Chapter 5

Plasma Nitriding of SMATed AISI 2205 Steel

5.1 Introduction

Duplex stainless steels are known for their high strength and corrosion resistance. However, low surface hardness limits their use in high wear resistant applications. A surface thermochemical treatment, like nitriding, is used to improve the surface properties by diffusion of nitrogen in the surface [1]. In addition to that, surface severe plastic deformation process, like shot peening, also enhances the nitriding kinetics by providing higher dislocations and grain boundaries, which act as the additional diffusion channels [1], and consequently, hardness and wear resistance of the surface are improved. Similar to the shot peening, surface-mechanical-attrition-treatment (SMAT) is also the severe plastic deformation process to produce the ultra-fine grains in the surface region of the steels [2–4]. However, SMAT is fundamentally different from the shot peening. SMAT modifies the coarse grains at the specimen surface to nano-grains through accumulative strain, which is obtained by continuous impact of the randomly moving balls ($\phi \sim 3$-$12$ mm) with a velocity in the range of 0.5 to 20 m/s for 15-$300$ min duration [2–4]. Nano-grains (15-50 nm size) are observed in the SMATed surface of AISI 304L and Ni-Cr-Mo steels [2, 5]. Standard details about the working principle of SMAT are available elsewhere [2–6].

Improvement in plasma-nitriding kinetics for AISI 316 steel [7] and low temperature boronizing of Ni-Cr-Mo steel [5] due to the SMAT is reported previously. Previous studies have reported that SMAT of AISI 316L [8] and AISI 316 [9] steels produces the thicker oxides on the surface, which restricts the nitrogen transfer through the surface during low temperature plasma-nitriding. It appears that, the effect of passivation of the severely deformed austenitic stainless steels on the plasma-nitriding behavior depends on the chemical composition of the stainless steel, atmosphere in which severe plastic deformation is conducted (vacuum or atmospheric condition) and the selection of plasma-nitriding parameters.

In the current study, AISI 2205 duplex stainless steel is selected. AISI 2205 steel is the dual phase material (typically, about 50% austenite and 50% ferrite). Due to its low
hardness, its application is restricted. A considerable amount of work has been reported in
the literature about the plasma-nitriding response of the SMATed steels. However, as per
our literature review, almost no information is available to correlate the passive behavior
of SMATed duplex stainless steel with the plasma-nitriding response.

This study is aimed to understand the effect of SMAT on the corrosion resistance of AISI
2205 steel through open circuit potential (OCP) measurement, electrochemical impedance
spectroscopy (EIS) and potentiodynamic polarization study. Furthermore, the knowledge
of corrosion study has been extended to understand the role of passivation and chemical
etching/cleaning on the plasma-nitriding behavior of the steel. Effect of surface roughness,
induced by the SMAT, on corrosion and nitriding behavior is also investigated by using the
intermediate step of polishing of the SMATed specimens.

5.2 Experimental

SMAT was performed on the commercially available AISI 2205 duplex stainless steel sheets.
Chemical composition of the steel is as follows (wt.-%): 0.027%C, 1.57%Mn, 22.95%Cr,
5.60%Ni, 3.08%Mo, 0.26%Si, 0.005%S, 0.025%P and balance Fe. Before SMAT the speci-
mens was undergone solution annealing at temperature 1100°C (2 h soaking) followed by
water quench. Specimens of size 20 mm × 70 mm × 4 mm were prepared from AISI 2205
steel sheets. Mirror polished specimens were prepared by using standard mechanical polish-
ing techniques of metallography.

In-house developed SMAT-setup was used in this study. This setup consisted of electro-
magnetically driven vibrating SMAT cabin (circular with φ 80 mm), where the frequency
of vibration was 100 Hz. Bearing steel-balls of 3 mm diameter (65 HRc) were used for
the SMAT. SMAT was performed on the specimens at atmospheric condition. Specimen
conditions, SMAT parameters and designation of the specimens are given in Table 5.1. Af-
fter SMATing, specimens were plasma-nitrided. Prior to the nitriding, the specimens were
degreased by ultrasonic cleaning in the acetone followed by cleaning with distilled water.
Plasma-nitriding parameters are given in the Table 5.2. In plasma nitriding, there is a prior
step of cleaning of specimen surface in H₂ atmosphere (H₂ plasma) for a particular duration
at the required nitriding temperature (or below that nitriding temperature), later nitriding
starts with the supply of N₂ gas. Cleaning of the specimens surface in hydrogen plasma is
referred as chemical etching/cleaning in this paper and rest of the chapters. Designation of
the plasma-nitried specimens are given in Table 5.1.

