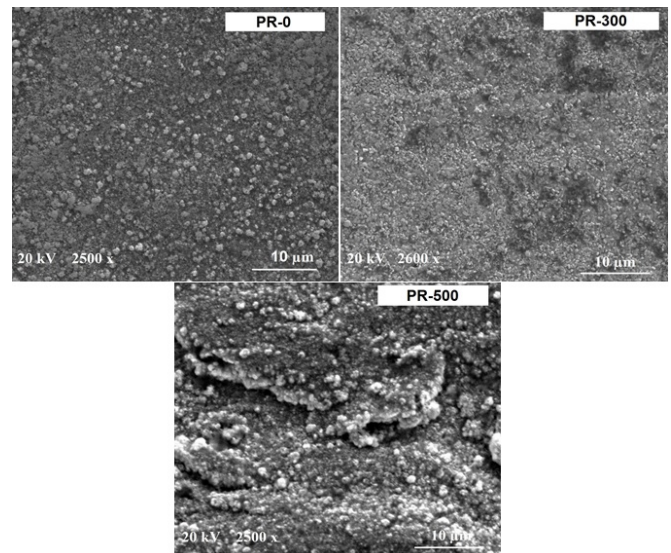


Figure 6: SEM images of corrosion tested PPN samples.

The PR-0 sample exhibits negligible corrosion due to the presence of dense nitrides with significant amount of chromium nitrides. In the case of PR-300 sample, the mixture of chromium and iron nitrides makes the surface more resistant to corrosion attack as it is seen from the SEM image. The PR-500 sample shows the presence of discontinuous nitrides and the variation in compound layer thickness, which makes the surface prone for corrosion attack.

Conclusions

Pulsed Plasma Nitriding process increases the surface hardness of AISI 4340 steel significantly. The surface hardness, compound layer and diffusion layer thickness are increased when pulse repetition time is reduced.

The formation of different nitride phases also depends on pulse repetition time. The plasma nitriding process increases the corrosion resistance of this steel. The corrosion resistance also depends on the pulse repetition time, since it controls the nature of nitrides formed on the surface.

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