

Chapter 2

Conventional DC Plasma Nitriding

As known before, the usual source for generating the plasma in plasma nitriding system is DC current (conventional or pulsed). This chapter just includes the results obtained by conventional DC plasma nitriding system on different grades of steels including stainless steels (austenitic, martensitic or precipitation hardening types), tool steels, and structural and constructional steels. This chapter consists of microstructural, mechanical, and corrosion properties obtained after conventional DC plasma nitriding of steels.

2.1 Microstructure

2.1.1 *Austenitic Stainless Steels*

The main phases present in the microstructure of plasma nitrided austenitic stainless steels are γ' -Fe₄N, ϵ -Fe₂₋₃N, and γ_N (expanded austenite). The expanded austenite (that is also called γ_N or s-phase) is formed by supersaturation of austenite FCC lattice by nitrogen atoms. The formation of this phase has two noticeable effects on XRD peaks of the nitrided layer: the broadening and shifting of the peaks to lower angles.

Here are the results of some experiments done to characterize the microstructure of plasma nitrided austenitic stainless steel.

Xu et al. [1] plasma nitrided AISI 304 austenitic stainless steel samples at temperatures of 400–420 and 500–520 °C, in atmosphere of 80 % N₂ + 20 % H₂, under pressure of 0.3 Pa and for 1 h. The microstructure of untreated sample (Fig. 2.1a) is composed of single phase γ -Fe. It can be seen from Fig. 2.1b that for 400 °C, all peaks are shifted to lower angles due to the formation of expanded austenite (γ_N) phase. It can be concluded from Fig. 2.1c that the layer produced at 500 °C is composed mainly of the α -ferrite and CrN phases.

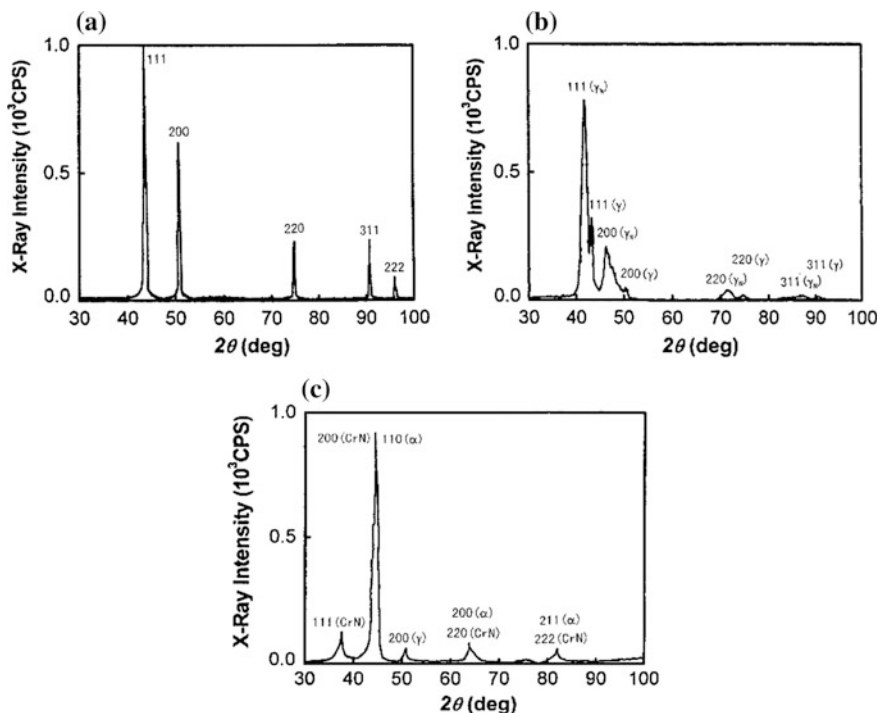


Fig. 2.1 XRD patterns of austenitic stainless steels. **a** Untreated, **b** after treatment at 400 °C and **c** after treatment at 500 °C [1]

According to TEM observations (Fig. 2.2), heavy stacking fault and high dislocation density regions have been observed for sample nitrided at 400 °C. Electron diffraction patterns indicated that an FCC phase had been produced. The lattice parameter of this phase was 0.372 nm, which was larger than that of the austenite (γ) parent phase. This phase is the mentioned expanded austenite (γ_N or s-phase). The formation of this phase induces stacking faults.

Figure 2.2 shows that, producing a bundle substructure is a result of nitrogen supersaturation and consequently decreasing of stacking fault energy.

A twinned relationship exists between bundles. These probably are deformation twins resulted from stress and strain which were produced from nitrogen supersaturation.

The microstructure of the plasma nitrided layer produced at 500 °C was made up of colonies displaying a lamellar structure. Each colony was reported to consist of α (ferrite or martensite) and CrN. With temperature enhancement, the diffusivity of substitutional atoms was increased. The bonding between chromium and nitrogen was stronger than that of other substitutional atoms with nitrogen, so that the CrN could nucleate and grow. Another suggestion for formation of CrN was decomposition of γ_N into α and CrN with increasing the temperature.

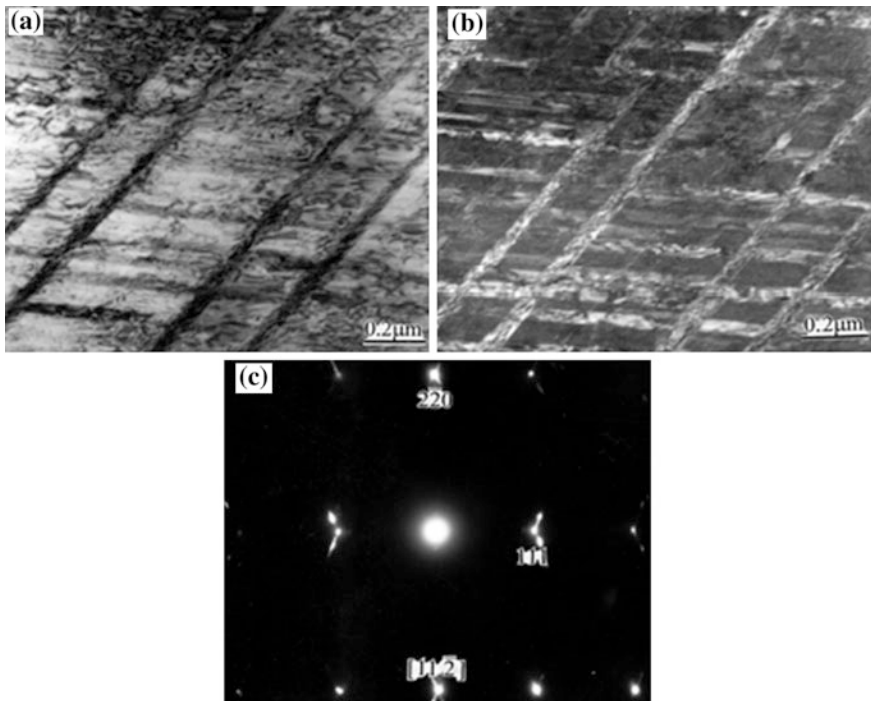


Fig. 2.2 TEM images showing stacking fault substructure of γ_N phase produced by plasma nitriding at 400 °C. **a** *Bright field*, **b** *dark field* and **c** electron diffraction pattern of **(a)** along [112] zone axis [1]

Wang et al. [2] plasma nitrided AISI 304L austenitic stainless steel with parameters listed in Table 2.1. There was no diffusion zone observed for none of the samples. However, it is obvious from Fig. 2.3 that the modified layer thickness is increased by temperature.

They also observed that, with an increase in temperature, the amount of γ_N decreased until 460 °C in which the γ_N completely disappeared. However, at 460 and 480 °C the CrN peaks started to get detected due to the precipitation of CrN which depletes the γ_N phase of chromium at 460 °C. This leads to the formation of a layer composed of expanded martensite (or austenite) and CrN.

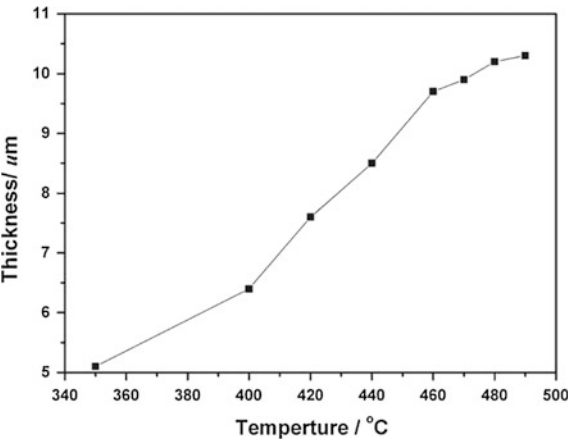
At 480 °C, just CrN and austenite of substrate were detected because of above-mentioned decomposition process as well as the chemical reaction of expanded austenite (γ_N) with the incident nitrogen species during the plasma nitriding treatment.

Stinville et al. [3] plasma nitrided AISI 316L austenitic stainless steel samples at 400 °C, in atmosphere of 60 % N_2 + 40 % H_2 , under pressure of 4.5 Pa and for 20 min–160 h. They detected γ_N phase. Also, increasing the temperature resulted in lowering the diffraction angle. They also reported an expansion of ~ 9 % in the direction normal to the surface and no expansion parallel to the surface for the

Table 2.1 The nitriding parameters used by Wang et al. [2]

Temperature (°C)	Duration (h)	Atmosphere ($\frac{N_2}{H_2}$)	Pressure (Pa)	Voltage (V)
350	4	$\frac{62}{240}$	600	520
400	4	$\frac{58}{196}$	600	520
420	4	$\frac{47}{201}$	600	520
460	4	$\frac{45}{180}$	600	520
480	4	$\frac{49}{199}$	600	520
420	4	$\frac{42}{172}$	400	520
400	4	$\frac{40}{161}$	400	520
350	4	$\frac{45}{186}$	400	520
400	4	$\frac{42}{168}$	200	520
420	8	$\frac{46}{191}$	600	520
400	8	$\frac{60}{246}$	600	520
350	8	$\frac{53}{220}$	600	520

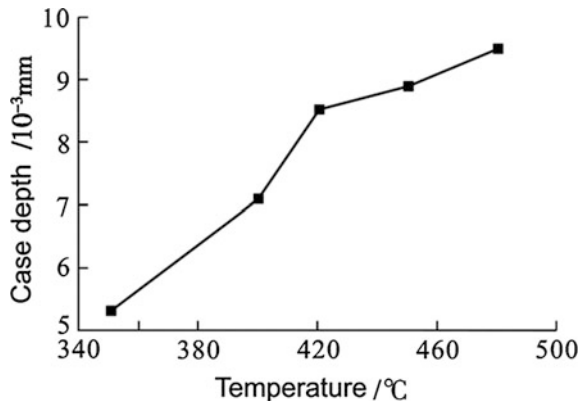
Fig. 2.3 Case depths of plasma nitrided AISI 304L samples treated at various temperatures [2]



nitrided layer. This led to the induction of high compressive stresses in the nitrided layer.

Li et al. [4] investigated plasma nitriding of AISI 316L austenitic stainless steel by applying these parameters: temperatures of 350, 400, 420, 450, and 480 °C, atmosphere of 20 % N₂ + 80 % H₂, pressure of 600 Pa and duration of 4 h. They observed no diffusion zone in any of the samples as reported by Wang et al. [2].

Fig. 2.4 Case depths of plasma nitrided AISI 316L austenitic stainless steel at various temperatures [4]



A dense case with thickness of approximately 5 μm produced at 350 °C which was less thicker than the layer formed at 480 °C. Besides, the layer formed at 480 °C showed a clear interface with substrate most probably because of the distinction between crystal structure of case and substrate. The thickness of treated layer is plotted in Fig. 2.4 as a function of temperature. It clearly can be seen in this figure that the thickness of the treated layer reaches a maximum value at 480 °C and the layer thickness shows an approximately linear behavior with temperature.

A high nitrogen concentration was seen at the surface of nitrided layer nitrided in various temperatures but at the same time. Due to a low diffusion rate at low temperatures, nitrogen penetration depth in the samples treated at 350 and 400 °C was less than that at temperatures higher than 420 °C.

In accordance with other researchers, they also saw that, the expanded austenite peaks were detected at lower temperatures and CrN was detected with increasing temperature. The reason for this action was given before. The broadening of γ_{N} peaks was probably due to the nitrogen gradient, residual stresses, and possible defect structure of the nitrided layers as mentioned before.

Egawa et al. [5] investigated the effect of some alloying elements on the microstructure of conventional DC plasma nitrided austenitic stainless steel samples nitrided with these parameters: temperatures of 400, 430, 440, and 470 °C, atmosphere of 80 % N_2 + 20 % H_2 , pressure of 667 Pa and duration of 4 h. In this study different austenitic stainless steel samples have been used: AISI 304, AISI 316, JIS-SUS 304J3, AISI 321, and AISI 347.

They found that with increasing temperature, the formation of CrN phase increased (according to Fig. 2.5) and appeared as dark phases after etching with marble's reagent.¹ So, two critical temperatures were defined: T_1 as the critical temperature where the “dark” phases are formed along the grain boundary and T_2 as the critical temperature where the dark phases are formed at the intergranular

¹mixture of equal parts of hydrochloric acid and CuSO_4 saturated aq. solution.

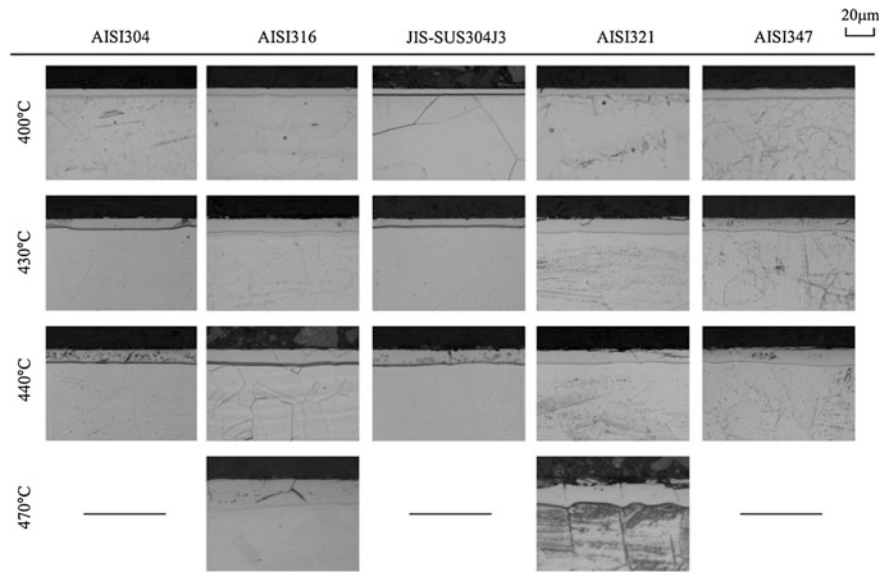


Fig. 2.5 Cross sections of the treated layers formed in various stainless steels after plasma nitriding at various temperatures for 4 h [5]

Table 2.2 Critical temperatures for formation of precipitations; at the grain boundaries (T_1) and at the intergranular regions (T_2) [5]

	304	316	304J3	321	347
T_1 (°C)	430–440	430–440	430–440	430–440	430–440
T_2 (°C)	430–440	460–470	430–440	460–470	430–440

regions. According to the authors, T_1 is independent of the chemical composition of substrate but T_2 is not constant (Table 2.2).

Molybdenum in AISI 316 and titanium in AISI 321 stabilize the structure of the expanded austenite. This stabilization is done by preventing the precipitation of chromium nitrides with attracting the surrounding nitrogen atoms. However, the formation of the nitride precipitation was not affected in JIS-SUS 304J3 because copper (existing in this steel) does not tend to attract nitrogen atoms. Despite the tendency of niobium in AISI 347 to attract nitrogen atoms, the T_2 temperature of AISI 347 was equal to that of AISI 304 because of combining with carbon.

They have noted that the behavior of layer thickness with temperature can be divided into two types: the first is when the layer grows slowly at low temperatures and then more rapidly above a critical temperature (AISI 304, J 304 and AISI 347) and the second is when an approximately linear increase in the layer thickness is shown with an increase in the temperature (AISI 316 and AISI 321). So in the first type, the precipitation of CrN accelerates the growth of the nitrided layer.

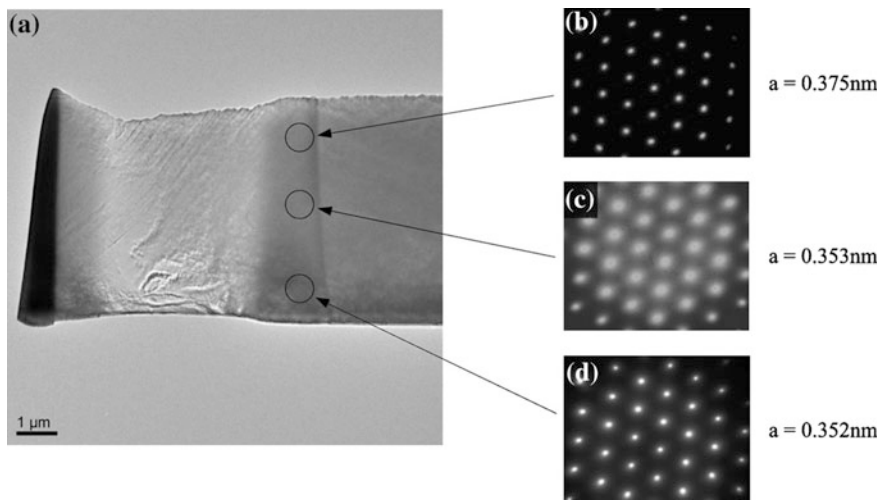


Fig. 2.6 a TEM image and b–d the selected area diffraction (SAD) patterns for the layers of the AISI 304 sample nitrided at 400 °C [5]

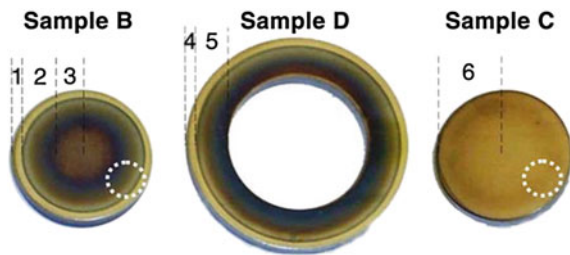
Figure 2.6 shows the increment of lattice parameters of the nitrided layers compared to the substrate austenite. Also, lattice parameter in the top part of the nitrided layer (Fig. 2.6b) was larger than that in the bottom region (Fig. 2.6d).

The formation of expanded austenite at low temperatures and CrN at high temperatures also was observed by Oliveira et al. [6]. They treated AISI 316L samples with applying these parameters: temperature of 350, 400, and 450 °C, atmosphere of 20 % N₂ + 80 % H₂, pressure of 667 Pa, and duration of 5 h. They observed the austenitic substrate and the growth of the nitrided layer, with the increasing nitriding temperatures. In the sample nitrided at 400 °C, the formation of only a white layer was observed. In the sample nitrided at 450 °C, emergence of the CrN precipitate in the white layer as well as a substantial increase of CrN precipitation in the sample nitrided at 500 °C, led to the formation of a second dark layer over the original white layer.

It was observed that the white layer was constituted mainly by the expanded austenite (γ_N). It was reported that in the case of sample plasma nitrided at low temperature (400 °C), γ_N peaks in XRD pattern appeared at lower angles compared to the substrate FCC austenite, indicating the larger lattice parameter of expanded austenite compared to the substrate austenite. This expansion was a result of the nitrogen supersaturation in austenite as mentioned by other authors before. Besides, CrN precipitates began to be detected with increasing temperature.

Olzon-Dionysio et al. [7] investigated the so-called “edge effect” phenomenon in plasma nitrided AISI 316L samples (Fig. 2.7). The thickness of all samples was 3.9 mm and diameter was 19.7 mm for samples A, B, and C. For sample D, the internal and external diameters were 19.7 and 31.6 mm, respectively. The plasma nitriding parameters were: temperature of 400 °C, atmosphere of 80 % N₂ + 20 % H₂, and duration of 4 h.

Fig. 2.7 Different regions of plasma nitrided samples according to their different colors [7]



According to Fig. 2.7, the borders of samples B and D (rings) were light gray, labeled 1 and 4, respectively. Toward the center, there was a region in shades of blue and brown, labeled 2 (sample B) and 5 (sample D). The central region of sample B is dark yellow, labeled as number 3. Sample C shows the same yellow shade and was labeled 6.