Electrochemical corrosion kinetics of SMATed (S1 and S2), SMAT-plus-polished (S2P)
and non-SMATed (NS) specimens was examined by using open circuit potential (OCP),
potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 3.5 wt.-
% NaCl solution. The electrochemical cell consists of three electrodes: (i) the specimen as a
Table 5.1: Designation of AISI 2205 stainless steel specimens and corresponding SMAT parameters.

<table>
<thead>
<tr>
<th>SMAT condition</th>
<th>SMAT parameters</th>
<th>SMATed + Nitriding</th>
<th>SMATed + Nitriding</th>
<th>SMATed + Nitriding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-SMAT</td>
<td>- - - - - -</td>
<td>NS</td>
<td>NSN1</td>
<td>NSN2</td>
</tr>
<tr>
<td>SMAT</td>
<td>3mm-130 balls-60 min</td>
<td>S1</td>
<td>S1N1</td>
<td>S1N2</td>
</tr>
<tr>
<td>SMAT</td>
<td>3mm-390 balls-60 min</td>
<td>S2</td>
<td>S2N1</td>
<td>S2N2</td>
</tr>
<tr>
<td>SMAT + polished</td>
<td>3mm-390 balls-60 min</td>
<td>S2P</td>
<td>S2PN1</td>
<td>S2PN2</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) patterns and grazing angle X-ray diffraction (GA-XRD) patterns were obtained by using Cu-Kα radiation with 0.03° step size for 2θ range from 30 to 85°. GA-XRD patterns were obtained from the surface of specimens at an incident angle of 2°. Compositional depth profiling of the samples was performed by Glow Discharge Optical Emission Spectroscopy (GD-OES, Horiba GD Profiler 2). The GD-OES technique allows to remove the atoms from the surface by sputtering and, after the emission of the excited species, photosensors for specific wavelength can detect the presence of atoms [10]. GDOES was used for qualitative estimation of nitrogen and carbon for the nitrided specimens. The GDOES measurements were performed as 630 Pa at 30 W with an acquisition time of 10 min, using 4 mm anode. Phase maps and inverse pole figure (IPF) maps of the cross-section of SMATed specimens were obtained by using electron back scattered diffraction (EBSD) scans. Optical microscopy was used to investigate the cross-sectional microstructures of the nitrided specimens. Berahi etchant (85 ml H₂O, 15 ml HCl and 1 g K₂S₂O₅) was used to reveal the microstructures. Microhardness was recorded by using 100 g load with dwell time...
Table 5.2: Process parameters for plasma-nitriding of the AISI 2205 steel specimens.

<table>
<thead>
<tr>
<th>Designation of nitriding cycle</th>
<th>Chemical etching/cleaning duration (min)</th>
<th>Cycle time excluding duration (h)</th>
<th>Gas chemical etching ratio</th>
<th>Gas flow N2:H2 (sccm)</th>
<th>Voltage (V)</th>
<th>Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>30</td>
<td>10</td>
<td>1:4</td>
<td>100:400</td>
<td>940</td>
<td>610-650</td>
</tr>
<tr>
<td>N2</td>
<td>120</td>
<td>10</td>
<td>1:4</td>
<td>100:400</td>
<td>940</td>
<td>610-650</td>
</tr>
<tr>
<td>N3</td>
<td>120</td>
<td>10</td>
<td>1:4</td>
<td>100:400</td>
<td>880</td>
<td>610-650</td>
</tr>
</tbody>
</table>

of 10 s. The microhardness values presented in this study were the average of 10 readings for each specimen. Surface roughness (R\text{a}) was measured by using portable surface profiler; and the average of 20 values were used.

5.3 Results and Discussion

5.3.1 Effect of SMAT on AISI 2205 steel

Considerable influence of SMAT on the hardness is observed for the AISI 2205 steel. Surface hardness of S1 and S2 specimens is about 446 HV(100 g) and 460 HV(100 g) respectively. However, the hardness of NS specimen is about 260 HV(100 g). Figure 5.1a shows the XRD patterns of the SMATed and nonSMATed specimens. Broadening of the austenite (\(\gamma\)) and ferrite (\(\alpha\)) peaks is observed for the SMATed specimens (see the insets in Fig. 5.1a), which indicates that the specimen surface is subjected to the refinement of grains, development of micro-strain and increase in the dislocation density during SMATing. GA-XRD (Fig. 5.1b) shows the peaks of \(\gamma\) and \(\alpha\) phases for all specimens. In GA-XRD patterns, the peaks of \(\gamma\) and \(\alpha\) phases are more clearly visible for NS and S2P specimens than the S1 and S2 specimens. This could suggest that the rough surface (i.e. the presence of crests and troughs due to the impact of balls) of the S1 and S2 specimens does not provide the sufficient bulk material for the diffraction of x-rays. Absence of any other peak, apart from the \(\gamma\) and \(\alpha\) phases, in GA-XRD patterns confirms no contamination of the specimen surface due to the SMAT.

