LOW-TEMPERATURE GAS-PHASE
CARBURIZING AND NITRIDING OF 17-7 PH
STAINLESS STEEL

by
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*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedicate to my parents, Hongping Wang and Qiuyue Shan, my girlfriend Hao Qu, and everyone in my life.
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Low-temperature Gas-phase Carburizing and Nitriding of 17-7 PH Stainless Steel

Abstract

by

DANQI WANG

Low-temperature carburization and low-temperature nitridation were successfully applied on 17-7 PH stainless steel and significantly improved the surface hardness. Via an isothermal martensite-to-austenite phase transformation, carbon- and nitrogen-supersaturated expanded austenite was achieved. Delta ferrite grains with astonishing amount (greater than 18 at.%) of carbon (nitrogen) were observed after carburization (nitridation). The interstitially-supersaturated ferrite shows a uniform contrast, i.e. no diffraction contrast from extended structural defects under transmission electron microscopy. Plates with uniform contrast were observed in ferrite grains near the interface between the carburized layer and bulk material after carburization. These plates are enriched in carbon but do not form any carbide.
A model based on segregation of carbon interstitials to dislocation cores is proposed, the featureless appearance being ascribed to strain field overlap of a massive dislocation network. As the carbon-dislocation binding energy is higher than that of carbon to iron in cementite, carbon atoms are able to segregate to the dislocations cores. With an extremely high dislocation density \((10^{13}/\text{cm}^2)\), ferrite can take up to several wt. pct. carbon without any phase transformation.

Similar mechanism holds for featureless nitrogen-supersaturated ferrite. But after nitriding at high temperature \((713 \text{ K})\), rocksalt-structured nitrides \(\text{MN}_{1-x}\) (\(M\) being Fe, Cr, Ni and Al) were observed in a Bain orientation relationship with respect to ferrite matrix. Low nitriding temperatures \((623 \text{ K} \text{ and } 653 \text{ K})\) prefer \(\text{M}_2\text{N}_{1-x}\) plate formation in ferrite. Continuing nitriding tends to dissolve \(\text{M}_2\text{N}_{1-x}\), forming featureless grain with \(\text{MN}_{1-x}\).

In spite of processing condition designed to eliminate long-range diffusion of substitutional solute atoms, decomposition of austenite into ferrite and nitride was observed to occur during low-temperature nitridation realized by enhanced diffusion along the austenite–ferrite interphase interface. \(\text{NiAl}\) formed in ferrite during both carburization and nitridation, but lost ordering afterwards in carbon- and nitrogen-supersaturated ferrite grains.
1. Introduction

1.1 Surface Engineering

Surface engineering is one of the fast growing research fields in metallurgical engineering practices. The major focus of surface engineering is to maximize the component lifetime in service. In order to achieve this goal, three separate fields are being investigated, i.e. the optimization of surface properties, the characterization of modified coatings and surfaces, and the technologies of surface modification [1].

The optimization of surface properties is mainly concerned with corrosion, wear, and fatigue performances of the treated surface. The characterization of modified surfaces and coatings focuses on the microstructure of the modification, i.e. their composition, morphology, and other properties of interest. The technology aspect of surface modification concerns more about new technology developments and improvements of any existing technologies.

There are plenty of technologies of coating and surface modifications developed over the years, like painting, electroplating, spraying, thermal and thermochemical treatments, such as carburization and nitridation. More recent advancements of coating technology are like physical and chemical vapor deposition, ion implantation. The carburization and nitridation are actually one kind of diffusion-based coating. Instead of introducing a distinct layer on top of the substrate, carburization and nitridation infuse interstitial
carbon and nitrogen atoms, respectively, without changing the fundamental structure of the substrate. For example, expanded austenite is usually achieved after carburization and nitridation, by expanding the original face centered cubic (FCC) lattice but still retaining the FCC characteristics. The technology is intended to produce a hard, corrosion-resistant, and fatigue-resistant surface with other beneficial properties.

1.2 Precipitation-hardening (PH) Stainless Steel
Stainless steels are a family of iron-based alloys with at least 10.5 at.% Cr in order to ensure the formation of adherent self-passivated Cr-rich Cr$_2$O$_3$ oxide film, which effectively protects the bulk material from rusting in atmospheric and many other industrial environments. Generally, there are austenitic, ferritic, and martensitic stainless steels, like 316L grade, 430 grade, and 410 grade, respectively. All of them are designed as single-phase stainless steels. However, austenitic grade suffers from low strength, while ferritic and martensitic grades are generally low in ductility. Therefore, new grades of stainless steels have been developed, like PH and duplex grades, which are designed to work in the gap between austenitic and ferritic stainless steels.

PH stainless steels were developed as a new grade of stainless steels characterized by a good combination of strength and ductility, and good corrosion resistance, working in the gap between the austenitic and the ferritic stainless steels. What makes PH grade stainless steels more appealing is that they are relatively easy to fabricate. Among the whole PH stainless steel family, which includes 13-8 Mo, 15-5, 17-4, 17-7 and et. al., 17-7 PH
stainless steel is commonly used as spring materials, for the reason mentioned earlier that it is soft enough to be formed into shape while it is still strong enough to be of practical use.