The depth of nitrided layer for sample C was $2.3 \pm 0.2 \mu\text{m}$. For sample B it was $1.5 \pm 0.1 \mu\text{m}$.

After plasma nitriding some phases such as γ_{N} , $\epsilon\text{-Fe}_{2+x}\text{N}$ (hexagonal), γ' (FCC), and chromium nitrides were detected as well as γ phase. The peaks for γ_{N} were in lower angles compared to γ peaks and had broader shapes as a result of nitrogen gradient.

The amount of γ phase in sample B was more than sample C, suggesting a thinner nitrided layer for sample B. The γ_{N} phase of the sample with ring (B) was closer to the γ phase than the sample without ring (C). It indicates that the γ_{N} phase presents more nitrogen atoms for C than B.

The existence of Cr_2N phase was reported on the surface of sample B. The formation of this phase can explain why the γ_{N} phase of this sample presents less nitrogen atoms than sample C which is due to the consumption of part of the nitrogen to form this Cr_2N phase.

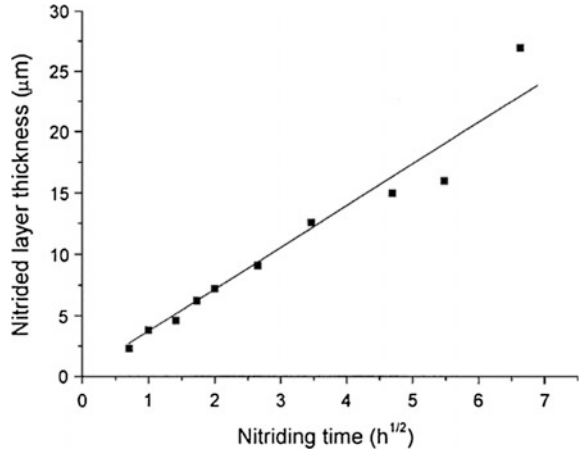
Although the nitriding temperature was 400°C , it reached 420°C in borders of sample because of edge effects. When reaching this temperature, the decomposition of metastable γ_{N} phase occurs due to reaching the solubility limit of nitrogen in the austenite structure and consequently chromium nitrides precipitates, which is relatively a stable phase. Consequently the γ_{N} phase decreased where samples B and D, which contain rings, showed smaller amounts of γ_{N} phase than C, without rings.

Nakajima et al. [8] studied the effects of solution treatment after plasma nitriding on the properties of the nitrided layer formed on AISI 304 austenitic stainless steel. The samples were solution treated at 1080°C for 30 min followed by plasma nitriding at 500°C for 8 h. The post-solution treatment was done at 1200°C for 1 h.

No grain growth was reported by the authors because the grain size remained almost constant as follows: 65, 73, and $69 \mu\text{m}$ for untreated, nitrided, and nitrided-annealed samples, respectively. The nitrided layer was reported to be $50 \mu\text{m}$ thick and mainly constituted by CrN.

Wang et al. [9] studied the effects of treatment duration on properties of plasma nitrided AISI 304 austenitic stainless steel. The plasma nitriding treatment was done under pressure of 100 Pa and atmosphere of ammonia at about 420°C for different durations.

Fig. 2.8 The variations of nitrated layer thickness with nitriding time [9]



At durations lower than 8 h, the layer was featureless. However for longer treatment times of above 12 h, some defects or precipitations appeared in the nitrated layers. A linear relationship was observed between the layer thickness and second root of the duration. This can be seen in Fig. 2.8. For treatment durations of 30 min and 44 h, the thicknesses of the nitride layer were 3 and 27 μm .

The microstructure of the nitride layer was reported to be composed of expanded austenite and substrate austenitic phase. The amount of both phases increased by treatment duration.

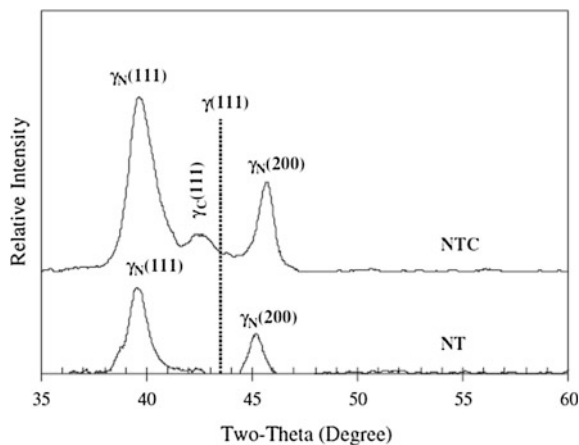
Sun et al. [10] evaluated the effect of CH_4 addition to the nitriding atmosphere on the properties of nitrated AISI 321 austenitic stainless steel. Plasma nitriding was done at range of 400–430 $^{\circ}C$ for 20 h under atmosphere of 80 % N_2 + 20 % H_2 . The addition of CH_4 was done with replacing H_2 with CH_4 with amount of 2–10 %. Three kinds of treatments were done: (1) nitriding in atmosphere of 80 % N_2 + 20 % H_2 for 5 h (NT), (2) treating in atmosphere of 95 % N_2 + 5 % CH_4 for 1 h and then nitriding in 80 % N_2 + 20 % H_2 atmosphere for 4 h (NT + NTC) and (3) treating in 95 % N_2 + 5 % CH_4 atmosphere for 5 h (NTC).

A double layer structure was observed for NTC and NT + NTC treatments in which an N-enriched layer is formed on the top and a C-enriched layer is formed under it. The thickest C-enriched layer was produced by NTC treatment as shown in Table 2.3. It can also be seen in this table that the thickness of the N-enriched layer produced by NTC and NTC+NT treatments was almost the same, which was even larger than that produced by just NT. It is obvious that the addition of carbon had a

Table 2.3 Layer thickness and surface hardness obtained from various treatments [10]

Treatment	Total thickness (μm)	N-enriched layer thickness (μm)	Surface hardness ($HV_{0.1}$)
NT	7.8	6.2	890
NT + NTC	12	9.2	1340
NTC	14	9.2	1530

Fig. 2.9 XRD patterns from surface of the samples nitrided without carbon addition (NT treatment) and with carbon (NTC treatment) addition at 420 °C for 5 h [10]



positive effect on increasing the thicknesses of N-enriched and the C-enriched layers. The improvement in hardness is also observed in this table.

As seen before, the formation of expanded austenite is common phenomenon in plasma nitriding of steels at low temperatures. This also happened for NTC treatment in which γ_C has been formed as well as γ_N . This γ_C phase is formed by supersaturation of austenite with carbon leading to lattice expansion. This is clearly seen in Fig. 2.9. The measured lattice parameter for γ_N and γ_C phases was about 0.395 and 0.371 nm, respectively, showing a significant expansion of 10 % for N-enriched and 3 % for C-enriched layers compared to 0.359 nm for austenite phase.

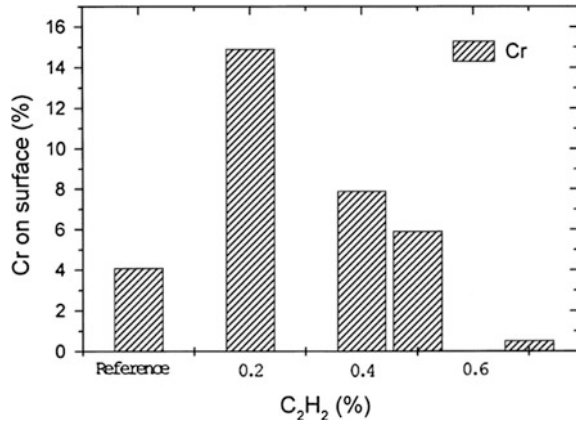
Carbon addition to the nitriding atmosphere also has reported to improve the uniformity of the layer. The sample treated with only plasma nitriding showed a nonuniform layer thickness. However, carbon addition to the atmosphere significantly improved the uniformity of the layer.

The effects of CH_4 amount have also been investigated. With addition of 2 % CH_4 , the modified zone was dominated by the N-enriched layer and had a thin C-enriched layer. Increasing the CH_4 level to 10 %, led to a further increase in thickness of the C-enriched layer and consequently the total layer thickness and the resultant N-enriched layer and C-enriched layer had similar thickness in this CH_4 amount. With a further increase in amount of CH_4 the C-enriched layer thickness increased, but with a reduction in the N-enriched layer thickness.

Borges et al. [11] studied the influences of different gas compositions of nitriding atmosphere as well as addition of C_2H_2 (acetylene) gas on properties of plasma nitrided AISI 304. Parameters of treatments were as follows: temperature of 400–600 °C, atmosphere of 95–100 % N_2 , 1–5 % H_2 , and 0–0.75 % C_2H_2 , pressure of between 5 and 10 torr.

Figure 2.10 presents the results of XPS analysis which shows the concentration of chromium on the nitride surface. It can be seen that the concentration of chromium decreased with both hydrogen and acetylene concentration.

Fig. 2.10 XPS results showing the chromium concentration on the nitride surface for different acetylene concentrations [11]



The amount of CrN formation was observed to directly be changed with the percent of hydrogen and acetylene in the nitriding atmosphere. However, the decrement of CrN was observed with temperature.

2.1.2 Martensitic Stainless Steels

Alphonsa et al. [12] studied plasma nitriding of AISI 420 martensitic stainless steel with these parameters: temperature of 530 °C, atmosphere of 20 % N_2 + 80 % H_2 , pressure of 300–400 Pa, and duration of 20 h.

The only phase detected in untreated surface was α -Fe whereas for plasma nitrided sample, ϵ - Fe_3N was detected in addition to α -Fe. The presence of CrN and traces of Fe_4N , in addition to the Fe_3N were also reported. The higher carbon content (>0.15 %) in AISI 420 was probably responsible for predominancy of Fe_3N .

The case depth was 61 μm . The microstructure over the case depth was different from that within the first 2–5 μm from the surface which shows the predominancy of the ϵ - Fe_3N phase.

The XPS spectrum of Fe2p shown in Fig. 2.11 consists of single peak Fe2p_{3/2} and Fe2p_{1/2} at 707 and 720.17 eV. It seems from this figure that the processing has not resulted in surface oxidation because the values of binding energies and also the shape of spectra which is asymmetric shape are in accordance with metallic Fe. Also, the Fe oxidation results in some changes such as large chemical shift and satellite structure in Fe2p spectrum, which are not observed here.

N1s spectrum (Fig. 2.12) with a binding energy of 397 eV is a peak typical of a metal nitride and confirms the formation of nitride. This peak belongs to both CrN and Fe_3N .

Fig. 2.11 Fe2p core-level XPS spectrum of plasma nitrided AISI 420 (*thin line*) along with the asymmetric Voigt function curve-fit (*thick line*). This figure clearly indicates that no oxidation occurred on the surface [12]

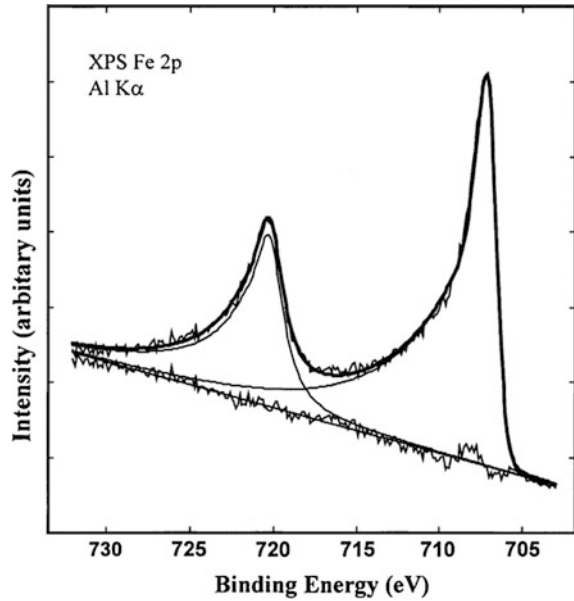
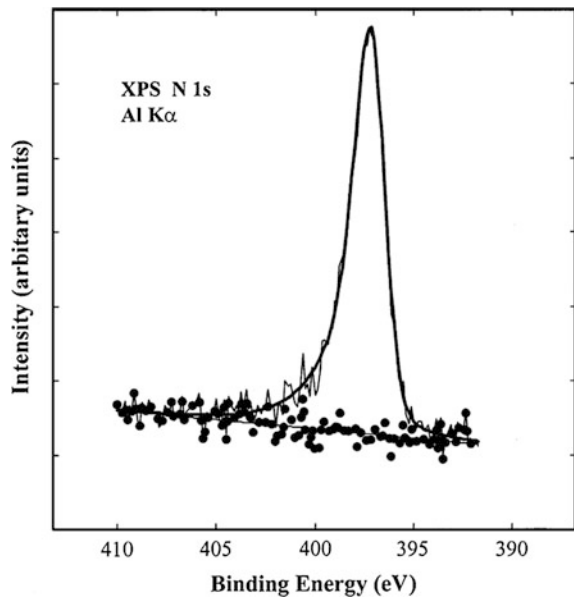
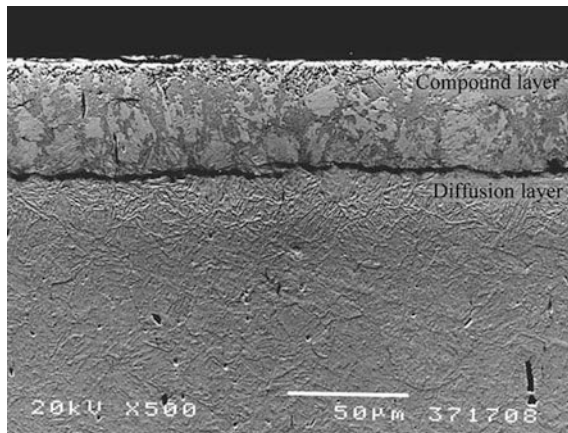


Fig. 2.12 N1s core-level XPS spectrum of plasma nitrided AISI 420 (*thin line*) superimposed with a single peak Voigt profile (*thick line*) indicating nitride formation [12]



Li et al. [13] investigated plasma nitriding properties of AISI 410 martensitic stainless steel. They did the treatment at temperatures of 420, 460, and 500 °C, in the atmosphere of 25 % N₂ + 75 % H₂, under pressure of 500 Pa for 20 h.

Fig. 2.13 Microstructure of AISI 410 martensitic stainless steel plasma nitrided at 420 °C [13]



The compound layer had a multiphase structure as indicated from composition variations in the layer in Fig. 2.13. The average thickness of the compound layer was 47, 86, and 135 μm for treating temperatures of 420, 460, and 500 °C, respectively. As seen in this figure, the microstructure in the diffusion zone is coarser than the substrate.

They reported that the untreated sample and the 420 °C nitrided surface consisted of mainly $\alpha\text{-Fe}$ and $\epsilon\text{-Fe}_{2-3}\text{N}$, respectively. Small amounts of $\gamma'\text{-Fe}_4\text{N}$ were also detected. The other phase detected was α_{N} or expanded martensite. This phase was formed by supersaturation of martensite by nitrogen atoms. No CrN peaks were detected by XRD analysis, indicating the prevention of the CrN formation in the surface of the AISI 410 steel when nitriding at 420 °C.

Increasing the treatment temperature to 460 °C, resulted in dominating of surface by $\gamma'\text{-Fe}_4\text{N}$, and reducing the amount of $\epsilon\text{-Fe}_{2-3}\text{N}$. CrN precipitates were also detected in the nitrided surface. Because of overlapping the peaks of α_{N} with those of CrN or ϵ , α_{N} could not be positively determined.

At 500 °C, the amount of $\gamma'\text{-Fe}_4\text{N}$ in the nitrided surface was further increased, but the amount of $\epsilon\text{-Fe}_{2-3}\text{N}$ became minor. It was believed that at 500 °C nitrogen in the α_{N} phase dissolved and combined with Cr in the steel to form stoichiometric CrN precipitates. This reduced the amount of nitrogen in solid solution, diminished the lattice expansion, and thus, shifted the XRD peak back to the position for $\alpha\text{-Fe}$.

Pinedo et al. [14] studied plasma nitriding of AISI 420 martensitic stainless steel. They did the treatment with these parameters: temperatures of 480, 500, 520, 540, and 560 °C, atmosphere of 75 % N_2 + 25 % H_2 , pressure of 250 Pa, and duration of 4 h.

They observed that increasing temperature resulted in thickening of the compound layer. No grain boundaries in nitrides network in the diffusion zone were observed. Also a clear interface between the diffusion zone and the substrate was observed for all nitriding temperatures.

The compound layer was found to consist of γ' -Fe₄N, ϵ -Fe₂₋₃N, and CrN nitrides.

Wu et al. [15] applied new and modified plasma nitriding methods to improve the properties of AISI 420 martensitic stainless steel. Cyclic plasma oxynitriding and cyclic plasma nitriding catalyzed by rare earth La were performed and compared with conventional plasma nitriding.

Conventional plasma nitriding was done in atmosphere of 70 % N₂ + 30 % H₂, at temperature of 560 °C for 25 h.

For cyclic plasma oxynitriding, some air entered in treatment atmosphere with amount of less than 5 % but the ratio of N₂/H₂ remained 7:3. For cyclic plasma nitriding catalyzed by La, four blocks of La were put directly in the four corners of the plasma nitriding furnace. The treatment cycle was as follows: nitriding at 560 °C for 3 h, cooling to room temperature in 30 min in an atmosphere of pure H₂, repeating of this stage for three times.

It was observed that the modified layer of the samples treated by conventional nitriding and cyclic plasma nitriding catalyzed by La, consisted of two layers of compound layer and diffusion zone in contrast with cyclic plasma oxynitrided samples that just had diffusion layer. The nitrided depths of the samples treated using conventional plasma nitriding, cyclic plasma oxynitriding, and cyclic plasma nitriding catalyzed by rare earth La in four cycles were 0.25, 0.35, and 0.64 mm, respectively.

The advantage of cyclic plasma oxynitriding technique was formation of a thicker layer in a shorter time so the role of some air was evaluated to be positive for accelerating the nitriding process. With developing the reaction between iron and oxygen in the plasma state, the formation of a loose and porous oxides on the surface was accelerated leading to absorbing a large amount of nitrogen by these active sites during the deoxidization process. The mentioned process led to a high nitrogen concentration in the nitrided case. Therefore a thicker nitrided case has been obtained with speeding up the nitrogen transportation.

Using La as a catalyst also increased the nitrogen diffusion on the surface. This occurred as a result of ionizing the La atoms and their sedimentation on the surface of the sample and activation of the surface by lattice distortion for increasing the diffusion of nitrogen atoms.

During cooling from nitriding temperature, the nitrogen-enriched ϵ phase has been transformed into less nitrogen containing γ' phase. This action has increased the interfaces and consequently the channels for diffusion of nitrogen. With reheating the sample, more nitrogen atoms diffused into the sample and the nitride layer grew thicker.

After treatment, all of the nitride layers were consisted of γ' , CrN and α . Some ϵ phase was also detected for the samples nitrided by conventional plasma nitriding in 25 h and cyclic plasma nitriding catalyzed by rare earth La in four cycles. For the sample treated by the cyclic plasma oxynitriding, traces of Fe₃O₄ have been also detected.

2.1.3 Precipitation Hardening Stainless Steels

Esfandiari et al. [16] studied plasma nitriding behavior of A286 (AISI 600) precipitation hardening stainless steel with following parameters: temperatures of 350, 370, 390, 420, 460, and 500 °C, atmosphere of 25 % N₂ + 75 % H₂, pressure of 500 Pa, and durations of 5, 10, 20, and 30 h.

They reported that the layer thickness varied from 1.2 μm (350 °C/5 h) to 60 μm (500 °C/30 h). Treating at 350 °C for 10 h resulted in transformation of the austenite phase in the modified layer into expanded austenite. At 420 °C in short time (5 h), surface of the nitrided samples mainly consisted of s-phase. Further increase in time (10 h and 20 h) caused γ'-Fe₄N and Cr₂N to start to form. Cr₂N phase was also formed at 500 °C. Therefore, it can be concluded that in precipitation hardening stainless steels, chromium nitride starts to form with increasing temperature as observed in case of austenitic stainless steels.