In our previous study [2], ‘peening intensity (PI)’ terminology is proposed to quantify the intensity of peening of the SMATed surface by flying balls. PI indicates the number of times the entire SMATed surface is impacted or peened by the balls during the total SMAT
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duration. Here, S1 SMAT condition induces 20 PI and S2 SMAT condition induces 45 PI. In other words, the specimen surface is impacted (by the 3 mm balls) for 20 times in S1 SMAT condition and that of 45 times in S2 SMAT condition. Higher surface hardness for the S2 SMAT condition is associated with the higher accumulative strain at the specimen surface. Temperature of the Fe-based alloys can increase to about 50-150°C during SMAT [11, 12]. This temperature is well below the 0.25T_m, where T_m is the melting point of the AISI 2205 steel in K and therefore, any modification in the refined grains of the SMATed surface is not expected.

Figure 5.1: a) X-ray diffraction (XRD) pattern of NS, S1 and S2 specimens. Insets indicate the broadening of peaks after SMAT, b) Grazing angle X-ray diffraction (GA-XRD) pattern of NS, S1, S2 and S2P specimens.
Figure 5.2 shows the IPF and phase maps of the cross-section of S1 and S2 specimens. Phase maps show the distribution of $\gamma$ and $\alpha$ grains across the cross-section. IPF maps of the SMATed regions show the variation in color density inside the grains, which is due to the misorientation (small variation in the orientation with respect to the parent grains) within the grains. This misorientation could occur to absorb the induced strain during SMATing [2]. The misorientation inside the grains also indicates the formation of sub-grains. Some unindexed regions are observed inside and along the grain boundaries. Such regions could be the highly deformed regions [2]. It is observed that the SMAT affected (deformed) region is thicker for S1 specimen than the S2 specimen. In S1 SMAT condition has lower number of the balls (130 balls) than S2 SMAT condition (390 balls). Therefore, S1 SMAT condition causes lower inter-collision and higher average vertical velocity of the balls [2]. This suggests that, the moving balls in S1 SMAT condition transfer the higher kinetic energy to the specimen surface and induce the higher deformed depth. However, as discussed above, the lower surface hardness of the specimen for S1 SMAT condition is due to the lower PI.

**Figure 5.2:** a) Inverse pole figure (IPF) and b) phase map of the cross-sectional of S1 specimen. c) IPF and d) phase map of the cross-section of S2 specimen.

Surface roughness of the specimens is increased to maximum 0.51 $\mu$m due to the SMAT (Table 5.3). Slightly smaller surface roughness is observed for the S2 specimen than S1 specimen. Higher number of balls in the SMAT cabin blunt down the crest (induced by the impact of balls during the initial period of SMAT) more effectively for S2 SMAT condition than the S1 SMAT condition.
5.3.2 Effect of SMAT on corrosion behavior of AISI 2205 steel

Figure 5.3a shows the variation of rest potential ($E_{rest}$) or open circuit potential (OCP) with respect to immersion time for the SMATed and non-SMATed specimens. SMATed specimens show the stable $E_{rest}$ after a little fluctuation during the initial period. S1 specimen achieves the stable $E_{rest}$ since the beginning of immersion. However, S2 specimen shows some fluctuation during the initial 800 s and then, it reaches the stable $E_{rest}$ at later stage of immersion.

It is observed that S1 SMAT condition gives the faster stabilization of passive film on the surface than the S2 SMAT condition. However, there is a more fluctuation in the $E_{rest}$, especially, in the range of 800 to 1200 s, for the polished S2P specimen, which suggests the delay in achieving the equilibrium state. Anodic shift for S1 and S2 specimens are quite similar (-225 mV for S1 and -275 mV for S2) and they are higher than NS (-325 mV). To understand the effect of surface roughness on corrosion, S2P specimen is prepared where roughness is reduced from 0.48 to 0.18 $\mu$m. Highest anodic shift is observed for the S2P as compared to S1, S2 and NS specimens. Figure 5.3b shows the potentiodynamic anodic polarization plots for the S1, S2 and NS specimens. Parameters extracted from these polarization plots are tabulated in Table 5.4. S1, S2 and S2P specimens show upward shift in the $E_{corr}$ values with respect to NS specimen. S1, S2 and S2P specimens show considerably lower passive current density ($i_{passive}$) than NS specimen. Pitting ($E_{pitt}$) or trans-passive ($E_{trans}$) potential values are about 1050 mV for S1, S2, S2P and NS specimens. However, $E_{pitt}$ for S1, S2, and S2P specimens are somewhat smaller than the NS specimen. This is due to the surface roughness/defects and/or accumulated strain at the specimen surface [13].

Polarization plots for S2, S2P and NS specimens (Fig. 5.3c) indicate the possible role of surface roughness on corrosion. Higher $E_{corr}$ and lower $i_{passive}$ are observed for S2P than S2 specimen. This suggests that the slight polishing of SMATed specimen of AISI 2205 steel can improve its corrosion property.

Nyquist plots obtained by using electrochemical impedance spectroscopy (EIS) for S1, S2, S2P and NS specimens are shown in Fig. 5.4a. These plots show capacitive semicircles for the non-SMATed and SMATed specimens. Typically, the larger radius of the capacitive semicircle indicates the more charge transfer resistance, which results in the lower dissolution.
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**Figure 5.3:** a) OCP or $E_{\text{rest}}$ potential variation respect to immersion duration of 1800 s for S1, S2, S2P and NS specimens, b) potentiodynamic polarization curves for S1, S2 and NS specimens, c) potentiodynamic polarization curves for S2, S2P and NS specimens of AISI 2205 stainless steel in 3.5% NaCl solution.

of the material [14]. Figure 5.4a shows the larger diameter of capacitive semicircle for S1, S2 and S2P than the NS specimen. The best data fitted equivalent circuit is shown in the Fig. 5.4a. The equivalent circuit consists of solution resistance ($R_s$), charge transfer resistance ($R_{ct}$) and constant phase element ($CPE$ or $Q_1$), which is necessary to account for the distribution of relaxation time resulted from the heterogeneities at the electrode surface [15]. The dots shown in the Fig. 5.4a are the experimental data points for the Nyquist plots; and lines are the best fitting results for the equivalent circuit. Impedance parameters obtained after the best fitting are tabulated in Table 5.5. Higher semicircle radius (shown in Nyquist plots) is associated with the formation of more compact and protective layer on the SMATed specimens than the non-SMATed specimen. S1-SMAT condition causes the higher charge transfer resistance than S2-SMAT condition. The highest resistance is observed for the S2P specimen, which could be due to the reduced surface roughness and
Table 5.4: Corrosion parameters evaluated by potentiodynamic polarization study for AISI 2205 steel.

<table>
<thead>
<tr>
<th>SMAT condition</th>
<th>$E_{corr}$ (mV$_{SCE}$)</th>
<th>$E_{pitt}$ (mV$_{SCE}$)</th>
<th>$i_{passive(at-150mV)}$ (µA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS</td>
<td>-444</td>
<td>1065</td>
<td>21.53</td>
</tr>
<tr>
<td>S1</td>
<td>-352</td>
<td>1042</td>
<td>8.93</td>
</tr>
<tr>
<td>S2</td>
<td>-371</td>
<td>-1051</td>
<td>15.85</td>
</tr>
<tr>
<td>S2P</td>
<td>-329</td>
<td>-1048</td>
<td>12.39</td>
</tr>
</tbody>
</table>

dense protective layer. Indeed, higher electrical potential can be developed at the peaks of rough surfaces than in the flat surfaces (according to the Maxwell’s equations). Bode phase and impedance (Fig. 5.4b) shows good agreement with the Nyquist plots. SMATed specimens show the higher phase angle maximum covering a large range of frequency in Bode impedance and phase plot compared to the non-SMATed specimen.

Table 5.5: Electrochemical parameters for SMAT and non-SMAT specimens for AISI 304L steel in 3.5 wt.% NaCl solution. Where, $R_s$-solution resistance, $n$-exponent, $Q_1$-constant phase element (CPE) and $R_{ct}$-charge transfer resistance.