At a constant temperature (specially low treating temperatures), a linear relationship was found between the square root of time and the thickness of the layer. Figure 2.14a shows the variations of the nitride layer thickness with the treatment time. The linear growth of the nitrided layer with the square root of time confirms the governing of layer growth by nitrogen solid diffusion.

Also as can be seen in Fig. 2.14b, the growth of nitrided layers can be divided into two regions: low-temperature (350–390 °C) region with slow growth and high-temperature (420–500 °C) region with a fast growth. The activation energies for these two regions are 115 and 104 kJ/mol, respectively.

Sobiecki et al. [17] did an investigation on plasma nitriding of H9S2 stainless steel (with chemical composition shown in Table 2.4) with conditions listed in Table 2.5.

In accordance with other researchers, they also found the dependence of the diffusion nitrided layer thickness on both the temperature and the duration of the process. The thickness of the layers produced by processes 1 and 3 was the same. According to their results, the composition of nitriding atmosphere did not change the thickness of the nitrided layer.

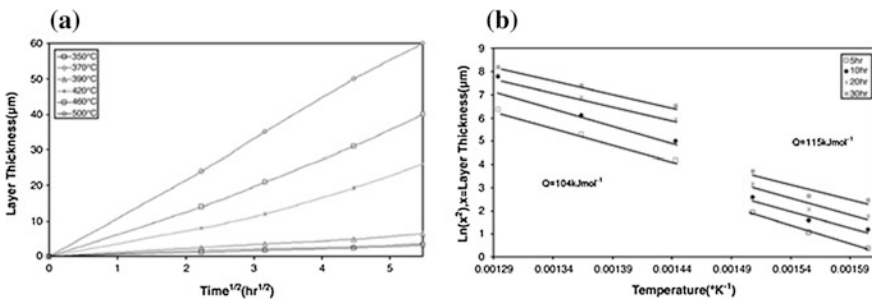


Fig. 2.14 Dependence of nitriding kinetics of A286 on **a** time and **b** temperature [16]

Table 2.4 Chemical composition of H9S2 steel [17]

C (%)	Mn (%)	Si (%)	Cr (%)	Ni (%)	Fe (%)
0.35–0.45	0.7	2	8–10	0.6	Balance

Table 2.5 Plasma nitriding parameters used by Sobiecki et al. [17]

No.	Temperature (°C)	Duration (h)	Atmosphere ($\frac{N_2}{H_2}$)
1	450	6	$\frac{1}{2}$
2	520	6	$\frac{1}{2}$
3	570	3	$\frac{1}{2}$
4	620	3	$\frac{1}{2}$
5	650	3	$\frac{1}{2}$
6	550	3	$\frac{1}{1}$
7	550	3	$\frac{2}{1}$
8	550	3	$\frac{1}{4}$

Li et al. [18] studied plasma nitriding of 17–4 precipitation hardening stainless steel. They applied these parameters: temperatures of 350, 400, 420, 450, and 480 °C, atmosphere of 20 % N₂ + 80 % H₂, pressure of 600 Pa, and duration of 4 h.

As can be seen in Fig. 2.15a, a 5 μm bright layer formed on the sample which was plasma nitrided at 350 °C for 4 h. However, for both of the samples treated with 420 °C/4 h and 480 °C/4 h conditions, an approximately 10 μm thick dark layer was observed (Fig. 2.15b, c). This indicated the susceptibility of this type of layer (from temperature above 400 °C processes) to etching in nital.

Nitrogen concentration profile across nitrided layers is shown in Fig. 2.16. At high temperatures, defect recombination (Frenkel pairs) resulted in a reduction in the surface stress and favoring nitrogen diffusion. Consequently, the highest nitrogen content of these nitrided layers was measured to be 12 wt% at 480 °C. Therefore, the nitrogen concentration at the surface of nitride layers formed with nitriding at 480 °C was higher and nitrogen penetration depth was deeper in comparison to the samples nitrided at temperatures less than 480 °C. Moreover, nitriding at increased temperature led to nitriding depths of more than 10 μm.

They have found that untreated sample mainly consisted of α phase. With the inward diffusion of the nitrogen, the FCC grain lattice was supersaturated by nitrogen to such extent that the transformation of alpha (α) into s-phase occurs. Therefore, at 350 and 400 °C, the main constituents of microstructure were a metastable “s-phase,” substrate alpha (α) and the α_N (expanded martensite). However, as seen before about austenitic stainless steels, at temperatures above 420 °C the s-phase peaks disappear. This was probably due to the depletion of the

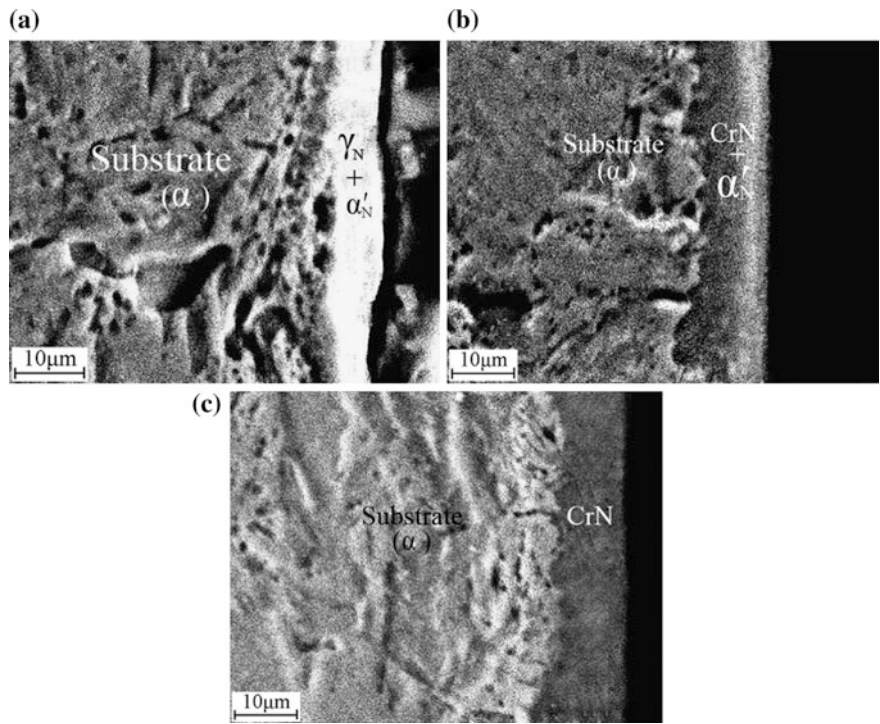
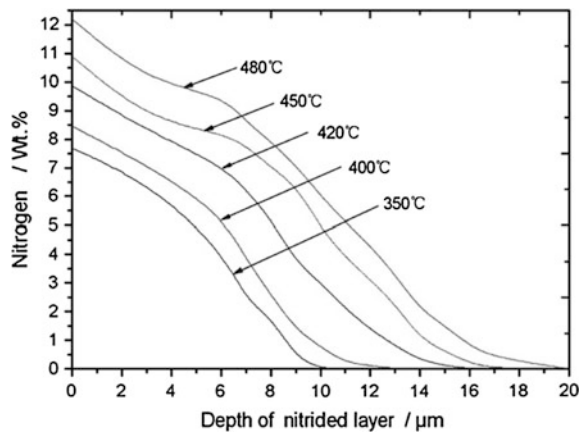


Fig. 2.15 Cross-sectional SEM micrographs of samples nitrided at various temperatures of **a** 350 °C, **b** 420 °C, and **c** 480 °C [18]

Fig. 2.16 Nitrogen concentration profile achieved at different temperatures for 4 h [18]



expanded phase of chromium at 420 °C resulted by CrN precipitation which results in the formation of a mixture layer of α_N and CrN (s-phase $\rightarrow \alpha_N + CrN$). Completely disappearing of α_N was possibly due to the decomposition of α_N into

alpha (α) and CrN. Furthermore, at temperature ≥ 450 °C the alpha (α) peak sharpened and returned to the unnitrided diffraction angle probably because of structure relaxation produced by the precipitation ($\alpha_N \rightarrow \alpha + \text{CrN}$).

Dong et al. [19] studied plasma nitriding of 17-4PH martensitic stainless steel and found almost the same results found by Li et al. [18]. They applied the following conditions: temperatures of 350, 370, 390, 420, 460, and 500 °C, atmosphere of 25 % N_2 + 75 % H_2 , pressure of 500 Pa, and durations of 10, 20 and 30 h.

For samples nitrided under 420 °C, a bright layer was observed. This was due not to have been attacked by etchant solution. However, the upper part of the layer treated at 420 °C for 20 h was slightly etched, indicating the nitrides precipitation during the treatment. With nitriding at 500 °C or above, the nitrided case became dark and grain boundaries in the treated case were preferentially etched. It should be noted that further increasing the nitriding temperature or time resulted in the development of the dark layer toward the layer/core interface.

The untreated sample mainly constituted by martensite and retained austenite (γ). High-temperature (≥ 460 °C) treated samples mainly consisted of chromium nitride (CrN) and γ' - Fe_4N . However, low-temperature nitrided samples were characterized by highly overlapped peaks and it was very difficult to characterize overlapped peaks of potential phases (γ' - Fe_4N , s-phase, α_N and CrN). Therefore, TEM was also used for further studies.

TEM observation of untreated 17-4PH stainless steel revealed the dominance of the lath martensite phase with the length of about 2–2.5 μm and width of 0.3–0.9 μm . A typical microstructure and corresponding SAD of $b = [100]_\alpha$ pattern are shown in Fig. 2.17. There were traces of retained austenite along the boundaries of martensite laths.

The maintained martensite features as well as micro twins and slip lines across martensite laths were observed for 350 °C/10 h treated sample. Also, the calculated lattice parameter ($a = 0.290$ nm) for this sample was larger than for the untreated samples ($a = 0.287$ nm). This difference can be ascribed to the supersaturation of nitrogen in the martensite. Also GDS (Glow Discharge Spectroscopy) results revealed the abundance of nitrogen amount in the nitrided layer compared to the solubility of nitrogen in the martensite lattice. Therefore, it can be concluded that the nitrided layer formed at temperatures below 420 °C is a nitrogen supersaturated martensite layer rather than a compound layer.

Microstructural observations revealed the existence of isolated s-phase grains in all the samples plasma nitrided at 420 °C and lower temperatures for 10 h. They also observed that α_N surrounded the s-phase and the size and distribution of the s-phase were similar to that of the retained austenite. From these findings and observations, it was concluded that the formation of s-phase in the martensitic 17-4PH stainless steel was resulted by the conversion of the retained austenite in the initial material. Therefore, the formation of s-phase was not as a continuous layer in plasma nitrided layers.

According to the results of TEM investigation (Fig. 2.18), when 17-4PH stainless steel was plasma nitrided at temperatures above 420 °C or at 420 °C for

Fig. 2.17 **a** *Bright* field TEM micrograph and **b** corresponding SAD pattern, $b = [100]$, of untreated 17-4PH stainless steel [19]

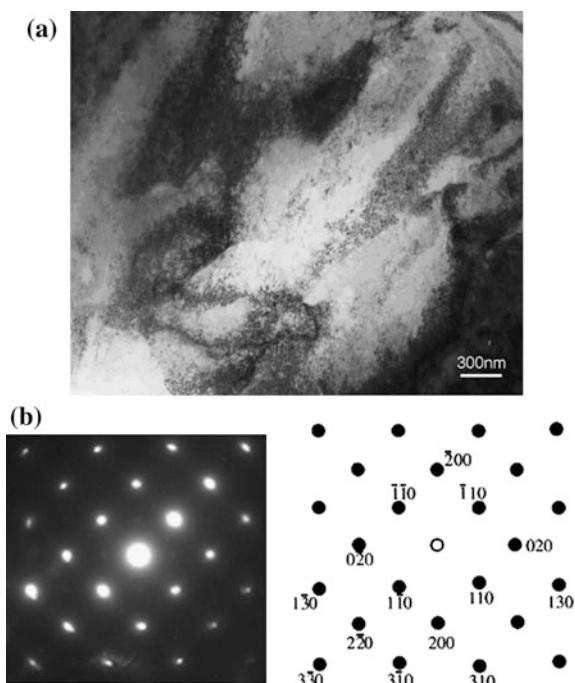
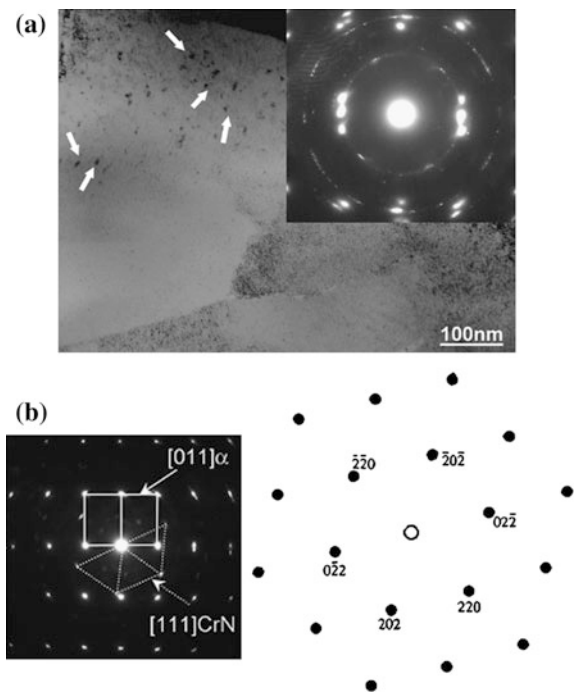


Fig. 2.18 **a** *Bright field TEM micrograph and*
b *corresponding SAD pattern*
from the CrN phase in
420 °C/20 h treated sample
[19]



more than 10 h, the decomposition of ϵ -phase into CrN and α -Fe occurred simultaneously with precipitation of CrN from α_N .

2.1.4 Tool Steels

Birol [20] investigated plasma nitriding behavior of the X32CrMoV33 hot work tool steel with these conditions: temperature of 520 °C, atmosphere of 100 % NH_3 , pressure of 100 Pa, and duration of 12 h.

The compound layer had the thickness of 6 μm and consisted of $\epsilon\text{-Fe}_{2-3}\text{N}$ phase.

Nouveau et al. [21] studied plasma nitriding of 90CrMoV8 tool steel at temperatures of 460, 500, and 520 °C, in atmosphere of 80 % N_2 + 20 % H_2 , under pressure of 500 Pa and for 6, 8, 10, and 12 h.

The Fe and all the iron nitride peaks were broadened and shifted to lower angles with treatment duration (with respect to untreated sample).

With increasing the treatment duration, γ' (110) and (200) peaks were broadened. The ϵ phase in all durations was present with high intensity as observed by Birol [20].

It was observed that in a fixed treatment duration, the Fe (110) peak widened and shifted toward the lower angles with respect to untreated steel ones, regardless of the process temperature. It can be implied that the temperature was less effective than duration. Also it was obvious that, the higher the temperature, the lower the angles and no trace of chromium nitrides was observed.

da Silva Rocha et al. [22] investigated plasma nitriding of AISI M2 high-speed steel. They applied these conditions: temperatures of 350, 400, 450, and 500 °C, atmosphere of 5 and 76 % N_2 + 95 and 24 % H_2 , pressure of 500 Pa, and duration of 30 min.

The untreated sample was constituted by the α -iron as well as carbides of the tool steel. A gas composition of 76 vol.% N_2 in the plasma resulted in the formation of a compound layer at 400 and at 500 °C composed of the ϵ -phase. At 500 °C alloying elements nitrides were formed and the primary and secondary carbides of steel transform to carbonitrides or even nitrides.

For lower nitrogen content in the gas, higher intensity of α -Fe, no compound layer at 500 °C, no ϵ -nitride, and some γ' -nitride were observed.

Figure 2.19 confirms XRD results. As can be seen in Fig. 2.19, no continuous compound layer was formed at the surface of samples nitrided in atmosphere of 5 vol.% N_2 . However, plasma nitriding in the atmosphere of 76 vol.% N_2 resulted in the formation of compound layer at all temperatures. As can be seen from Fig. 2.19 and Table 2.6, 5 vol.% N_2 led to the formation of a thin diffusion zone only. The depth of the diffusion zone increased from 4 to 6 μm to about 16–20 μm with temperature. However, with 76 vol.% N_2 , both compound layer thickness (from 0.5 to 2.3 μm) and depth of diffusion zone increased with temperature (from 8 μm to about 30 μm).

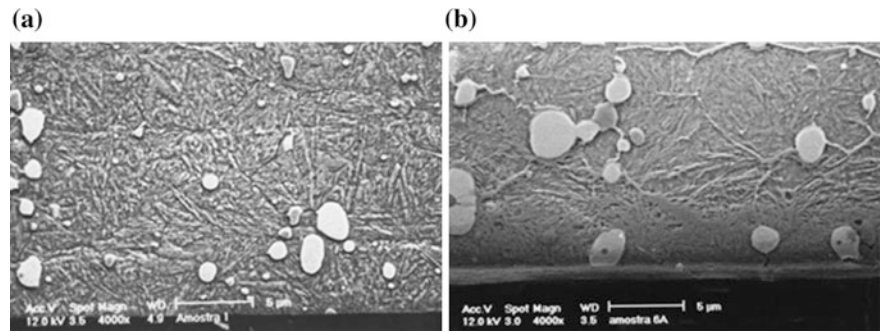


Fig. 2.19 SEM Cross-sectional images of a sample plasma nitrided at 500 °C for 30 min in atmosphere of **a** 5 vol.% N₂ and **b** 76 vol.% N₂ [22]

Table 2.6 Compound layer and diffusion zone thicknesses of samples plasma nitrided at different temperatures and with different gas compositions [22]

Parameters	Compound layer (µm)		Diffusion zone	
	Metallography	GDOS	Metallography	GDOS
350 °C, 5 % N ₂	–	–	6.0	4.0
350 °C, 76 % N ₂	0.5	0.4	8	4.0
400 °C, 5 % N ₂	–	Not measured	6.5	Not measured
400 °C, 76 % N ₂	0.7	Not measured	6.5	Not measured
450 °C, 5 % N ₂	–	Not measured	12.5	Not measured
450 °C, 76 % N ₂	1.3	Not measured	14	Not measured
500 °C, 5 % N ₂	–	–	16.0	23.4
500 °C, 76 % N ₂	2.3	2.8	24.0	32.6

Pessin et al. [23] studied plasma nitriding of AISI M2 high-speed steel with parameters presented here: temperatures of 450 and 500 °C, atmosphere of 25 % N₂ + 75 % H₂, pressures of 200, 400 and 900 Pa, and duration of 60 min.

Table 2.7 summarizes the results of metallographic analysis and X-ray diffraction. The X-ray diffraction patterns for two of the conditions used are shown in Fig. 2.20. Although the microstructural analysis of all samples did not reveal a compound layer, it can be seen from Table 2.7 and Fig. 2.20 that the γ' -phase was formed at 500 °C and the ϵ -phase was observed for both temperatures, which indicated the formation of compound layer. It can be observed that the nitride formation ratio ϵ/γ' decreases when temperature is increased.

Increasing of pressure from 200 to 400 and 900 Pa at 500 °C resulted in the formation of γ' -Fe₄N and ϵ -Fe₂₋₃N phases, although only ϵ -nitrides were observed at 450 °C.

According to Table 2.7, it is obvious that samples nitrided at 400 Pa exhibited deeper case depths than those nitrided at 200 and 900 Pa. This can be due to better plasma distribution and nitriding efficiency in this pressure.