<table>
<thead>
<tr>
<th>SMAT condition</th>
<th>$R_s$ (ohm cm$^2$)</th>
<th>$n$</th>
<th>$Q_1$ (ohm $s^n$cm$^{-2}$)</th>
<th>$R_{ct}$ (ohm cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS</td>
<td>5.644</td>
<td>0.837</td>
<td>70.66×10$^{-6}$</td>
<td>6.44×10$^4$</td>
</tr>
<tr>
<td>S1</td>
<td>6.305</td>
<td>0.808</td>
<td>77.19×10$^{-6}$</td>
<td>3.32×10$^5$</td>
</tr>
<tr>
<td>S2</td>
<td>5.21</td>
<td>0.821</td>
<td>94.51×10$^{-6}$</td>
<td>2.25×10$^5$</td>
</tr>
<tr>
<td>S2P</td>
<td>4.715</td>
<td>0.861</td>
<td>49.91×10$^{-6}$</td>
<td>5.31×10$^5$</td>
</tr>
</tbody>
</table>

The improvement in the corrosion resistance of the SMATed specimens is in agreement with the work conducted by Splinter et al. [16] on nanocrystalline Ni-P alloy, where they have reported that the high volume of grain boundaries and triple junction enhances the diffusion of oxygen in the passive layer. Knoner et al. [17] have also reported the enhanced diffusivity of oxygen (which is about three orders of magnitude higher) in the nanocrystalline yttria-doped ZrO$_2$ (n-ZrO$_2$ · 6.9 mol% Y$_2$O$_3$) than the single crystal counterpart. In the recent work on the SMATed AISI 316L steel [18] has reported the formation of thicker oxide layer due to the higher diffusivity of oxygen in the nanocrystalline SMATed surface than the microcrystalline non-SMATed material. It is likely that the improvement in corrosion resistance...
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Figure 5.4: a) Nyquist and b) Bode plots for NS, S1, S2 and S2P AISI 2205 stainless steel specimens in 3.5% NaCl solution. Randle circuit was used for the best fitting of the experimental Nyquist impedance data.

The resistance of the SMATed AISI 2205 steel in the present study is due to the stable and thicker oxides on the SMATed surface. In case of non-SMATed AISI 2205 steel, Donik et al. [19] have reported that the passive layer, at room temperature, consists of outer iron-oxides layer followed by chromium-rich oxides layer. Thickness of the air-borne passive film on duplex stainless steel is about 1.8 nm [20]. However, with increasing passivation potential, passive film thickness can vary from 3-5 nm [20].
5.3.3 Plasma nitriding of SMATed and non-SMATed AISI 2205 steel at 500°C

i) Microstructure and thickness of the nitrided layer

Figure 5.5 shows the optical micrographs of the cross-section the specimens nitrided by using cycle-N1 and cycle-N2 (Table 5.1 and 5.2). Non-nitrided core of the specimens shows yellow colored $\gamma$ grains and dark-blue colored $\alpha$ grains in the optical micrographs. Single layer morphology is observed in the nitrided layer of the specimens. Yellow color of the nitrided layer in optical micrographs suggests that the nitrided layer is composed of $\gamma$ and/or expanded austenite ($\gamma_N$) phase. This is further confirmed by the XRD in subsequent paragraph. Deep holes/patches in the nitrided layer, which appear dark in the optical micrographs, could be formed as a result of the selective material removal by etching action [21]. Nitrided layer of the specimens nitrided by using cycle-N2 shows more dark spots/patches than the cycle-N1. Total thickness of the nitrided layer is about 11-14 $\mu$m for cycle-N1 and 14-18 $\mu$m for cycle-N2. For a particular nitriding cycle, SMATed specimens show thicker nitrided layer (by about 1.5-3 $\mu$m) than the non-SMATed specimens (see Fig. 5.5a). However, S2PN1 specimen shows somewhat reduced thickness of the nitride layer as compared to the other specimens (Fig. 5.5d and Fig. 5.6a). Figure 5.6b shows higher surface hardness for the nitrided SMATed specimens than the nitrided non-SMATed specimens. Higher surface hardness is observed for the nitrided S1 specimen than the nitrided S2 specimen, which indicates the effective peening in case of S1 condition. S2N2 and S2PN2 specimens show the quite similar surface hardness.