Table 2.7 Iron nitrides identified (X-ray analysis) and layer depth (GDOS test) [23]

	Temperature					
	450 °C			500 °C		
	200 Pa	400 Pa	900 Pa	200 Pa	400 Pa	900 Pa
Compound layer composition	–	ε	ε	–	ε and γ′	ε and γ′
Layers depth (μm)	22	36	31	31	57	32

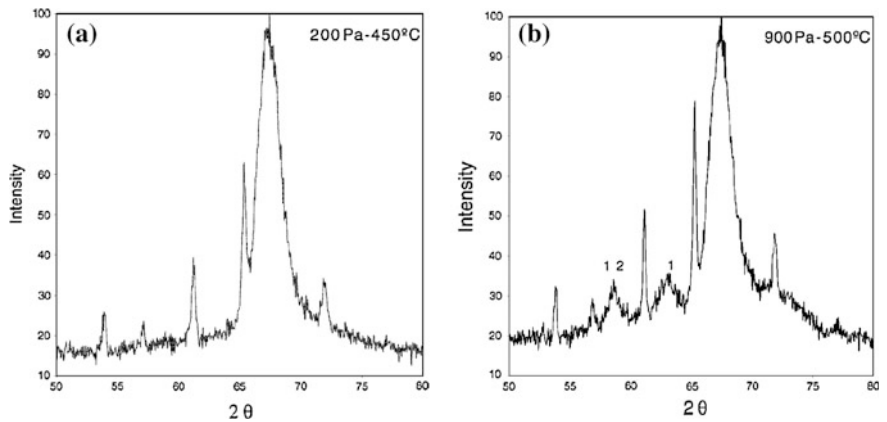


Fig. 2.20 XRD patterns showing **a** the absence of compound layer and **b** the characteristic peaks of ε (1) and γ′ (2) nitrides [23]

2.1.5 Structural and Constructional Steels

Li et al. [24] studied plasma nitriding of 709M40 low alloy steel with applying these parameters: temperature of 500 °C, atmospheres of 25 % N₂ + 75 % H₂ and 65 % N₂ + 35 % H₂, pressure of 500 Pa, and durations of 3, 10 and 40 h.

The samples were treated at 500 °C for 10 h with two nitrogen potentials. Both of the conditions produced a similar case. The compound layer was mainly consisted of γ′-Fe₄N with traces of ε-Fe₂₋₃N. The average thickness of the compound layer was 4.3 μm (for 25 % N₂) and 7.5 μm (for 65 % N₂).

Karaoğlu [25] investigated plasma nitriding of AISI 5140 low-alloy steel. The applied parameters are presented in Table 2.8.

The nitrided samples consisted of a compound layer and a diffusion zone. As can be seen in Table 2.9, increasing time and/or temperature increased the thickness of the diffusion layer by increasing the nitrogen diffusion through the layer. It seems that, increasing the nitrogen content in gas mixture resulted in decreasing the case depth. Also it can be indicated from Table 2.9 that the process temperature is the most effective parameter on the thickness of compound layer. It was reported that at the same temperature, the amount of ε-phase decreased but that of γ′ increased with time. Also increasing the process temperature caused

Table 2.8 Plasma nitriding conditions used by Karaoğlu [25]

Group	Temperature (°C)	Duration (h)	Atmosphere ($\frac{N_2}{H_2}$)	Pressure (Pa)	Voltage (V)
1.500.20	500	1	$\frac{20}{80}$	1000	400–600
4.500.20	500	4	$\frac{20}{80}$	1000	400–600
12.500.20	500	12	$\frac{20}{80}$	1000	400–600
4.450.20	450	4	$\frac{20}{80}$	1000	400–600
4.550.20	550	4	$\frac{20}{80}$	1000	400–600
4.500.60	500	4	$\frac{60}{40}$	1000	400–600

Table 2.9 Maximum case depth and compound layer thickness values obtained with applying different process parameters [25]

	Specimen group					
	1.500.20	4.500.20	12.500.20	4.450.20	4.550.20	4.500.60
Surface hardness (HV)	760	986	862	943	810	940
Case depth (μm)	166	320	496	247	424	306
Compound layer (μm)	2.5	5.5	7	2	11	7.5

an increase in the amount of γ' phase but reduced the amount of ε phase. Lowering the nitrogen content in the nitriding atmosphere led to an increase in the formation of γ' but a reduction in formation of ε .

Karakan et al. [26] studied plasma nitriding of AISI 5140 steel by means of different gas mixtures of 10 % H_2 + 90 % N_2 , 10 % Ar + 90 % N_2 , 90 % Ar + 10 % N_2 , 90 % H_2 + 10 % N_2 , 10 % Ar + 10 % H_2 + 80 % N_2 , 80 % Ar + 10 % H_2 + 10 % N_2 , 10 % Ar + 80 % H_2 + 10 % N_2 . The treatment temperature and duration were 450 °C and 4 h. Figures 2.29 and 2.30 show XRD results for AISI 5140 low-alloy steel plasma nitrided under various gas mixtures. As seen clearly in these figures, multiphase (γ and ε) iron nitrides formed on the surface of plasma nitrided low-alloy steel.

Figure 2.21 shows the XRD results of the plasma nitrided specimens at gas mixtures of 10 % H_2 + 90 % N_2 and 10 % Ar + 90 % N_2 . For as much as the intensity of ε phase was not high, α -Fe phase was clearly observed when Ar- N_2 mixtures were used as nitriding atmosphere. Gas mixture of 10 % Ar + 90 % N_2 led to the formation of a thin compound layer because the amount of Ar in the gas mixture was not sufficient to create diffusion. It was observed that the presence of at least 20 % Ar in dual gas mixture is necessary to form a compound layer and to increase surface hardness. However, using 10 % H_2 gas mixture formed a compound layer because the ionization energy of H_2 is lower than that of Ar.

Fig. 2.21 XRD patterns of plasma nitrided AISI 5140 steel for gas mixtures of 10 % H_2 + 90 % N_2 (a) and 10 % Ar + 90% N_2 (b) [26]

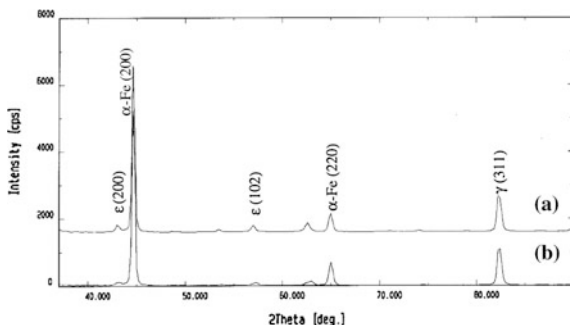


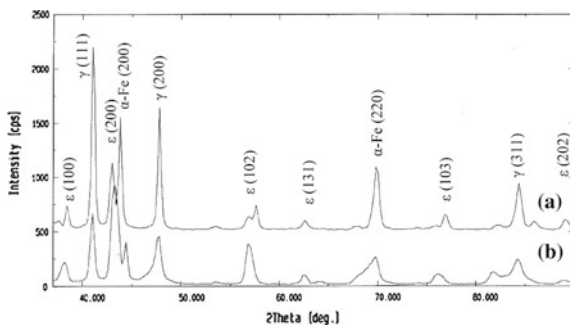
Figure 2.22 illustrates the XRD results of the samples plasma nitrided at gas mixtures of 90 % H_2 + 10 % N_2 and 90 % Ar + 10 % N_2 . While the intensity of ϵ decreased for Ar- N_2 mixtures, the intensity of γ increased for H_2 - N_2 mixtures.

When the amount of Ar in the gas mixture increased, the intensity of compound layer phases increased.

Mahboubi et al. [22] investigated plasma nitriding of DIN 1.6959 low alloy steel. They have applied these conditions: temperatures of 350, 400, 450, 500, and 550 °C, atmosphere of 75 % N_2 + 25 % H_2 , pressure of 400 Pa, and duration of 5 h.

According to Fig. 2.23, the compound layer is observable for all samples. Plasma nitriding at 550 °C led to a more uniform interface between compound layer and diffusion zone. However for samples nitrided at 350 and 450 °C, the compound layer extended into the grain boundaries at some areas along the interface. This can be due to the grain boundary and volume diffusion coefficients which are temperature dependent. At low treatment temperatures, the mobility of nitrogen atoms was low and penetration was done more easily at less compact diffusion routes such as grain boundaries. Therefore, nitrogen atoms diffusing along the boundaries will be able to penetrate much deeper than atoms that only diffuse through the more compact areas such as grains (lattice diffusion). Increasing treatment temperature

Fig. 2.22 XRD patterns of plasma nitrided AISI 5140 steel for gas mixtures of 90 % Ar + 10 % N_2 (a) and 90 % H_2 + 10 % N_2 (b) [26]



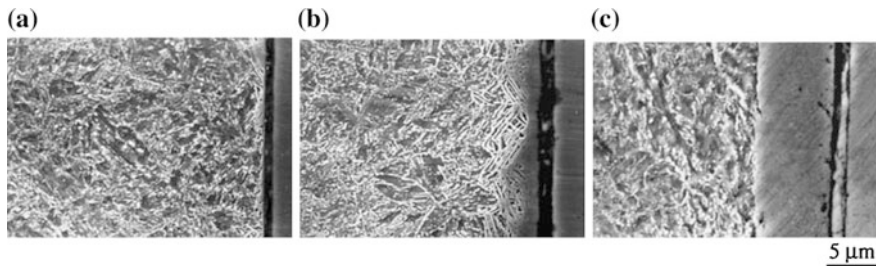


Fig. 2.23 SEM images of the surface layers of the samples plasma nitrided at various **a** 350, **b** 450, and **c** 550 °C [27]

led to the increment of the nitrogen atoms mobility. Thus, lattice diffusion dominated and the penetration of nitrogen atoms through grains occurred more easily, leading to the formation of a more uniform compound layer.

They have observed that the thickness of compound layer and diffusion zone generally increased with increasing temperature because the growth of the compound layer is controlled by diffusion of nitrogen through this layer.

The compound layer of all samples mainly consisted of ϵ and γ' nitrides. Their intensities increased with temperature due to the diffusion kinetics explained before. However the intensity of iron peaks decreased. This can be explained by prevention of the incident X-ray from reaching the substrate with layer thickening.

Yasavol et al. [28] investigated the effects of post-oxidizing treatment on properties of plasma nitrided AISI 4130 steel. The plasma nitriding treatment was done under pressure of 4 mbar and gas atmosphere of 75 % N_2 + 25 % H_2 at temperature of 550 °C. Post-oxidizing treatment was done under pressure of 4 mbar and at temperatures of 400 and 500 °C. Three gas mixtures were used for this treatment: 25 % O_2 + 75 % H_2 , 10 % O_2 + 90 % H_2 , and 100 % O_2 .

After post-oxidizing treatment, the presence of several phases was reported such as Fe_3N , Fe_4N , Fe_2O_3 , Fe_3O_4 , and Fe. This may be due to the fact: with growing the oxide layer during oxidation treatment, the nitrogen atoms were released. One part of these released atoms which diffused into the matrix and the interface of oxide and nitride layer. Therefore, the transformation of γ' - Fe_4N to ϵ - Fe_3N occurred. The presence of Fe in the microstructure was attributed to two phenomena: (1) decomposition of γ' to $\gamma' + (\alpha\text{-Fe}_3N)$ which occurs due to exposure to treatment temperature during plasma oxidizing, which produces α iron and (2) more penetration of the X-ray beam into deeper depth of the substrate because of lower absorption coefficient of iron oxides compared to that of iron nitrides.

For oxidizing atmosphere of 100 % O_2 , Fe_2O_3 and Fe_3O_4 phases were detected. With adding hydrogen and using the above-mentioned gas mixtures, the amount of oxide phases decreased. Also as the oxygen content decreased in the oxidizing atmosphere, the decrement in the amount of Fe_3O_4 was more than Fe_2O_3 .

The thickness of compound layer was reported to be 12 μm , while that of oxide layer was observed to be 1, 1.3, and 1.6 μm for oxidizing atmospheres of 25 % O_2 + 75 % H_2 , 10 % O_2 + 90 % H_2 , and 100 % O_2 .

Alsaran et al. [29] also investigated the effects of post-plasma oxidizing treatment on the properties of AISI 5140 steel. Plasma nitriding was done at 500 $^{\circ}\text{C}$, under atmosphere of 40 % N_2 + 60 % H_2 and pressure of 5 mbar for 4 h. The post-oxidizing treatment was done at 500 $^{\circ}\text{C}$ for 15, 30, and 60 min under a pressure of 2 mbar and atmosphere of only nitrogen.

With plasma oxidizing for 30 min, a 0.4 μm thick oxide layer was reported to be formed on the nitride layer of 5 μm thick. For nitrided sample, only nitride phases of γ' - Fe_4N and ε - Fe_3N as well as small amount of oxide (resulted from insufficient evacuation) were detected. For durations more than 15 min, the oxide layer made of two oxide phases of Fe_2O_3 and Fe_3O_4 was formed. In lower durations and early stages of oxidation, Fe_3O_4 was formed however with further durations, the intensities of both oxides enhanced. For duration of 60 min, α -Fe peaks also arose. This can be attributed to thinning of compound layer owing to sputtering effect and lower absorption coefficient of iron oxides.

Alsaran et al. [30] investigated the effects of post-aging treatment on the plasma nitrided AISI 4140 steel. They plasma nitrided samples with following parameters: atmosphere of 50 % N_2 + 50 % H_2 , duration of 1 h, temperature of 575 $^{\circ}\text{C}$, and pressure of 1000 Pa. The samples were quenched and then the post-aging treatment was done at 400 $^{\circ}\text{C}$, for durations of 0.5, 1, 4, 8, and 12 h in a gas mixture of 50 % H_2 + 50 % Ar.

The microstructure of both quenched and post-aged samples consisted of compound layer and diffusion zone. As seen in Fig. 2.24, two distinct layers of γ' and ε phases are distinguishable and their separating line is obvious. The compound layer had the thickness of almost 20 μm . The quenching after nitriding resulted in the formation of α_{N} phase. After aging, a new needle-shaped α'' phase was initiated

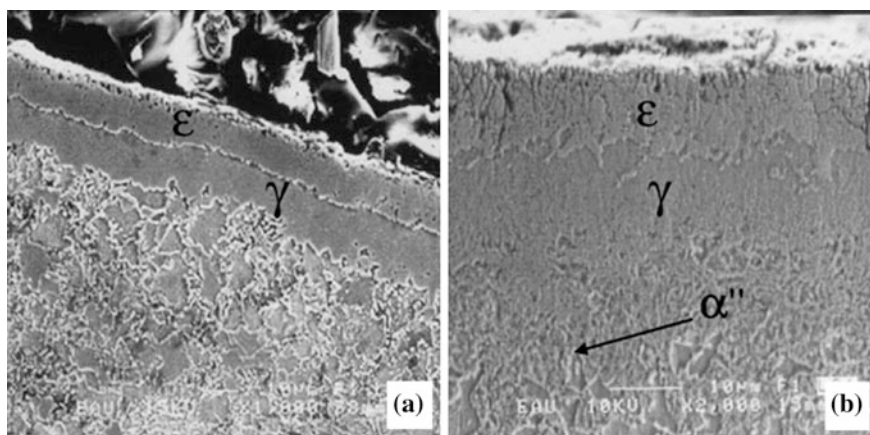


Fig. 2.24 SEM micrographs of specimens **a** quenched and **b** plasma post-aged for 1 h [30]

from martensite. The most intense α'' phase was observed for duration of 1 h because of the increasing possibility of nitrogen diffusion due to ion bombardment.

After aging treatment the amount of γ' and ε phases decreased and α phase was detected. The decomposition of nitride phases resulted in the releasing of nitrogen and its diffusion into the α phase. This supersaturated phase also was transformed to more stable α'' -Fe₁₆N₂. The amount of this phase reached its maximum value for the duration of 1 h.

Alves et al. [31] studied the effect of three different cooling rates on the microstructural properties of the AISI 1010 steel. Plasma nitriding procedure was done with following parameters: atmosphere of 20 % N₂ + 80 % H₂, temperatures of 500 and 580 °C, duration of 2 h, and pressure of 500 Pa. Three cooling method was applied on the nitrided samples: (1) cooling naturally on the sample holder, (2) cooling on a cold surface and (3) cooling in an oil medium.

In the case of nitriding at 500 °C, two distinct layers of compound layer (of 4 μ m) and diffusion zone were observed. For cooling procedures of 2 and 3, a clear boundary was not observed between diffusion zone and the substrate. For the sample cooled on the holder with total nitrided layer of 300 μ m, two diffusion zones were distinguished: First, a zone nearer to the surface with the thickness of 30 μ m with no nitride precipitation and second zone just after that toward the core composed of γ' -Fe₄N with small precipitates of α'' -Fe₁₆N₂ phase formed near the substrate interface.

In the case of treatment at 580 °C, the thickness of compound layer increased to 17 μ m. Moreover, for all three samples another layer of 23 μ m was observed between compound zone and diffusion layer named transformation zone. This layer consisted of nitride precipitates in grain boundaries for cooling on the substrate. However no nitride precipitate was observed for two others.

The same two-part diffusion zone was also observed for this sample except the thickness of first zone extended to 110 μ m. Again, no precipitate for first zone and two nitrides of γ' and α'' were detected for the first and second layer, respectively.

The compound layer of all samples (nitrided at two temperatures and cooled in three ways) was constituted by ε -Fe₂₋₃N and γ' -Fe₄N. For nitriding at 500 °C, the amount of ε and γ' was 10 and 90 % for substrate cooling and 17 and 83 % for oil cooling. This refers to the fact that, γ' -Fe₄N is formed by transformation of ε -Fe₂₋₃N phase and by rapid cooling this transformation is hindered and the amount of ε phase remains higher. For the samples nitrided at 580 °C, phase constituents in three depths are presented in Table 2.10. The presence of γ -Fe was attributed to the difference between the real temperature of the sample and the nominal temperature and reaching the temperature to austenitization area.

Ashrafizadeh [32] studied the plasma nitriding of Ck45 and En40B (32CrMo12) structural steels and compared with gas nitriding. Plasma nitriding was done for 5 h and gas nitriding was done for 70 h.

It was observed that the compound layer formed for gas nitriding was thicker and mainly constituted by γ' and ε phases as well as some iron oxide (Fe₃O₄) while that of plasma nitrided sample composed of just γ' . This difference in thickness was attributed to the sputtering and material removal of the surface in plasma nitriding.

Table 2.10 Phases obtained during a progressive wear in surface of nitrided samples for depths of 35 and 65 μm at temperature of 580 °C [31]

Position	Cooling	Phases
Diffusion zone 1 (depth of 65 μm)	Substrate holder	γ-Fe and α-Fe
	Oil reservoir	γ-Fe and α-Fe
Transformation one (depth of 35 μm)	Substrate holder	γ'-Fe ₄ N, ε-Fe ₂₋₃ N, γ-Fe and α-Fe
	Oil reservoir	γ'-Fe ₄ N, ε-Fe ₂₋₃ N, γ-Fe and α-Fe
Compound layer (surface)	Substrate holder	γ'-Fe ₄ N and ε-Fe ₂₋₃ N
	Oil reservoir	γ'-Fe ₄ N and ε-Fe ₂₋₃ N

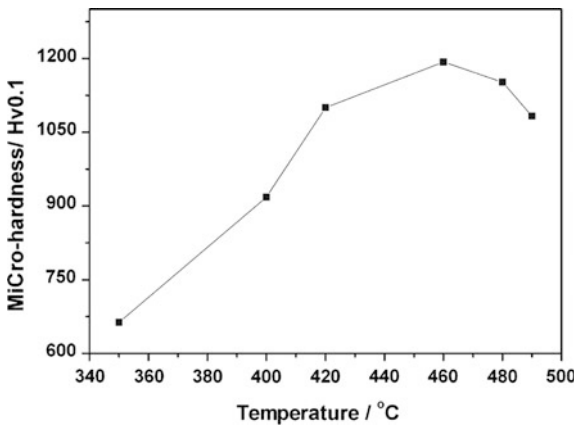
For both gas and plasma nitriding and for both steels, a diffusion zone was observed below the compound layer in which nitrogen dissolves in the ferritic phase and forms nitrides. For En40B steel, alloying elements with higher affinity to nitrogen formed precipitates.

2.2 Mechanical Properties

2.2.1 Austenitic Stainless Steels

According to Wang et al. [2] (see Sect. 2.1.1), the microhardness for AISI 304L austenitic stainless steel increased with temperature with maximum value of 1200 HV_{0.1} at 460 °C as shown in Fig. 2.25. This increase was probably due to the formation of chromium nitrides.

Fig. 2.25 Microhardness of AISI 304L austenitic stainless steel plasma nitrided at various temperatures [2]



They have found that, increasing nitriding temperature from 350 to 480 °C, increases the wear rate slightly, which is still much lower than that of the unnitrided material. Formation of a hard s-phase layer was the reason for achieving the lowest wear rate at 350 °C. Increasing chromium nitrides concentration in the modified layer corresponded for decreasing wear resistance with increasing temperature. The highest wear rate belongs to 480 °C treated sample where a single CrN nitride layer was produced.

According to the studies of Stinville et al. [3] (see Sect. 2.1.1) about the fatigue life of plasma nitrided AISI 316L steel, plasma nitriding led to an increase of the total stress amplitude during the whole cyclic deformation test. As seen in Fig. 2.26, this effect was not symmetric.

They estimated a residual compressive stress value of 1.7–3 GPa for plasma nitrided samples. An improvement was also seen in the number of cycles to failure as a function of the nitriding duration. This can be ascribed to the pressure of residual compressive stress. The residual compressive stress (3 GPa) and the fatigue life (5.5×10^4 cycles) reached their maximum value. In longer durations the fatigue life decreased because some grains are lost favoring an early crack initiation.

Egawa et al. [5] (see Sect. 2.1.1) also found that wear properties of JIS-SUS 304J3 stainless steel were improved by plasma nitriding. Friction coefficient of the samples (plasma nitrided at 400 °C) was almost the same against 304 and 52,100 balls. However, friction coefficient against an alumina ball was 0.55 while that of untreated specimen was 0.7.

Also they reported that the wear volume of the nitrided samples was less than one tenth of those of untreated specimens.

Li et al. [4] (see Sect. 2.1.1) did some experiments to find a relationship between surface hardness and plasma nitriding temperature for AISI 316L austenitic

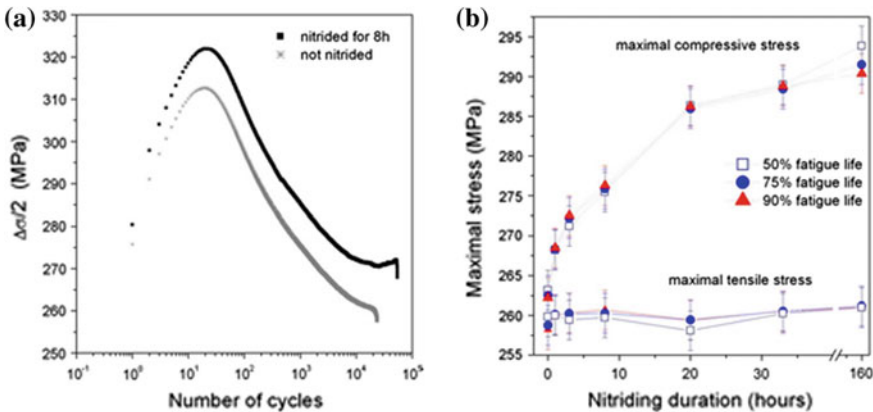


Fig. 2.26 **a** Cyclic stress amplitude evolution during fatigue tests for untreated and 8 h treated specimens for a $\Delta\epsilon_p/2 = 2 \times 10^{-3}$ plastic strain amplitude and **b** maximal compressive (*dotted line*) and tensile (*full lines*) stresses at different stages of the fatigue life for $\Delta\epsilon_p/2 = 2 \times 10^{-3}$ plastic strain amplitude [3]

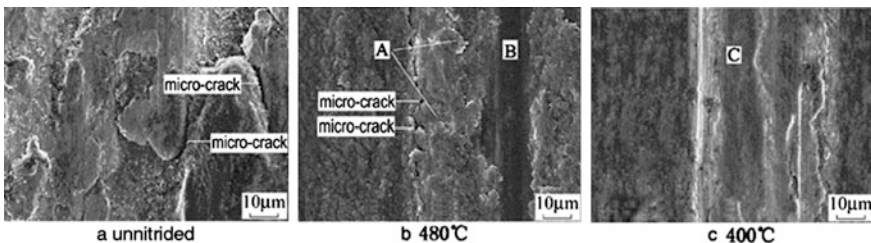
Table 2.11 Wear rate of AISI 316L austenitic stainless steel plasma nitrided with different parameters [4]

Process	Process parameters	Phase composition	Surface microhardness (HV _{0.1})	Wear rate (mg km ⁻¹)
No. 0	Unnitrided	γ (Matrix)	219	2.06
No. 1	480 °C $\times$ 600 Pa $\times$ 4 h	CrN	1117	0.98
No. 2	450 °C $\times$ 600 Pa $\times$ 4 h	CrN + S-phase	1089	0.58
No. 3	420 °C $\times$ 600 Pa $\times$ 4 h	CrN + S-phase	939	0.33
No. 4	400 °C $\times$ 600 Pa $\times$ 4 h	S-phase	763	0.21
No. 5	350 °C $\times$ 600 Pa $\times$ 4 h	S-phase	735	0.22

stainless steel. They found a very steep trend for microhardness increasing on the surface of the sample (as found by Wang et al. [2] shown in Fig. 2.25) when nitrided at temperatures below 400 °C, but it turned to a gradual trend when temperature reached beyond 450 °C. The formation of chromium nitrides corresponded for this dramatic increasing in hardness. However this can have a deleterious effect and lead to decreasing of wear resistance as reported by the authors.

As can be seen in Table 2.11, plasma nitriding improved wear resistance of steels with respect to untreated ones. The rate of wear completely depends on the treatment temperature. The lowest wear rate obtained with nitriding at 400 °C led to the formation of a hard s-phase layer corresponding for the low wear rate. In addition, increasing temperature led to the increment of chromium nitrides formation and this was ascribed to the reduction in dry sliding wear resistance. More existing chromium nitrides in the layer deteriorated wear resistance of AISI 316L steel. The dry sliding wear rate of nitrided steel reached a maximum value at 480 °C where a single CrN nitride layer was produced. Therefore, 350 and 400 °C nitriding temperatures led to the best wear properties because of maximum amount of s-phase and no chromium nitride.

Figure 2.27 shows the SEM images of the worn surfaces of both unnitrided and nitrided AISI 316L samples after dry sliding against the GCr15 at room temperature. As seen in Fig. 2.27a, wear of the unnitrided sample was so severe. As a result

**Fig. 2.27** Appearance of wear surfaces of AISI 316L austenitic stainless steel: **a** unnitrided, **b** nitrided at 480 °C and **c** nitrided at 400 °C [4]

of this severe wear, the surface became very rough and experienced microcracks, peeling off, and small wear debris distributed on the wear track. The wear process began with asperity fracture and consequently, small amounts of wear particles were produced via asperity fracture. These particles then crushed down between slider and sample and then facilitated to adhesive and abrasive wear on the unnitrided samples with increasing sliding distance. Moreover, the detaching of material from the surface of the steel, its plastic deformation between slider and sample, formation of the consequent microcracks, and peeling off the materials from the surface led to the higher wear rate.

Figure 2.27b shows a typical morphology of the worn surfaces of CrN layer formed at 480 °C. Two distinct areas are distinguishable in the worn track (indicated as “A” and “B” in this figure). The area “A” was so rough and exposed signs of plastic deformation. This can be ascribed to local flash temperature at the rubbing interface which can be high enough to soften the asperities in contact area and cause their deformation under initial high contact stress. It can be considered to be aggregates of fine wear debris generated from area “B” with increasing sliding distance. The microcracks observed were because of a CrN layer formed on the surface. Although despite these microcracks, the wear rate of this sample was much lower than that of unnitrided sample.

Figure 2.27c shows a typical morphology of the worn surfaces of s-phase layer formed at 400 °C. As seen in the figure, some shallow and wide grooves were produced along the wear direction (e.g., region “C” in Fig. 2.27c). It can be concluded that the dry sliding wear resistance of single expanded austenite layer was better than single chromium nitrides layer. This can be due to the nitrogen dissolved in austenite lattice which would increase the hardness of plasma nitrided layer. As a result, wear resistance increases due to the ductile behavior of s-phase in scratching and in abrasion.

Oliveira et al. [6] (see Sect. 2.1.1) also proved increase of surface hardness by plasma nitriding. The nitride layer obtained at 500 °C possessed higher microhardness value (~ 1050 HV) in comparison to the samples nitrided at 400 °C (~ 853 HV) and 450 °C (~ 950 HV), as well as a larger case depth, probably due to the formation of chromium nitrides and the high nitrogen concentration on the white layer. An abrupt fall was observed beneath the nitrides layer (20 μm). Later, N increased until the depth of 40 μm , forming the s-phase. This was corresponding for high hardness obtained. After that the N content decreased to reach the substrate.

Olzon-Dionysio et al. [7] also have done hardness measurements to study edge effect (see Sect. 2.1.1). Figure 2.28 depicts hardness values in different regions on the surface of the nitrided samples (regions 1–6 on the samples B, C, and D according to Fig. 2.7). The mean hardness value for each region is represented by a continuous line. The indent penetration during hardness measurements was between approximately 0.66 μm for region 4 and 1.3 μm for region 2.

Hardness reached a maximum value in regions 1 and 4 and then decreased abruptly in regions 2 and 5. There was a small interface region toward the center of

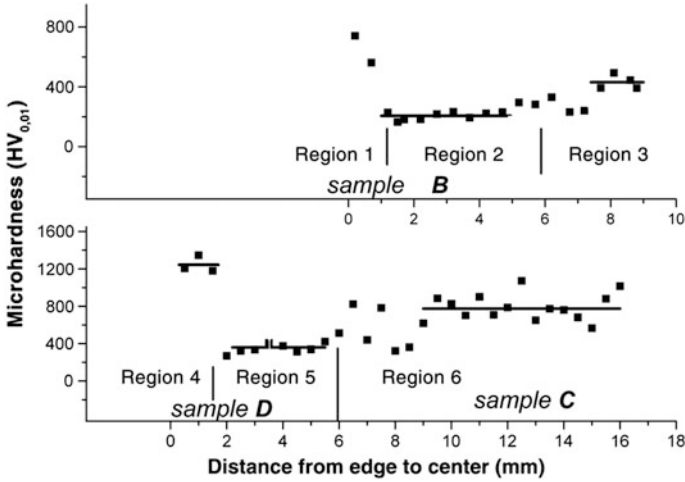


Fig. 2.28 Surface hardness values in different regions of the nitrided samples B, C, and D [7]

the sample after which hardness increased again and tended to stabilize in central regions 3 and 6.

The estimated extension of regions marked in Fig. 2.7 is presented in Table 2.12. As can be seen, despite their different diameters, the extension of equivalent regions in samples B (1 and 4) and D (2 and 5) agrees to be better than 98 %.

According to Table 2.12, the rings formed in samples B and D had the same characteristics. This shows that the formation of the rings does not seem to depend on sample geometry, at least not in their current dimensions.

It should be noted that these hardness results were in agreement with XRD results. For example, the existence of Cr_2N phase (with hardness of more than 1479 HV) on sample B can be the reason for the highest hardness values on the ring region.

Nakajima et al. [8] (see Sect. 2.1.1) evaluated the mechanical properties of AISI 304 austenitic stainless steel samples after post-solution treatment.

The surface hardness of the nitrided sample was reported to be 1360 HV with a rapid decrease to hardness of the untreated core of 153 HV within 0.1 mm. For post-solution treated sample the hardness was 280 HV, however, with higher core hardness compared to the just nitrided one. The hardness of the sample solution treated at 1200 °C for 45 min reached to the hardness of untreated sample in depth of 1 mm. This trend was also reported for durations of 60 and 90 min. Although the interior hardness for these two samples was higher compared to that of 45 min. It can be due to the resolving of the nitrides and diffusion of nitrogen to deeper distances.

Table 2.12 Measurements of region extension and mean hardness values for samples B, C, and D [7]

Position	Border or ring		Intermediate		Central	
	B	D	B	D	B	C
Sample						
Region	1	4	2	5	3	6
Extension (mm)	1.31 ± 0.06	1.33 ± 0.05	4.72 ± 0.08	4.63 ± 0.07	3.82 ± 0.09	9.85 ± 0.08
Mean hardness (HV _{0.01})	652 ± 70	1244 ± 90	206 ± 20	360 ± 30	431 ± 40	775 ± 80

Table 2.13 Mechanical properties of unnitrided, nitrided, and post-solution treated specimens [8]

Specimen	0.2 % proof stress $\sigma_{0.2}$ (MPa)	Tensile strength σ_B (MPa)	Elongation δ (%)	Reduction of area φ (%)
Untreated	268	606	62	83
Nitrided	263	616	65	77
Nitrided and post-solution treated	282	640	62	78

Table 2.13 presents the mechanical properties of the samples. As can be seen, tensile properties were improved after post-solution treatment. This can be due to the fact that, the compound layer formed on the plasma nitrided sample was very hard, thin, and brittle. Therefore, it cannot reply well to tensile tests and consequently deteriorates the mechanical properties.

In laboratory air, fatigue limits of the untreated, nitrided, and post-solution treated samples were 290, 380, and 340 MPa, respectively. Due to the higher surface hardness of the nitrided sample, it had the highest fatigue limit among the samples.

In 3 % NaCl solution, fatigue limit was reported to remain the same as for laboratory air condition. However, for nitrided and post-solution-treated samples, the fatigue limit was reported to decrease due to the sensitization phenomenon and formation of chromium depleted zone. However, the fatigue life of the post-solution treated sample was obvious in comparison with unnitrided sample. The mechanisms for this increase in fatigue strength were reported as follows: the precipitation of chromium nitride (CrN), the solid solution of nitrogen, and slower crack growth rates in this sample compared to untreated sample. A fine precipitation of nitride was reported to correspond for this behavior.

Wang et al. [9] (see Sect. 2.1.1) have the effect of nitriding duration on the hardness of nitrided AISI 304.

It was reported that, surface hardness increased by nitriding time. This was attributed to thickening of the nitride layer and reducing the substrate effect on the surface hardness. For treatment time of 5 h, the hardness of the sample increased by approximately a factor of 5 compared with the unnitrided sample. The extremely high microhardness values observed were attributed to the large compressive stresses formed in the modified layers after nitriding.

Sun et al. [10] (see Sect. 2.1.1) studied the effects of carbon addition to the nitriding atmosphere on properties of AISI 321. Figure 2.29 shows the comparison between hardness profiles of samples treated with only nitriding and nitriding with CH_4 addition. As seen, the only nitrided sample showed a sudden decrease of hardness in the interface. However, the hardness drop became slight with carbon addition and this is an advantage of this process.

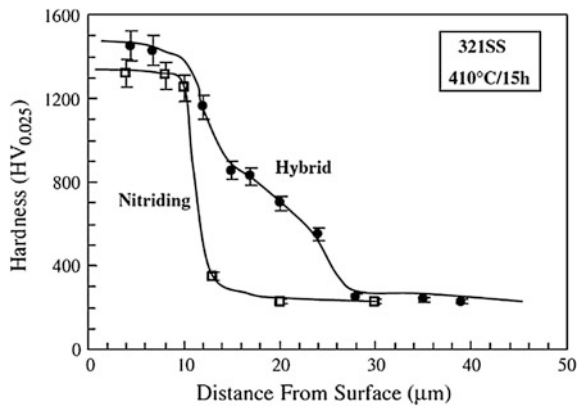


Fig. 2.29 Hardness profiles across the treated layers produced by nitriding alone and nitriding with carbon addition at 410 °C for 15 h [10]

2.2.2 Martensitic Stainless Steels

Alphonsa et al. [12] (see Sect. 2.1.2) also showed the increasing of hardness by nitrogen content in AISI 420 martensitic stainless steel. As can be seen in Fig. 2.30, the microhardness was maximum up to the depth of ~60 μm, at which the nitrogen concentration reduced very fast. The reduced nitrogen content resulted in a reduction in surface hardness, and the hardness value reached that of the base material by about 80–90 μm micrometers. This figure clearly shows the direct relation between nitrogen concentration and hardness in the case depth.

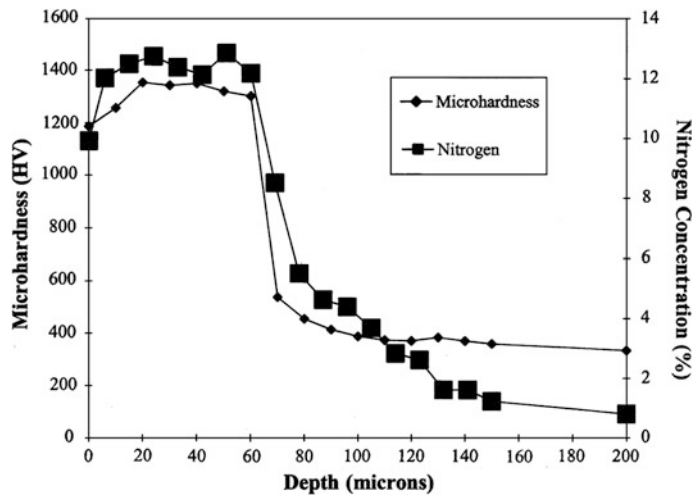


Fig. 2.30 Nitrogen concentration and microhardness values across the cross section of plasma nitrided AISI 420 [12]

Li et al. [13] (see Sect. 2.1.2) drew a conclusion about the relationship between hardness and treatment temperature for AISI 410. The increase in surface hardness was higher for the lower temperature nitrided steel. The surface hardness was 262 HV_{0.1} for untreated sample and 1210, 1204, and 1113 HV_{0.1} for samples nitrided at 420, 460, and 500 °C, respectively. The hardness dropped quickly and reached to the substrate value in the diffusion layer. This is suggesting that hardening in the diffusion zone was small. The effective case depths (with hardness of 350 HK_{0.1}) were 77, 166, and 186 µm, respectively, for the samples nitrided at 420, 460, and 500 °C.

Pinedo et al. [14] (see Sect. 2.1.2) observed the nitriding beneficial effect on hardness improvement resulted by precipitation of fine and homogeneous nitrides (γ' -Fe₄N, ϵ -Fe₂₋₃N and CrN) on diffusion zone (Fig. 2.31). As seen in this figure, the hardness profiles experienced a sharp decrease after the maximum hardness plateau. The shape of nitrogen profile was coincident with hardness profiles across the nitrided case.

Sobiecki et al. [17] (see Sect. 2.1.2) concluded that for H9S2 steel, plasma nitriding above 600 °C was the least favorable. The smallest microhardness values were 5.39 and 6.57 GPa obtained at these temperatures.

Wu et al. [15] (see Sect. 2.1.2) evaluated the effects of two new plasma nitriding methods on mechanical properties of AISI 420. The methods were cyclic plasma oxynitriding and cyclic plasma nitriding catalyzed by rare earth La.

The microhardness of the untreated sample was 285 HV_{0.05}, while that of the conventional plasma nitrided sample was 920 HV_{0.05}. The surface microhardness of the samples treated using cyclic plasma oxynitriding and cyclic plasma nitriding catalyzed by rare earth La in four cycles, were 942 HV_{0.05} and 957 HV_{0.05} respectively. The higher surface microhardness resulted by these two methods was attributed to higher concentration of nitrogen on the surface. The hardness drop along the cross section resulted by conventional DC plasma nitriding was abrupt in contrast to two new methods applied. Also a higher hardness and higher nitrogen diffusion depth were observed by increasing the treatment cycles.

As can be seen in Fig. 2.32, wear behavior of the samples nitrided with three methods was similar in initial stages until 120 min but it was changed beyond this

Fig. 2.31 Hardness profiles obtained for each nitriding temperature [14]

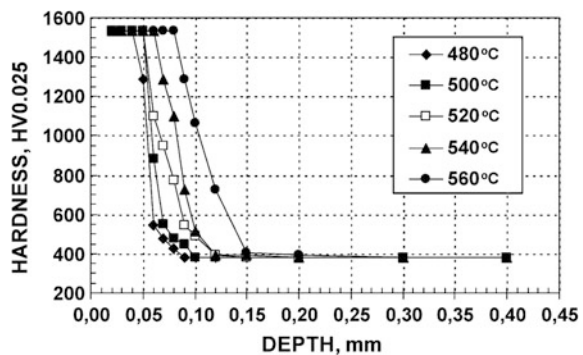
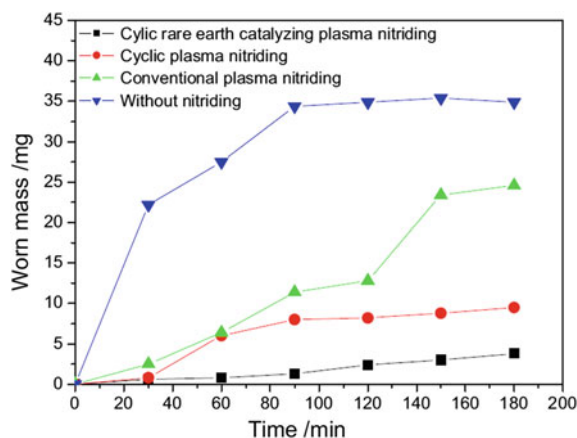


Fig. 2.32 Weight loss curves of nitrided and unnitrided AISI 420 martensitic stainless steel [15]



time. The weight loss after 180 min was 34.9, 24.6, and 9.5 mg for the untreated sample, conventional plasma nitrided sample and cyclic plasma oxynitrided sample, respectively. However, the weight loss for the sample treated by cyclic plasma nitriding catalyzed by rare earth La was 3.8 mg probably due to the higher nitrogen diffusion depth. Further densification of the surface of the nitrided case and the generation of small nitrides and consequently inducing high compressive residual stress and improving the strength, and plasticity of the nitrided layers were also counted as La functions.