ii) Phase analysis of nitrided layers

XRD patterns recorded for the specimens nitrided by using cycle-N1 and cycle-N2 are shown in Fig. 5.7a and Fig. 5.7b respectively. SMATed specimens nitrided by using both cycles show the peaks corresponding to CrN and expanded austenite ($\gamma_N$). Peak shift of $\gamma_N$ is significant for the nitrided specimens with respect to the position of $\gamma$ peaks in NS specimen. This shift is associated with the presence of high nitrogen content in the nitrided layer. It has been reported in the previous studies that the $\alpha$ phase present in the duplex stainless steel transforms to $\gamma_N$ during nitriding since nitrogen is the austenite stabilizer [22–24]. Formation of $\gamma_N$ is also reported in literature in case of plasma nitrided martensitic stainless steel [25]. Nitrided SMATed specimens show higher intensity of the CrN peaks than that of the nitrided non-SMATed specimen in both the cycles. This indicates the higher proportion of CrN in the nitrided layer of SMATed specimens. Shen et al. [1] have observed the enhancement in the precipitation of CrN for the ‘shot peened’ AISI 304 steel. They have reported that the higher defect density, like slip bands and dislocations, acts as...
Figure 5.5: Optical micrographs of the cross-section of the nitrided specimens: a) NSN1, b) S1N1, c) S2N1, d) S2PN1, e) NSN2, f) S1N2, g) S2N2 and h) S2PN2. Cross-section of the specimens is etched with Berahi etchant for 50 s.
the ‘short ways’ (i.e. additional diffusion channels) for nitrogen and Cr atoms to enhance the CrN formation. These observations in the literature support the enhancement in CrN precipitation for the SMATed specimens in the present study. SMATed specimens nitrided by using cycle-N2 show higher intensity of the CrN peaks than the SMATed specimens nitrided by using cycle-N1. Surface hardness values for the SMATed specimens are in the range of 1300 to 1500 HV(100 g) and 1530 to 1675 HV(100 g) for cycle-N1 and for cycle-N2 respectively (see Fig. 5.6b). Higher surface hardness and intensity of the CrN peaks in XRD for the cycle-N2 confirm the higher CrN precipitation.

It has been reported in the previous study [26] that, in plasma-nitriding process, hydrogen removes oxygen from the surface by forming H$_2$O (chemical etching). Since

![Figure 5.6: a) Nitrided layer thickness and b) surface microhardness for NS, S1, S2 and S2P specimens.](image-url)
hydrogen is the lightest element, it can only remove oxygen from the surface, instead of sputtering Fe atoms. Considering the action of hydrogen, the above results indicate that 30 min of chemical etching in cycle-N1 is not sufficient for the entire removal of surface oxide-layer. Therefore, during subsequent nitriding-cycle, some duration of the total nitriding time is consumed to overcome the potential barrier (for nitrogen incorporation into the specimen surface) by oxide layer, and consequently, ‘effective’ nitriding time is reduced. Here, the effective nitriding time \( (t_{\text{eff}}) \) is defined as the total nitriding time minus time required for oxide removal during nitriding cycle.

Figure 5.7: XRD pattern of the non-SMATed and SMATed specimens nitrided by using a) cycle-N1 and b) cycle-N2.

Based on the substantial removal of the surface oxides in the cycle-N2, it can be infer that, the total ‘effective’ nitriding time for the nitrogen diffusion is more in case of cycle-N2 than the cycle-N1. Higher available cycle time for nitrogen diffusion is realized by the greater CrN precipitation for the specimens nitrided by using cycle-N2 (Fig. 5.7). Enhancement in the precipitation of CrN with increase in the duration of plasma-nitriding for AISI 321 steel is reported in Ref. [27].

In this study, the role of enhanced corrosion resistance, due to the thick and stable surface oxides (caused by SMAT effect), on the nitriding behavior is clearly observed. S2P specimen has the highest charge transfer resistance, which indicates the presence of thicker and stable passive layer (see Fig. 5.4). Therefore, for S2PN1 specimen, the nitrided layer
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thickness (Fig. 5.5d) is the thinnest among the nitrided SMATed and non-SMATed specimens. This is quite unusual behavior as compared to the nitriding response of SMATed AISI 316 steel [14], where the polishing of the SMATed surface of AISI 316 steel has resulted in the thicker nitrided layer.

Thinnest thickness of the nitrided layer for S2PN1 specimen confirms that 30 min of chemical etching is not sufficient to remove the entire passive layer. S2P, S1 and S2 specimens show the improved corrosion resistance as compared to the NS specimen (Fig. 5.4). Thicker nitrided layer for S1N1 and S2N1 specimens than the NSN1 specimen suggests that the passive layer on the S1 and S2 specimens is less stable and thinner than S2P specimen. Therefore, the potential barrier by passive/oxide layer after 30 min of chemical etching is lesser for S1 and S2 specimens than that of S2P specimen. If passive layer is removed properly before nitriding, SMATed specimens result in the thicker nitrided layer. In case of cycle-N2, polished specimen shows the comparable nitrided layer thickness to its rough counterparts (S1N2 and S2N2). Therefore, it appears that 120 min chemical etching is resulted in the substantial removal of the oxide layer from the SMATed surface, even for the polished specimen, as compared to the lower chemical etching time (30 min). This indicates that the \( t_{eff} \) for cycle-N1 is less than the cycle-N2 (i.e. \( t_{N2}^{eff} > t_{N1}^{eff} \)).