Marchev et al. [33] (see Sect. 2.1.2) investigated the wear properties of AISI 410 martensitic stainless steel nitrided at different temperatures for different durations.

Plasma nitriding treatments were done at 400–566 °C in atmosphere of 65 % N_2 + 35 % H_2 under pressure of 2.7–2.8 torr for durations between 6 and 120 h.

It was concluded that lower nitriding temperatures as well as longer durations led to higher wear resistance and lower friction coefficient when compared to higher temperatures treated samples as well as untreated sample. This can be seen from the obtained data presented in Table 2.14.

2.2.3 Precipitation Hardening Stainless Steels

According to Esfandiari et al. [16] (see Sect. 2.1.3) for A286 (AISI 600) stainless steel, at low temperatures (≤ 420 °C) the surface hardness increased by time. However, the surface hardness of the high-temperature (460 and 500 °C) treated samples initially increased by time but after a maximum point, decreased.

Plasma nitriding at low temperatures led to the formation of s-phase. The hardness of this phase is very high which is due to the solid solution hardening mechanism. However, with increasing the nitriding temperature up to 460 °C (the critical temperature for the formation of chromium nitrides) the surface hardness of

Table 2.14 Results from friction and wear experiments on nitrided AISI 410 martensitic stainless steel samples [33]

Treatment temperature (°C)	Treatment time (h)	Number of rotations	Wear depth (μm)	Appearance of wear surface	Friction coefficient (μ_{avg})
None	None	24,000	17.1	Adhesion and pitting	0.7–0.8
400	96	50,000	13.7	–	0.2
400	120	50,000	10.2	Mild abrasion	Lower than 0.1
455	96	50,000	28.6	Abrasion and plastic deformation	0.4–0.5
465	96	50,000	24.8	Plastic deformation and platelet formation: batl fracture	0.4–0.5

nitrided samples increased. This effective hardness increment can be ascribed to the precipitation of fine chromium nitride particles as well as solid solution. However, with further increasing of treatment temperature to 500 °C, the decreased effect of solid solution hardening effect reduced the surface hardness.

After dry sliding wear test, the wear volume loss was very high for untreated samples. The wear volume loss was 0.6 mm³ for untreated sample and 0.01, 0.004, and 0.001 mm³ for samples treated at 350, 420, and 500 °C. Also, the wide and deep wear tracks were visible after test indicating poor wear resistance. However, wear tracks on the plasma nitrided samples were shallow and superficial. Increasing treatment time resulted in improving wear resistance because of thickening of the layer.

Wear tests revealed the fact that for untreated samples, the wear mechanism was adhesive. However, in plasma nitrided samples, wear occurred in mild micro-abrasion and oxidative wear modes, in contrast to the severe adhesive and abrasive wear.

Increasing hardness with temperature was also reported by Li et al. [18] (see Sect. 2.1.3). The surface hardness varied between 950 HV_{0.1} and 1270 HV_{0.1} for samples treated at temperatures of about 350 and 480 °C, respectively. The maximum hardness value was 1270 HV_{0.1} which was measured from the surface of sample nitrided at 480 °C. This was about 3.5 times as hard as the untreated sample (362 HV_{0.1}). Due to close relation of microstructure with the properties, the formation of chromium nitrides caused an abrupt increase in hardness at temperature 420 °C.

They also investigated wear behavior of this steel. It was found that, the treatment temperature affected surface roughness after plasma nitriding (Table 2.15). The interaction between ions and the sample surface through the superficial sputtering (existing on the cathode surface) corresponded for this roughness variation. An increasing treatment temperature resulted in increasing energy of incident species and consequently rougher surface. Therefore, increasing temperature more

Table 2.15 Wear rate of 17-4PH stainless steel nitrided at different parameters [18]

Process parameters	No. 0 unnitrided	No. 1 480 °C/600 Pa/4 h	No. 2 450 °C/600 Pa/4 h	No. 3 420 °C/600 Pa/4 h	No. 4 400 °C/600 Pa/4 h	No. 5 350 °C/600 Pa/4 h
Phase composition	α (Matrix)	CrN + α	CrN + α	CrN + α'_N	S-phase + α'_N	S-phase + α'_N
Microhardness (HV _{0.1})	362	1278	1187	1140	1022	973
Roughness R _s (µm)	0.05	0.25	0.21	0.18	0.11	0.10
Roughness R _{max} (µm)	0.1	2.4	2.3	2.1	1.32	1.12
Wear rate (mg km ⁻¹)	10.35	1.94	1.85	1.49	0.85	1.27

than 400 °C can have deleterious effect on the wear behavior of the plasma nitrided sample.

According to Table 2.15, the highest dry sliding wear resistance was obtained at treatment temperature of 400 °C. The wear resistance of the 400 °C/4 h treated sample was higher than the 350 °C/4 h treated one since the layer formed at 400 °C was thicker and harder in comparison to layer formed at 350 °C. The other important factor in good wear resistance was the formation of s-phase.

The wear of the untreated 17-4PH is dominantly characterized by strong adhesion, abrasion, and oxidation mechanism (as mentioned before).

Existence of microcracks and flake-like debris with slight plastic deformation on the worn surface of the 480 °C/4 h treated sample, indicated occurring of a mild adhesive and abrasive wear. Therefore, dry sliding wear resistance of nitrided samples was improved. The surface roughness of treated sample reduced the contact area compared to the untreated one and consequently increased the pressure on the asperities. Therefore flattening of the asperities occurred as a result of greater local plastic deformation. Consequently the contact area increased and reduced the contact pressure, leading to a mild adhesive wear and abrasive wear mechanism. Although the surface roughness was higher compared to the unnitrided surface, its wear rate was lower than that of the unnitrided samples. This was due to the formation of a hard and rigid chromium nitride (CrN) layer on the 480 °C/4 h treated sample surface. The oxidative film can play the role of lubricant during the test and reduce the friction between slider and sample.

The worn surface of the 400 °C/4 h treated samples showed smooth worn surface without microcracks. For the 400 °C/4 h, treated layer was composed of s-phase and α_N . Due to the ductile behavior of s-phase in scratching and abrasion, the formation of s-phase during plasma nitriding improved the wear resistance. The surface roughness of this sample increased the contact area with GCr15 even more, compared to the 480 °C/4 h treated sample. This led to the reduction of initial asperity deformation and polishing. Therefore, dry sliding wear resistance of the 400 °C/4 h treated sample was improved compared to that of the 480 °C/4 h treated sample.

2.2.4 Tool Steels

Hardness measurements done by Birol [20] (see Sect. 2.1.4) in case of plasma nitrided X32CrMoV33 steel confirmed the microstructure observations mentioned in Sect. 2.1.4. As shown in Fig. 2.33, hardness decreased sharply from surface to the core. The highest hardness belonged to the surface due to the nitrides precipitation and to the supersaturation with nitrogen of the BCC matrix in the diffusion zone. The case depth which was estimated from the hardness profile to be approximately 150 μm , was consistent with the etching response of the surface layer. The atomic Fe:N ratio in the compound layer was close to 3. This ratio decreased through the substrate.

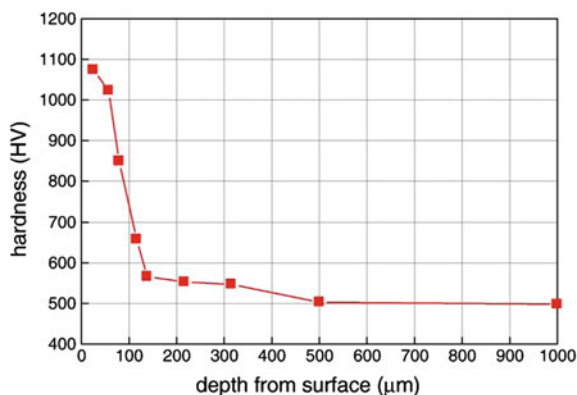


Fig. 2.33 Hardness variations with depth from the surface of the plasma nitrided hot work tool steel sample [20]

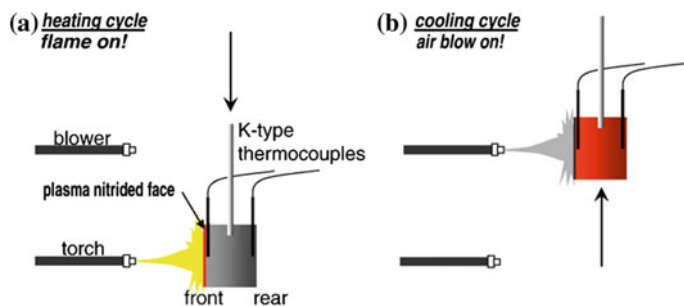


Fig. 2.34 Schematic of thermal fatigue test setup for the: **a** heating and **b** cooling cycles [20]

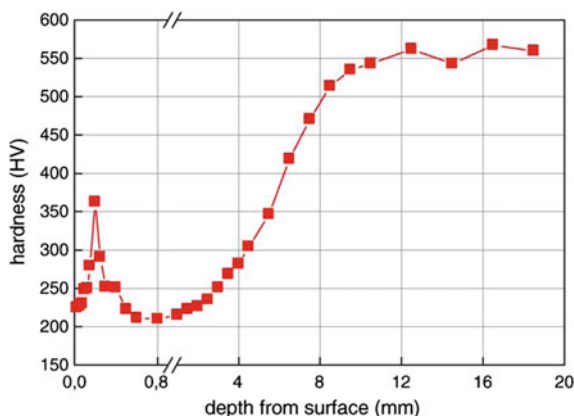
Thermal fatigue test was done to approximate thermal loading conditions. Plasma nitrided samples were cycled between 750 and 450 °C. The experimental setup for this test is presented in Fig. 2.34.

The thermal fatigue life of the nitrided tool steel obtained by test was much shorter than expected. Therefore, plasma nitriding resulted in a decrease in thermal fatigue life.

The first oxide to form on the surface of the steel is Fe_3O_4 and with further oxidation transforms into Fe_2O_3 . The failure of the oxide scale was enhanced because of the poor adherence and limited ductility of these oxides. Reduction of adhesive strength of the oxide film on the substrate occurred due to the thermal expansion mismatch with the underlying metal and the consequent compressive stresses. Isotherm annealing (at 750 °C for 6 h) retained the oxide scales on the surface.

This oxidation and removal and reoxidation resulted in a dimple profile on the front face. The resistance to oxidation was improved by plasma nitriding. This can

Fig. 2.35 Hardness variations versus depth from the surface of the plasma nitrided hot work tool steel sample after 500 thermal cycles [20]



be confirmed by formation of a thin Fe_3O_4 layer on the nitrided surface after isothermal annealing at 750 °C for 1 h under a vacuum of 10^{-3} Pa. Therefore, the oxidation of nitrided tool steel occurred more easily than the hot work tool steel, probably due to the fast-diffusion paths which were created by population of defects in the surface.

According to Fig. 2.35, the surface hardening caused by plasma nitriding was completely eliminated during thermal fatigue. The tempered martensitic structure was replaced by fine, equiaxed ferritic grains implying a dynamic recrystallization process during thermal cycling. This was ascribed to thermal stresses generated at the surface during thermal fatigue test.

Nouveau et al. [21] (see Sect. 2.1.4) have observed improving mechanical properties of 90CrMoV8 tool steel by plasma nitriding.

At constant temperature of 500 °C, hardness of subsurface was measured to be around 1250 (10 and 12 h) or 1050 (6 and 8 h) HV while the hardness of bulk was 650 HV. With increasing the treatment duration from 6 to 12 h, the hardened layer thickness varied from approximately 40–120 μm .

The nitrogen content severely decreased from surface toward the bulk. Nitriding at 500 °C for 10 h led to the highest nitrogen content and the hardest layer.

At 460 °C, a very thin hardened layer (40 μm thick) was obtained with a hardness of around 1150 HV (Fig. 2.36b). At 460 °C, the thickness of the diffusion layer was too low for withstanding the severe abrasion occurring in wood machining. As Fig. 2.36 shows, the diffusion layer consisted of two parts: compound layer as outer part and hardened bulk material as inner part. The top surface of 520 °C nitrided sample was less hard than the one nitrided at 500 °C and above a 100 μm depth the microhardness reduced to 300 HV.

For above-mentioned reasons, the optimal nitriding parameters were selected as temperature of 500 °C and duration of 10 h.

Pessin et al. [23] (see Sect. 2.1.4) observed the significant improvement in the wear resistance after plasma nitriding for AISI M2 tool steel. The obtained results are shown in Table 2.16.

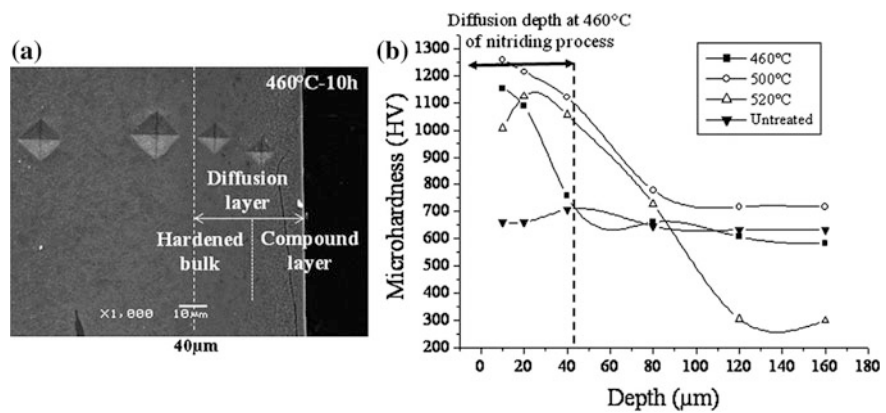


Fig. 2.36 a SEM cross-section micrograph for the steel nitrided at 460 °C for 10 h, and b hardness variations with depth for steels nitrided at different temperatures for 10 h [21]

Table 2.16 Surface hardness, friction coefficient, scar length, and wear depth [23]

	Temperature					
	450 °C			500 °C		
	200 Pa	400 Pa	900 Pa	200 Pa	400 Pa	900 Pa
Surface hardness (HV _{0.2})	1178	1274	1263	1260	1286	1272
Friction coefficient	0.80	0.25	0.25	0.80	0.25	0.25
Scar length (mm)	2.9	1.3	1.8	2.5	1.3	1.3
Wear depth (μm)	42.1	8.5	16.2	31.3	8.5	8.5

The high friction coefficient ($\mu = 0.95$) caused significant adhesion on the surface of the untreated specimen. The existence of a thin compound layer significantly reduced the adhesive wear and friction coefficient ($\mu = 0.25$) and consequently improved wear resistance. The samples plasma nitrided at 200 Pa showed spalling during the wear test, which was believed to be due to the lack of a compound layer. The high friction coefficient measured on the diffusion zone ($\mu = 0.80$) resulted in high shear stresses on the sample surface, which combined with its low toughness produces a significant material loss. Due to the hardness increase from nitride precipitation in the diffusion zone, the plastic deformation capability of the material was reduced, resulting in a brittle fracture mechanism.

2.2.5 Structural and Constructional Steels

Şengül et al. [34] studied the effects of plasma nitriding on fatigue crack growth on AISI 4140 steel under variable amplitude loading. They used these parameters for

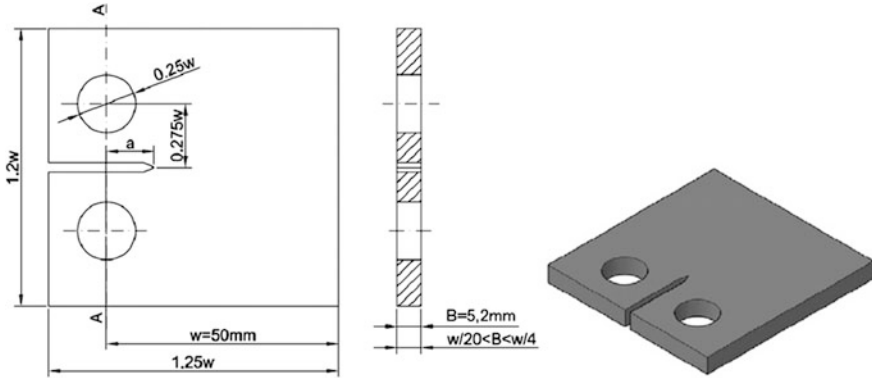


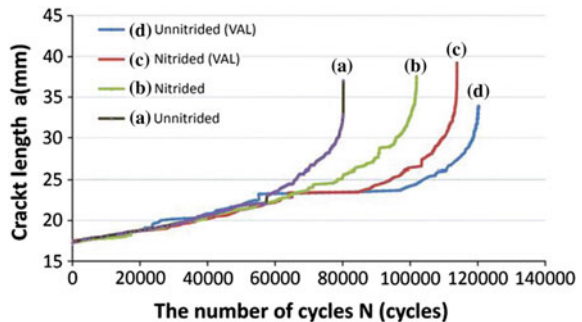
Fig. 2.37 Dimensions of the CT specimen used for testing [34]

nitriding: temperature of 500 °C, duration of 2 h, atmosphere of 50 % N₂ + 50 % H₂, and pressure of 500 Pa. The compact tension (CT) specimens (Fig. 2.37) were fabricated in L–T orientation, i.e., the load was applied in the longitudinal direction and the crack was in the transverse direction. Fatigue crack growth (FCG) tests were done in two conditions to evaluate fatigue life of samples: Constant amplitude loading (CAL) and Variable amplitude loading (VAL). Constant amplitude loading was defined as fatigue under cyclic loading with constant amplitude and a constant mean load. Much larger retardations were observable in tests with a high peak load added to constant amplitude loading. Such high loads were frequently called overloads. If constant amplitude loading includes one or more overload cycles, then this is called variable amplitude loading.

For the nitrided sample, the maximum hardness was achieved on the surface. The substrate hardness in the unnitrided condition was measured at 200 HV_{0.025}.

Plasma nitriding treatment improved the fatigue crack growth limit under constant amplitude loading (Fig. 2.38a, b). These improvements were the result of the hardening of the material surface in the plasma nitriding case. The hardened surface caused by the plasma nitriding treatment increased resistance to the fatigue crack growth rate.

Fig. 2.38 Crack development diagram of compact samples of 4140 steel: **a** unnitrided, **b** nitrided, **c** nitrided with 10 cycles overload, and **d** unnitrided with 10 cycles overload [34]



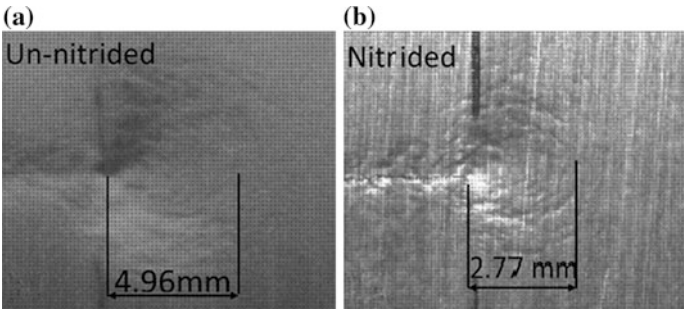


Fig. 2.39 The surface images of the plastic zone after overloading for: **a** unnitrided and **b** nitrided sample [34]

For unnitrided specimens under the variable amplitude loading condition (during the retardation period), the crack growth significantly decreased. On the other hand, the plasma nitriding process under the variable amplitude loading condition decreased the life of fatigue crack growth (Fig. 2.38c).