iii) GDOES of nitrided layer

Qualitative distribution of nitrogen and carbon along the depth of SMATed and non-SMATed specimen (determined by using GDOES) are shown in the Fig. 5.8. Slightly deeper nitrogen depth profiles for the S1N1 and S2N1 specimens than NSN1 (Fig. 5.8a) indicates the effect of SMAT on nitriding. However, the shortest nitrogen depth profile for S2PN1 specimen (Fig. 5.8a) further confirms that \( t_{eff}^{S2PN1} < t_{eff}^{S1N1} < t_{eff}^{NSN1} \) due to the highest corrosion resistance for S2P. Figure 5.8b shows thicker nitrogen depth profile for the S2PN2 specimen than for S2PN1 specimen, which further confirms that \( t_{eff}^{N2} > t_{eff}^{N1} \).

Interestingly, a considerable carbon uptake is observed in the present work at the interface between nitrided layer and non-nitrided core (Fig. 5.8a and b) even without supply of any carbon carrying gas during plasma nitriding. There are few studies which have reported the source and uptake of this carbon in the nitrided layer during plasma nitriding in the absence of carbon carrying gas [28, 29]. Presence of this carbon uptake can be explained as follows. During sputter cleaning (chemical etching) carbon is taken up from the furnace walls and accumulated on the surface of steel specimens [28]. Oxygen released from the chemical etching of passive layer on the steel specimen reacts with the carbon contamination and forms CO gas [30]. Generation of CO creates the carburizing potential near to the specimen surface. High temperature of the chemical etching process and the availability of carburizing potential cause the carbon enrichment of the specimen surface. Carbon enriched
steel surface can create the obstacle for nitrogen incorporation in the specimen surface during the subsequent nitriding process (due to the deficiency of octahedral interstitial sites for thermodynamically equilibrium absorption of nitrogen atoms). During nitriding process, this carbon enriched zone is pushed in the forward direction [29]. Carbon does not pickup in the nitride layer during nitriding (as evident in GDOES plots) because the carbon contamination can now react with nitrogen and forms volatile CN [28] which could vent out before reacting with the steel surface.

Figure 5.8: Composition depth profile for a) Specimens nitrided by using cycle-N1 and b) S2PN1 and S2PN2 for comparison of nitriding response of polished specimens of AISI 2205 steel.

The presence of passive layer and carbon enriched region are the possible obstacles in the nitriding process. Extent of these obstacles during nitriding process depends on: (i) the duration of chemical etching prior to the nitriding process, (ii) the stability of passive layer (higher stability of the passive layer requires higher duration to etch completely) and (iii) the duration required to push the carbon enriched zone in the forward direction. Now, the previous definition of $t_{eff}$ can be refined further as the total nitriding time minus the time required to overcome the obstacles. Duration of the obstacle of carbon enrichment is possibly independent of non-SMAT, SMAT, N1 and N2 conditions. However, if the duration of chemical etching is less and/or the stability of passive layer is more, significant obstacles can enter in to the nitriding process and therefore, the effective nitriding time reduces considerably. The duration of chemical etching and the stability of passive layer play significant role in the nitriding behavior of non-SMATed and SMATed specimens in the current work.
5.3.4 Low temperature (400°C) plasma nitriding of SMATed AISI 2205 steel

Low temperature nitriding at 400°C is performed with the 120 min of chemical etching/cleaning duration. Low temperature is resulted in the thinner nitrided layers as shown in the Fig. 5.9a-d. Substantial gain is not observed in the nitrided layer thickness for the SMATed specimens. However, there is a substantial increase in the surface hardness for the SMATed specimens (i.e. S1N3, S2N3) compared to the non-SMATed nitrided specimen (i.e. NSN3) as shown in Fig. 5.9e even with the 1-2 µm thick nitrided layer. This gain in surface hardness is due to the thin nitrided layer obtained on the surface and the deformed SMATed surface beneath the nitrided layer which has already higher hardness due to SMAT action. It can be observed that the polished specimen and its rough counterpart show the same hardness, which indicates the 120 min of chemical etching time has resulted in the substantial removal of passive layer from the surface at 400°C.

![Image of micrographs and hardness graph]

**Figure 5.9:** Optical micrographs of the cross-section of plasma nitrided specimens by using cycle-N3: a) NSN3, b) S1N3, c) S2N3 and d) S2PN3. e) Surface microhardness for non-SMATed and plasma nitrided specimens (cycle-N3).

The qualitative nitrogen concentration along the depth is shown in Fig. 5.10a. The X-ray diffraction pattern in Fig. 5.10b shows the $\gamma_N$ peaks for the nitrided layer along with the $\gamma$ and $\alpha$ from the non-nitrided matrix. Unlike the specimens nitrided using cycle-N1 and cycle-N2 there is an absence of CrN peaks in XRD, This indicates that the low temperature has suppressed the CrN formation even in the SMATed specimens.
5.3.5 Mechanism for nitriding behavior of SMATed AISI 2205 steel

In the present study, SMAT is performed on the AISI 2205 steel by using two SMAT conditions, where number of balls (130 and 390 number of balls) is varied in the SMAT cabin to vary the PI. It appears that SMAT action enhances the surface hardness due to the rise in dislocation density and the refinement of grains. Moreover, rise in the corrosion resistance of the SMATed specimens, due to the formation of stable passive/oxide layer, is also observed. Slight polishing of the SMATed surface further enhances the stability of passive layer on the AISI 2205 steel. This improved corrosion resistance (passive layer formation) hinders the nitrogen transfer to the surface during nitriding process. It appears that low chemical etching time (30 min in the present study) does not remove effectively the passive layer from the steel surface. Removal of the passive layer from the polished SMATed surface is even more difficult during chemical etching because the passive layer is more stable and thicker (Nyquist plots show the highest charge transfer resistance for the polished SMATed specimen). Such passive film, if not chemical cleaned or etched properly, the total ‘effective’ nitriding time for the nitrogen diffusion is reduced. This assumption is well supported by the nitriding response of the polished SMATed specimen (S2PN1), where the passive nature is very strong (S2P) and the nitried layer is smallest for this specimen among the SMATed and non-SMATed specimens. However, for the same surface condition (S2P), longer chemical etching time (120 min) is more effective in the removal
of the passive/oxide layer, and therefore, more effective nitriding time is available for the actual nitrogen diffusion in the surface (S2PN2). As a consequence, higher surface hardness (due to the enhanced CrN precipitation) and thicker nitrided layer is observed. Thus, longer chemical etching/cleaning time can be combined in a synergic way with the SMAT process in order to enhance the nitriding kinetics and to achieve the higher surface hardness.

Figure 5.11: Mechanism for nitrided layer formation in a) non-SMATed and b) non-SMATed specimens.

The phase transformation during the formation of nitrided layer in cycle-N1 and cycle-N2 for the non-SMATed and SMATed specimen is shown in Fig. 5.11. Stage-I in Fig. 5.11a shows the initial condition of non-SMATed specimen surface, where the nitrogen is ready to be diffused into the surface. In stage-II, the pre-existing α and γ of the duplex stainless steel transforms to γ and γ_N respectively and simultaneously, precipitates of CrN forms in both the phases of nitrided layer. The increase in duration of nitriding results in the
transformation of $\gamma \rightarrow \gamma_N$, and increase in the diffusional depth of nitrogen and CrN precipitation (i.e. stage-III and stage-IV). Since the overall $t_{eff}$ in cycle-N2 is higher than the cycle-N1, NS specimen reaches the stage-III in cycle-N1 and stage-IV in cycle-N2.

Figure 5.11b shows the phase transformation for the SMATed specimen. The major difference in the phase transformation during the nitriding compared to non-SMATed specimen is the availability of higher defects (i.e. dislocations and boundaries) in the SMATed surface. The sequence of stages of phase transformation is similar to that of non-SMATed specimen. However, there is enhanced precipitation of the CrN nitrides, and diffusion of nitrogen is deeper due to the additional pathways provided by the defects.

5.4 Conclusions

1. SMAT of AISI 2205 steel improved the surface hardness by about 80% as compared to the non-SMATed specimen. This improvement in the hardness was the result of rise in the dislocation density and grain refinement in the SMATed surface.

2. Corrosion resistance of the steel was improved after SMAT. Slight polishing of the SMATed surface further enhanced the corrosion resistance of the steel. This improvement was associated with the formation of stable and thick passive/oxide layer.

3. Improved passivity behavior of the SMATed surface hindered the nitrogen transfer in the plasma-nitriding process. Shorter chemical etching time (30 min) resulted in the thinner nitrided layer on the specimen. However, longer chemical etching time (120 min) was successful in the removal of passive layer from the SMATed surface and therefore, resulted in the slightly thicker nitrided layer.

4. Surface hardness of the nitrided SMATed specimens was higher than the nitrided non-SMATed specimens. This was due to the higher CrN precipitation in the nitrided layer of the SMATed specimens.
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References


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