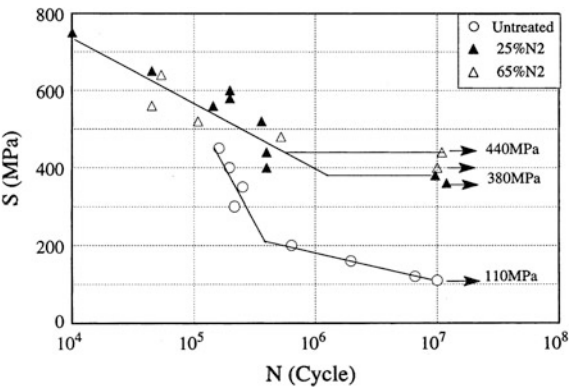
According to Fig. 2.39 after overloading, the surface of the plastic zone for unnitrided sample was greater than nitrided one. During overloading, the hard nitride layer resisted surface movement and consequently swelled and peeled off. This resistance prevented more growth of plastic zone, therefore, a shorter retardation period was caused by overloading.

Li et al. [24] (see Sect. 2.1.5) investigated fretting fatigue properties of plasma nitrided 709M40 steel.

They found that the average thickness of the compound layer was increased from 4.3 to 7.5 μm when the nitrogen content in the atmosphere increased from 25 to 65 %. The average hardness of the compound layer (surface hardness) was 840 $\text{HV}_{0.1}$. The residual stress in the nitrided case was compressive and its magnitude gradually reduced with increasing distance from the surface.

As shown in Fig. 2.40, plasma nitriding significantly improved fretting fatigue strengths. The improvements were ascribed to the existence of compound layer,

Fig. 2.40 Fretting fatigue S–N curves of unnitrided and plasma nitrided 709M40 samples. Plasma nitriding was performed at 500 °C for 10 h, with nitrogen potentials of 25 and 65 % [24]



diffusion layer, compressive residual stress, and also friction coefficient of the plasma nitrided steel.

Comparing fretting fatigue S-N curves in Fig. 2.40 shows the effect of compound layer. This change in fretting fatigue strength can only be attributed to the different compound layer produced at two nitrogen potentials. Probably, the high hardness of the compound layer increased the resistance to fretting surface damage and surface crack initiation. The thicker compound layer acted as a thicker hard coating and provided more protection against fretting. As a result, the fretting fatigue strength improved.

Compared with traditional nitriding methods, plasma nitriding produced much more ductile compound layer due to the sputtering effect during the plasma nitriding.

Increasing nitriding time led to an increase in the case hardness and case depth. Nitriding durations of 3, 10, and 40 h at 500 °C produced case depths of 187, 340, and 552 μm , respectively. The hardest diffusion zone was achieved by the longer nitriding duration of 40 h.

The fretting fatigue strengths (10^7 cycles) of the nitrided samples were similar. This can be proved by Fig. 2.41 (10 and 40 h treated samples). As for the 3 h nitrided sample, despite significant difference with others in case depth, there was little difference in fretting fatigue strength. It can be concluded that, case depth and a high case hardness in the diffusion zone were not major factors in determining the fretting fatigue strength.

Introducing compressive residual stresses led to improvements in fatigue life. In contrast, degradation was caused by introducing tensile residual stresses.

Table 2.17 summarizes the surface hardness, the surface residual stress and the case depth of the nitrided samples. Nitriding for 3 h produced a high compound layer hardness (794 $\text{HV}_{0.1}$) and a high surface compressive residual stress (-502 MPa). The combination of these properties significantly increased the fretting fatigue strength (10^7 cycles) of the steel from 110 to 340 MPa. However, since the compound layer was thin (3.1 μm), and the compressive residual stress distribution was only to a very shallow depth, once cracks are initiated at high stresses

Fig. 2.41 Fretting fatigue S-N curves of 709M40 samples plasma nitrided at 500 °C for 3, 10, and 40 h with nitrogen potential of 25 % [24]

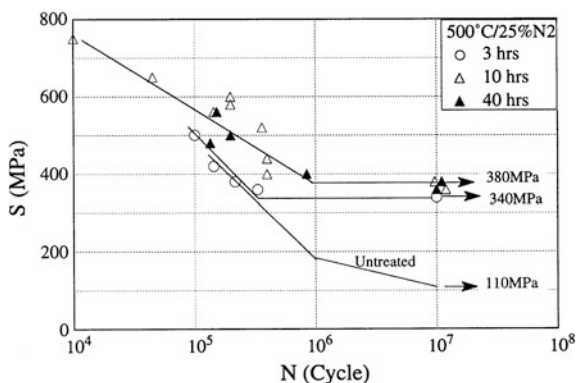


Table 2.17 Influence of nitriding time (at 500 °C in 25 % N₂:75 % H₂) on properties of nitrided samples [24]

Nitriding time (h)	3	10	40
Surface hardness, HV _{0.1}	794	845	789
Compound layer thickness (μm)	3.1	4.7	6.3
Surface residual stress (MPa)	−502	−498	−385
Case depth (μm)	187	340	552

from the contact surfaces, the hard compound layer and the shallow compressive residual stress depth could not have any further influence on the propagation of the cracks. Therefore, it can be concluded that to improve the fretting fatigue behavior of nitrided samples, a hard and relatively thick compound layer and a high and deep compressive residual stress are required. However, longer duration and deep case depth are not necessary.

Karaoglu [25] (see Sect. 2.1.5) studied the effects of plasma nitriding on the mechanical properties of AISI 5140 steel. According to Table 2.9, longer durations at 500 °C or performing the treatment at 550 °C led to decrease in hardness.

Among the treated samples, the highest initial wear rate after 400 m sliding and maximum total wear after 200 m sliding belonged to 455,020 and 150,020 samples, respectively.

The charts of friction coefficient (μ) versus sliding distance showed that at the steady-state period, the friction coefficient values of plasma nitrided samples were slightly greater than the untreated samples. The maximum resistance to wear was shown by the maximum hardness. This can reveal the importance of surface hardness with respect to wear rate.

The thick compound layer (composed of $\gamma' + \epsilon$) produced on the high-temperature (550 °C) treated samples was extremely brittle and increased the wear rate of the material. The particles generated from the breakdown of the thick compound layers at the beginning of the wear tests changed the wear mechanism from adhesive to abrasive. Therefore, the wear rate increased with thickening the compound layer.

The large and predominantly metallic debris particles from the unnitrided sample (Fig. 2.42a) were in line with the severe wear experienced by that sample. However, the wear debris produced from the nitrided sample was a mixture of plate-like large products of early periods and very fine brown powders (Fig. 2.42b). The oxidized appearance of the worn surface and the generation of oxide wear debris indicated the dominancy of mild oxidative wear in the wear of the nitrided samples.

Karakan et al. [26] (see Sect. 2.1.5) studied hardness changes with different gas mixtures (Table 2.18). They found that maximum hardness was in the range of 760–770 HV_{0.05} for the atmosphere of 10 % N₂ + 90 % H₂.

According to Mahboubi et al. [27] (see Sect. 2.1.5), nitriding at low temperature (350 °C), lowered the nitrogen uptake and precipitate (nitride) density and consequently the hardening effect. With increasing the nitriding temperature to 550 °C,

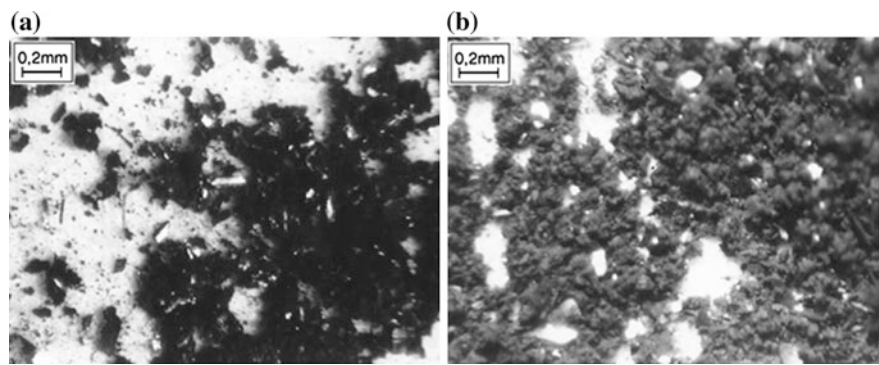


Fig. 2.42 Morphology of wear debris particles for **a** unnitrided and **b** plasma nitrided AISI 5140 (in a 20 % N₂ + 80 % H₂ gas mixture for 4 h at 500 °C) [25]

Table 2.18 Variations in the compound layer thickness, the case depth, and surface hardness with gas mixtures [26]

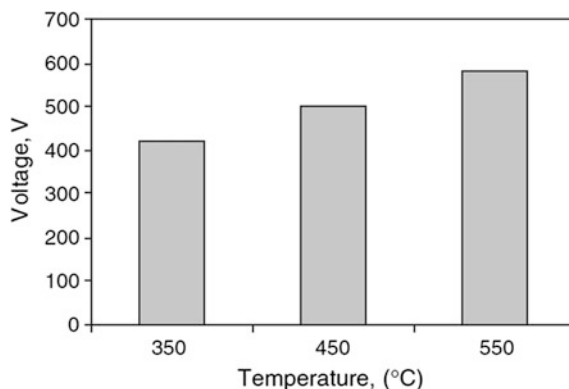
Plasma nitriding parameters			Compound layer (μm)	Case depth (μm)	Surface hardness (HV)
Time (h)	Temperature (°C)	Gas mixture			
4	450	90 % N ₂ + 10 % H ₂	4–5	160–190	540–550
4	450	10 % N ₂ + 90 % H ₂	2–2.5	210–240	760–770
4	450	90 % N ₂ + 10 % Ar	–	35–65	290–300
4	450	10 % N ₂ + 90 % Ar	8–10	60–90	470–480
4	450	80 % N ₂ + 10 % H ₂ + 10 % Ar	5–6	110–140	470–480
4	450	10 % N ₂ + 10 % H ₂ + 80 % Ar	5.5–6.5	90–120	500–510
4	450	10 % N ₂ + 80 % H ₂ + 10 % Ar	2–3	185–215	700–710

both precipitate growth and tempering of the matrix significantly enhanced and the precipitates got larger in size and lower in number leading to lower hardness. Therefore, it was observed that plasma nitriding of DIN 1.6959 steel at 500 °C produced the optimum nitride precipitate size and density, and resulted in the highest surface hardness.

Increasing the treatment temperature increased the roughness of the surface due to the severe sputtering of the substrate caused by nitrogen ions and higher applied voltage required for the treatment. As a result, the kinetic energy of the incident ions (or atoms) increased (Fig. 2.43). At low treatment temperatures, the formation of nitrides resulted in volumetric expansion and surface relief and consequently increment of the surface roughness.

Yasavol et al. [28] (see Sect. 2.1.5) investigated the effects of post-oxidizing treatment under different atmospheres on mechanical properties of 4130 steel. Plasma nitriding treatment improved the surface hardness from 230 HV_{0.05} for

Fig. 2.43 Applied voltage at different plasma nitriding temperatures [27]



untreated sample to 870 HV_{0.05} for plasma nitrided sample. This improvement was owing to the formation of γ' -Fe₄N nitride phase. However, the following oxidizing treatment decreased the improved surface hardness due to the lower hardness of oxide layer compared to nitride layer. The hardness of the layer formed under atmosphere of 25 % O₂ + 75 % H₂, was higher compared to two others due to two reasons: (1) the higher hardness of Fe₃O₄ phase and (2) the interface of this oxide film that is denser than that of Fe₂O₃ phase. Besides, there was more coincidence in the white layer and Fe₃O₄ interface than in the white layer and Fe₂O₃ interface. Also oxidizing at 500 °C, led to higher surface microhardness because of thicker oxide layer and the formation of more Fe₃O₄ phase compared to oxidizing at 400 °C.

Alsaran et al. [29] (see Sect. 2.1.5) investigated the effects of post-plasma oxidizing on the mechanical properties of AISI 5140 steel.

The maximum surface hardness was obtained for plasma nitrided sample due to the formation of hard ϵ -Fe₃N iron nitride. The oxide layer formation lowered the surface hardness.

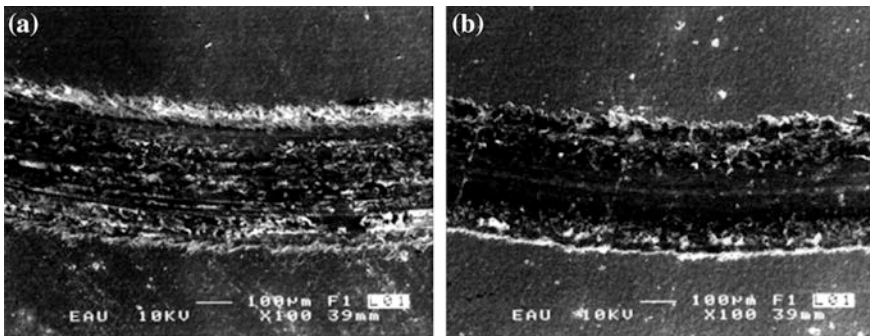
Post-oxidizing treatment had a beneficial effect on the wear behavior of nitrided sample. The lowest wear rate and friction coefficient belonged to the sample oxidized for 15 and 30 min, respectively. All of the data obtained for mechanical properties as well as the layers' thicknesses are presented in Table 2.19. The friction coefficient and wear rate for the sample post-oxidized for 60 min were higher compared with that of other oxidizing times. This was because of the failure of oxide layer by spallation (as a result of sputtering) despite the growing oxide layer with prolonging oxidation.

The improvement of wear resistance was also observed by SEM observation. As seen in Fig. 2.44, the wear track of the sample only nitrided was wider than that of nitrided-oxidized sample. Besides, some abrasive particles were also seen for just nitrided sample. This was attributed to the presence of a hard and brittle compound layer composed of two nitride phases.

Alsaran et al. [30] (see Sect. 2.1.5) studied the effects of post-aging treatment on mechanical properties of AISI 4140 steel.

Table 2.19 Properties of plasma nitrided and post-oxidized AISI 5140 steel [29]

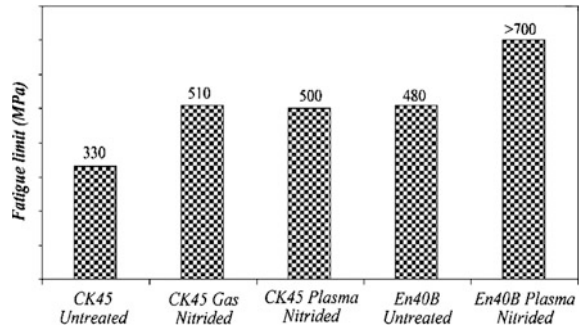
Treatments	Compound layer (μm)	Oxide layer (μm)	Surface hardness ($\text{HV}_{0.025}$)	Surface roughness (R_a)	Friction coefficient	Wear rate ($\text{mm}^3/\text{Nm} \times 10^6$)
Nitrided	5.5–6.5	–	945–1000	0.15	0.38–0.41	4.84
Nitrided + 15 min post-oxidized	5–6	0.3–0.35	500–530	0.17	0.27–0.3	2.50
Nitrided + 30 min post-oxidized	5–5.5	0.35–0.4	480–520	0.16	0.23–0.25	3.22
Nitrided + 60 min post-oxidized	2–2.5	0.5–0.7	380–420	0.18	0.3–0.32	4.29

**Fig. 2.44** SEM images of samples **a** plasma nitrided and **b** post-oxidized for 30 min after plasma nitriding [29]

The positive effect of post-aging treatment on the hardness was reported. The fact that hardness was high was related to the size and main crystal structure of α'' . The post-aging treatment caused the lattice to be distorted and consequently the dislocation movement to be hindered and the hardness to be increased. The maximum hardness was achieved by duration of 1 h. The hardness was increased by post-aging duration until 1 h, however decreased after that due to the overaging. In this stage, the α'' phase was decomposed and therefore the coherency between the main lattice structure and this phase begun to disappear. The minimum hardness was achieved by duration of 12 h due to the growing of precipitates.

The minimum friction coefficient of 0.4 was achieved for post-aging duration of 0.5 h, while the maximum friction coefficient of 0.6 was obtained for a post-aging duration of 12 h. The minimum wear track width was observed for duration of 1 h. Because of higher hardness of compound layer formed on the surface of nitrided-quenched samples, the wear rate and abrasive particles were higher for this sample. The post-aging treatment resulted in the lower wear rate due to the hardening of diffusion layer. Also the lowest wear rate belonged to the sample post-aged for 1 h.

Fig. 2.45 Fatigue limits of the samples [32]



Ashrafizadeh [32] (see Sect. 2.1.5) compared the plasma and gas nitriding of Ck45 and En40B steels.

The lowest hardness of plasma nitrided Ck45 steel achieved was 470 HV and that of En40B was above 900 HV with a steep gradient. The hardness of compound layers of Ck45 and En40B was in the range of 500–800 HV and 900–1100 HV, respectively. This difference referred to the amount of absorbed nitrogen and type of nitrides formed in these two steels that were nitrides of iron and alloying elements in Ck45 and En40B, respectively. The lower nitriding depth of En40B was attributed to the higher content of carbon and alloying elements which had inhibiting effect on the nitrogen diffusion.

Fatigue limits of the untreated and nitrided samples are presented in Fig. 2.45. The improvement in fatigue limit for Ck45 steel was 52 % and for En40B was 46 % and higher depending on the treatment time. However for gas nitriding and Ck45 steel, no improvement of fatigue limit was observed even for duration of 70 h. Also it was found that compound layer had no significant effect on the fatigue limit in contrast to diffusion zone. The improvement of fatigue limit was due to two main reasons: higher case hardness and compressive residual stress. The increment of residual stress was caused by nitrogen being taken into solution in the matrix and the formation of nitride precipitates. It was concluded that gas nitriding is not suitable to improve the mechanical properties as it needs longer durations and produces thicker compound layers which is not suitable for some applications.

2.3 Corrosion Behavior

2.3.1 Austenitic Stainless Steels

Olzon-Dionysio et al. [7] (see Sect. 2.1.1) found that, the nitrided sample C (region 6 in Fig. 2.7) showed a more positive E_{corr} value than the nitrided sample B

(regions 1 and 2). Moreover, the E_{corr} value of the unnitrided sample was lower than that of nitrided sample.

The corrosion current density value (for $E = 1.0$ V) obtained for sample C was about $8.0 \times 10^3 \mu\text{A cm}^{-2}$ while it was about $9 \times 10^4 \mu\text{A cm}^{-2}$ for sample B. This showed the lowering of the current density for this sample, indicating a lower pits dissolution rate. This may be caused by two factors

- (1) The concentration of the hexagonal ϵ (Fe_{2+x}N) phase in the center (sample C, 38 %) was larger than in the border (sample B, 18.4 %). The hexagonal ϵ (Fe_{2+x}N) phase can reduce the dissolution rate of pits formed in the presence of aggressive ions.
- (2) The nitrogen concentration in sample C was larger than in sample B, which changed pH and had a neutralizing effect on the acid pits of the corrosion surface.

Therefore, the sample with a ring showed lower corrosion resistance compared to the sample without it. Sample C showed the best corrosion resistance.

Egawa et al. [5] (see Sect. 2.1.1) found that for austenitic stainless steel, low temperatures (according to critical temperatures presented in Table 2.2) should be used to hamper the formation of dark phase discussed before. Also, the current density to maintain passivity on the plasma nitrided AISI 316 is higher than that of the untreated one. However in the case of other steels, plasma nitriding deteriorated corrosion resistance.

Nakajima et al. [8] (see Sect. 2.1.1) studied the effect of solution treatment after plasma nitriding on corrosion behavior of AISI 304.

After doing the anodic polarization test, pitting was reported as the main corrosion mechanism in the samples. The main reason for corrosion was found to be the formation of chromium nitride and consequently the depletion of boundaries. Also the surface of untreated sample was occupied uniformly by many corrosion pits.

2.3.2 Martensitic Stainless Steels

Li et al. [13] (see Sect. 2.1.2) observed that untreated AISI 410 sample did not show passivation layer and the current density increased with a high rate after the corrosion potential (Fig. 2.46). This could be due to the breakdown of the passive layer and localized corrosion. Also the untreated AISI 410 steel sample was severely experienced crevice corrosion and pitting corrosion during the polarization test (Fig. 2.47a).

As seen in Fig. 2.40, after plasma nitriding, the corrosion potential (E_{corr}) increased from -312 mV for the unnitrided sample to -190 , -30 , and -205 mV for the samples nitrided at 420, 460, and 500 °C nitrided samples, respectively.

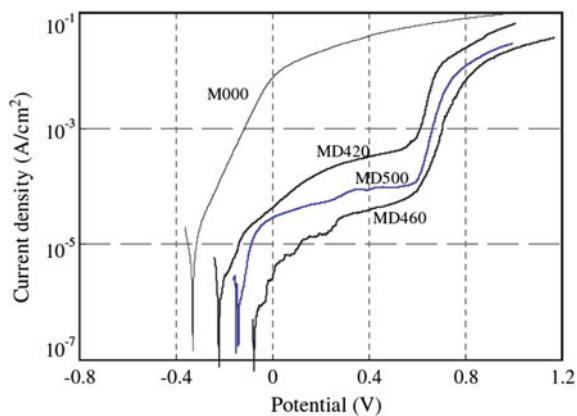


Fig. 2.46 Polarization curves of unnnitrided and plasma nitrided AISI 410 steel in 3.5 wt% NaCl solution [13]

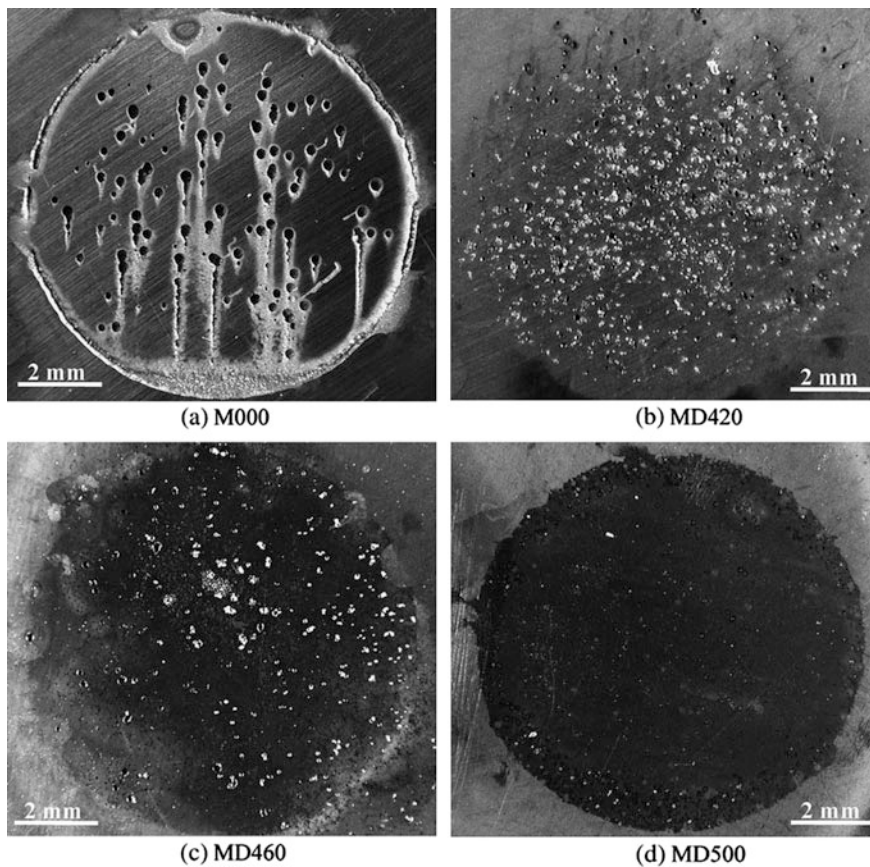


Fig. 2.47 Corrosion scars on **a** unnnitrided and **b** 420 °C, **c** 460 °C, and **d** 500 °C nitrided AISI 410 martensitic stainless steel surface after electrochemical corrosion tests in 3.5 % NaCl solution [13]

It can be inferred from current densities in Fig. 2.46 that, corrosion rate for nitrided samples was much lower than that of the unnitrided one. It can also be indicated from this figure that pitting also occurred for all the nitrided samples which can be inferred from the sudden increase in current density after the passivation region. The pitting potential was about 600 mV for all the nitrided samples while it is much higher than -250 mV for the unnitrided sample.

It was reported that corrosion resistance of the AISI 410 martensitic stainless steel was improved by plasma nitriding indicated by the higher corrosion potential, higher pitting potentials, and lower current density of the nitrided samples. This improvement was also confirmed by corroded surface examination after polarization tests. Figure 2.47 shows that no crevice corrosion occurred in nitrided sample and the corrosion pits on a nitrided surface were smaller in size and fewer in number in comparison with the unnitrided sample. Besides, nitriding at 420 °C resulted in less resistance to pitting corrosion than the 460 and 500 °C. This completely agrees with Fig. 2.46 that the sample MD420 had the highest current densities among all nitrided samples.

The results of immersion tests in 1 % HCl solution also confirmed that plasma nitriding led to improving corrosion resistance of AISI 410 martensitic stainless steel. The average corrosion rate for unnitrided sample was $478 \text{ g m}^{-2} \text{ d}^{-1}$ in the 1 % HCl solution. It decreased to 141, 246, and $307 \text{ g m}^{-2} \text{ d}^{-1}$ for samples nitrided at 420, 460, and 500 °C, respectively. The iron nitrides formed on AISI 410 stainless steel surface could be responsible for good corrosion resistance and protect the substrate from being attacked by corrosive environment. The formation of an iron nitride compound layer was believed to be the main reason for improving corrosion resistance of the AISI 410 after plasma nitriding. With formation of a compound layer composed of γ' and/or ϵ iron nitride on the plasma nitrided surface, the effectiveness of chromium nitride formation in the corrosion resistance of the AISI 410 stainless steel faded.

In contrast to the results of electrochemical tests, the least corrosion rate belonged to the sample MD420 with the lowest weight loss among three nitrided samples. This inconsistency can rise from differing of test methods.

The surface of unnitrided sample was rough and severe pitting corrosion occurred after immersion test. However, the surface of nitrided samples was smooth.

Despite the chromium nitride precipitation at 460 and 500 °C, electrochemical and immersion corrosion tests revealed improving the corrosion resistance of the AISI 410 martensitic stainless steel at all three temperatures. This showed that the chromium nitride precipitation criteria for corrosion resistance of austenitic stainless steels may not be applicable to martensitic stainless steels.

For the untreated and 420 °C nitrided samples, the chromium content was higher in the near surface region probably due to the formation of chromium oxide passive film on the surface. The chromium content in the 460 °C treated surface was higher in the near surface region. However, precipitation of chromium nitride and the consequent depletion of free chromium in the iron matrix may have hindered the formation of a protective passive film. When nitriding at 500 °C, passive film was

not formed on the nitrided surface because of (1) the lower chromium content in the top surface and (2) the chromium nitride precipitation.

2.3.3 Precipitation Hardening Stainless Steels

Sobiecki et al. [17] (see Sect. 2.1.3) found that the corrosion resistance of H9S2 steel was improved with plasma nitriding. This was inferred from the corrosion potential shifting from -250 to -500 mV. However, the corrosion current values were slightly increased compared to the untreated steel due to the formation of chromium nitride precipitations during nitriding above 500 °C.

Esfandiari et al. [16] (see Sect. 2.1.3) observed the improvement of corrosion resistance in the case of A286 precipitation hardening stainless steel by plasma nitriding (as shown in Fig. 2.48). However, it is clear from corrosion current densities that at temperatures below 420 °C, increasing the process time decreased corrosion resistance.

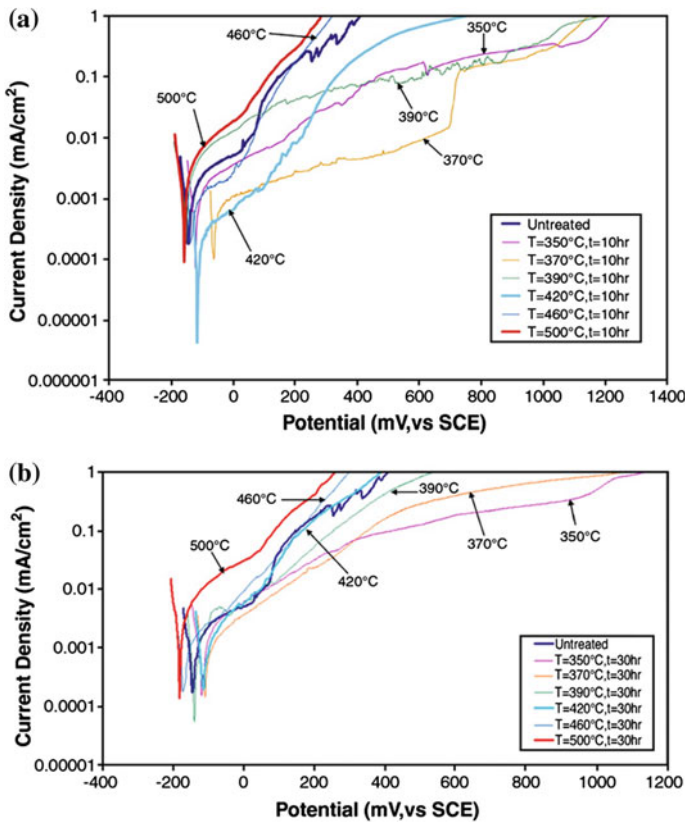


Fig. 2.48 Corrosion behavior of A286 samples plasma nitrided for **a** 10 h and **b** 30 h [16]

The evaluation of corrosion behavior of nitrided A286 precipitation hardening stainless steel in NaCl solutions showed two results: (1) nitriding at low temperature led to better pitting resistance than the untreated material and (2) nitriding at high temperature significantly deteriorated the corrosion resistance of A286 stainless steel. Also, results of corrosion test clearly indicated that plasma nitriding at low temperature, improved corrosion resistance of nitrided A286 stainless steel compared to the untreated sample because of the elimination of pitting corrosion in presence of a chloride-containing solution (Fig. 2.48). Thus, it was concluded that high nitrogen content corresponded for the above-mentioned improved corrosion resistance due to the formation of s-phase layer. However, it should be mentioned that, the beneficial effect of nitrogen only appeared when nitrogen is in solid solution, and the nitrided layer was a single phase. So that, CrN formation deteriorated the corrosion resistance of the stainless steel.

Corrosion-wear resistance of the untreated A286 steel was very low. This was proved by deep (18 μm) and wide wear tracks on the sample surface as seen in Fig. 2.49a, whereas, wear tracks on the surface of plasma nitrided samples were shallow (5–9 μm) and superficial as seen in Fig. 2.49b. Corrosion-wear resistance of 350 $^{\circ}\text{C}/10$ h nitrided sample was improved only about 25 % related to the untreated one.

Although the 420 $^{\circ}\text{C}/10$ h treated samples showed better corrosion resistance, the corrosion-wear resistance of the 420 $^{\circ}\text{C}/10$ h and 500 $^{\circ}\text{C}/10$ h treated samples were the same. Therefore, both layer hardness and thickness played an important role in the corrosion-wear process.

2.3.4 Tool Steels

Nouveau et al. [21] (see Sect. 2.1.4) evaluated corrosion properties of 90CrMoV8 tool steel used for wood machining. For testing corrosion properties the authors simulated the liquid oozed out during wood machining called “wood juice.”

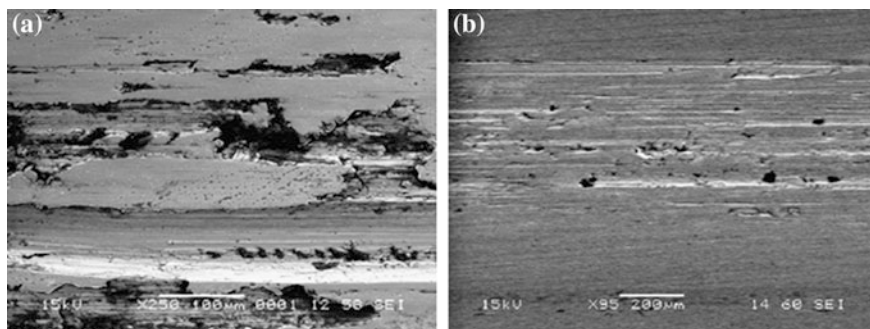


Fig. 2.49 SEM micrographs of the wear tracks on **a** untreated and **b** 420 $^{\circ}\text{C}/10$ h treated A286 stainless steel after corrosion-wear test (10 N, 10 h) [16]

In electrochemical measurements, untreated steel behaved as a passive material which was characterized by a high corrosion potential value (-307 mV/ECS), a very low corrosion rate (~ 37 nA/cm²) as well as a wide passive domain of about 250 mV. However, after plasma nitriding treatment, the extent of the passive domain for nitrided surfaces was reduced (~ 150 mV) indicating that the corrosion tendency was higher in terms of more negative potential and increased corrosion rates. The passivation of treated surfaces owed to the predominance of ϵ -phase nitrides and also to the absence of CrN precipitates. For too short nitriding times (6 h), surface experienced pitting, while prolonging the treatment (12 h), led to the cracking of the corroded surface. Therefore, it showed that long duration treatments were recommended for achieving a thick very hard layer, which is interesting from a tribological point of view. Furthermore, due to the release of potentially aggressive liquids during the wood machining, tools need also to be corrosion resistant (Fig. 2.50 and Table 2.20). Therefore, the best nitriding condition was 500 °C for 10 h.

2.3.5 Structural and Constructional Steels

Yasavol et al. [28] (see Sect. 2.1.5) evaluated the post-oxidizing treatment effects on corrosion properties of AISI 4130 steel seen in Table 2.21. Post-oxidizing treatment using 100 % O₂ led to lower corrosion resistance compared to other atmospheres despite the thickest oxide layer formed using this atmosphere. This behavior was attributed to the presence of both Fe₂O₃ and Fe₃O₄. However, the sample oxidized under atmosphere of 25 % O₂ + 75 % H₂ showed a better corrosion resistance due to the formation of a dense oxide layer despite its lower thickness compared to 100 % O₂. The decrement of oxygen content led to even lower corrosion rate. However, an increase in the oxidizing temperature to 500 °C degraded the corrosion resistance due to the formation of a thin and non-compact oxide layer.

In all of the oxidizing atmospheres, the corrosion resistance was improved compared to only plasma nitriding. This was due to the formation of a dense oxide layer and filling the pits of compound layer.

Alsaran et al. [29] (see Sect. 2.1.5) also studied the effects of post-oxidizing treatment on corrosion behavior of AISI 5140 steel.

It was observed that both plasma nitriding and plasma nitriding-post-oxidizing treatments significantly improved the corrosion resistance of the samples. The untreated samples showed a low corrosion potential (-720 mV) and very high anodic currents indicating an active behavior. For all of the treated samples a good resistance to general corrosion was observed in comparison with untreated specimen, however all of them were subjected to pitting corrosion. As seen in Fig. 2.51, after the potentiodynamic polarization tests, corrosion pits resulting from local passivity breakdown were distributed on the surface. This behavior could be ascribed to the presence of hematite as the main constituent of oxide layer due to the

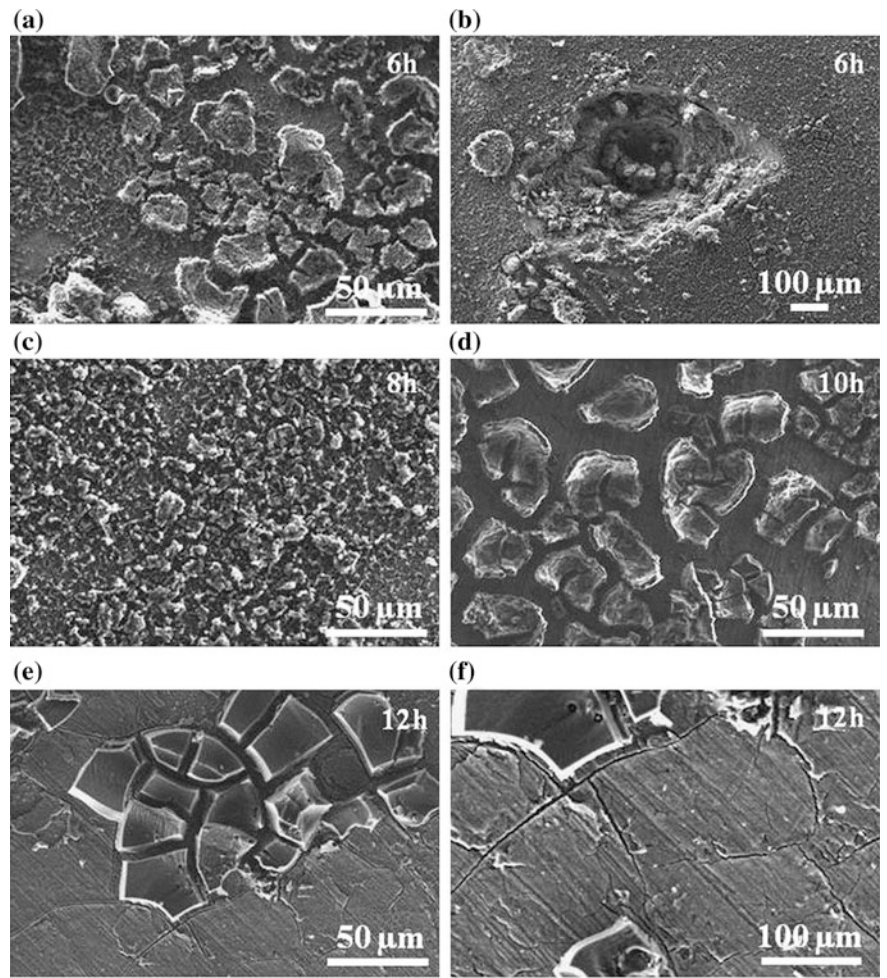


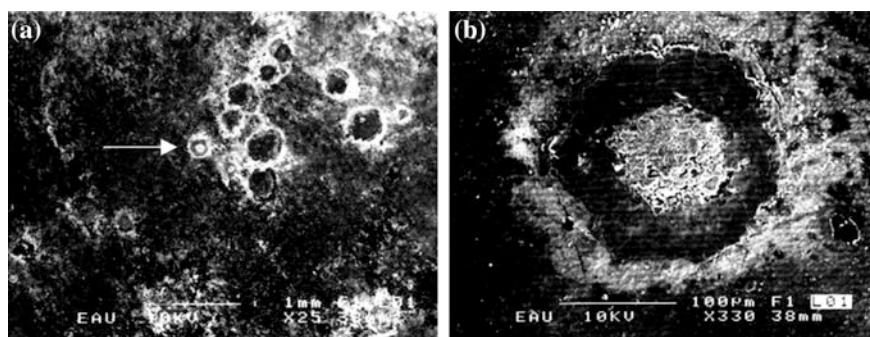
Fig. 2.50 SEM micrographs showing the surface morphologies of corroded nitrided steel samples after 24 h corrosion tests [21]

Table 2.20 Electrochemical parameters of the different samples deduced from polarization curves [21]

	Untreated steel	6 h at 500 °C	8 h at 500 °C	10 h at 500 °C	12 h at 500 °C
E_{corr} (mV/ECS)	-307	-559	-569	-582	-575
I_{corr} (nA/cm ²)	37	233	417	392	347
Passive domain extent (mV)	255	87	150	157	156

Table 2.21 The results of corrosion test on nitrided-post-oxidized samples [28]

Plasma oxidizing treatment parameters	I_{corr} (A/cm ²)	E_{corr} (V)	Corrosion rate (mm/year)
500 °C, 25 % O ₂ + 75 % H ₂	6.92×10^{-9}	−0.09	0.0057
500 °C, 10 % O ₂ + 90 % H ₂	3.39×10^{-8}	−0.20	0.0121
500 °C, 100 % O ₂	8.87×10^{-8}	−0.30	0.0089
400 °C, 25 % O ₂ + 75 % H ₂	9.09×10^{-7}	−0.39	0.0077

**Fig. 2.51** SEM micrographs showing the surface of corroded sample post-oxidized for 60 min **a** after plasma nitriding and **b** one pit [29]

porous and low-adherent nature of hematite which was grown during oxidation treatment. The higher corrosion potential (−255 mV) belonged to the sample post-oxidized for 15 min which was higher than that of the plasma nitrided sample. The lowest anodic currents were obtained for durations of 15 and 30 min whereas the highest anodic currents were observed for duration of 60 min. This was owing to the fact that increasing of oxidation time led to the spallation and consequently failure of the oxides.

Alsaran et al. [30] (see Sect. 2.1.5) studied the effects of post-aging treatment on corrosion resistance of plasma nitrided AISI 4140 steel.

Among post-aged samples, the best result was obtained for post-aging duration of 1 h. The corrosion resistance was inversely related with duration. However the corrosion resistance of just plasma nitrided sample was higher than quenched and post-aged samples.

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