PH stainless steel can be classified into three groups, i.e., martensitic, semiaustenitic, and austenitic. Martensitic grade renders a fully martensitic microstructure in the annealed condition, like 13-8 Mo and 17-4. Austenitic PH stainless steels, on the other hand, are entirely austenitic in both annealed and age-hardening conditions, like A286 and 17-10. Semiaustenitic PH stainless steel grade like 17-7 PH stainless steel is generated with the addition of adequate but not sufficiently high amount of austenite stabilizer (Ni), in which austenite is stable at room temperature but not stable with respect to mechanical driving force. In the mill-annealed condition (condition A, to be shown in Fig. 1.1), the microstructure of the semiaustenitic PH stainless steels is dominated by austenite. The austenite in the semiaustenitic PH stainless steel is designed to be unstable and can be transformed to martensite by mechanical or heat treatment. The transformed martensite can be further hardened by coherent precipitates after aging. Specifically for 17-7 PH stainless steel, the addition of Al ($\approx 2$ at.%) enables the precipitation of B2-structured NiAl during the aging. The composition of 17-7 is summarized in Table 1.1, along with several other common alloys.

| Table 1.1 Composition of stainless steels, 17-7 PH, 316L, 2205, and PH 13-8 Mo. |
|---|---|---|---|---|---|---|---|---|
| At.% | Cr | Ni | Al | Mn | Si | Mo | C | Fe |

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The standard process procedure of 17-7 PH stainless steel is shown in the Fig. 1.1 below [2]. The steel is mill annealed at a sufficiently high temperature in order to get rid of any pre-existed carbide and makes the microstructure fully austenite, so called condition A. After cooling down to the room temperature, the microstructure partially transforms to martensite, due to a higher-than-room-temperature martensite-starting temperature (M_s). Nevertheless, the major phase in the microstructure is still austenite. Besides transformed martensite, there are residual delta ferrite grains in the alloy after solidification. The morphology of the ferrite grains is stringer shape, due to the surrounding equiaxed austenite grains. The stringers of ferrite cannot further transform into austenite due to the high Cr and low Ni contents as a result of the partition of Cr and Ni between ferrite and austenite phases during solidification.
The age-hardening phase of 17-7 PH stainless steel is NiAl, which is B2 (CsCl) structure with a lattice parameter of 0.2887 nm, as shown in Fig. 1.2. NiAl has a primitive cubic structure with space group of Pm3m, whose lattice parameter is very close to body-centered cubic (BCC) ferrite (0.2881 nm from as-received material), enabling it to be fully coherent with ferrite matrix.
The product in condition T can be achieved after austenite conditioning followed by a fast cooling (within one hour) to room temperature. The microstructure of the alloy in condition T is predominately martensite with retained austenite and delta ferrite. After precipitation-hardening procedure (aging), alloy in condition TH 1050 can be obtained. The only difference between conditions T and TH 1050 is the precipitation of sub-micrometer NiAl. Alloys in condition A 1750, R 100, and RH 950 can be achieved by different heat treatments. Cold-rolled alloy is supplied in condition C, and after aging, condition CH 900 can be achieved.

In this study, low-temperature carburized and nitrided 17-7 PH stainless steel in condition A was investigated, while preliminary results were collected from 17-7 in conditions T and TH.
1.3 Low-temperature carburization and nitridation on austenitic stainless steels

Traditionally, carburization and nitridation are performed in a relatively high temperature range and work well for plain low-alloying steels. Within the hardened layer of several millimeters, formation of carbides and nitrides does not significantly deteriorate the component properties. More importantly, the residual stresses and more retained austenite introduced in this layer could significantly improve the performance of the carburized materials. However, the conventional carburization and nitridation do not work for stainless steels, because of its high Cr content. At elevated treatment temperatures, it is inevitable to induce the formation of Cr-rich carbide or nitride, which depletes the Cr from the matrix and compromises its corrosion resistance. Therefore, low-temperature carburization and nitridation were developed to circumvent this problem for austenitic stainless steels. The essence of low-temperature carburization and nitridation is the inhibition of the carbide and nitride formation kinetically. In the processing temperature range, the diffusivity of interstitial atoms (both carbon and nitrogen) is orders of magnitude higher than that of substitutional alloying elements, like Fe, Cr, and Ni. For example, at 723 ~ 773 K, the diffusivity of carbon is in the range $10^{-16} \sim 10^{-17}$ m$^2$s$^{-1}$, while the diffusivity of Cr at the same temperature range is $\approx 10^{-21}$ m$^2$s$^{-1}$ [3].

The low-temperature carburization and nitridation are most extensively studied for austenitic stainless steels, because of their low surface hardness and poor wear resistance, which limit their practical applications. Successful carburization and nitridation can
significantly improve the mechanical performances of the materials, like surface hardness, wear resistance, fatigue resistance [4-8]. This is due to the formation of interstitial-supersaturated austenite, namely expanded austenite. The expanded austenite, so-called S-phase, was initially discovered and demonstrated that it is possible to enhance the surface hardness without compromising the corrosion resistance of the stainless steels after surface processing [9, 10]. The name of “expanded austenite” was first proposed by Leyland [10] to describe the surface obtained after low-temperature carburization and nitridation. The name of “expanded austenite” clearly indicates that despite of significant amount of interstitial atoms, the characteristics of original FCC structure retain. It is a precipitate-free single phase with colossal supersaturated interstitial atoms (carbon and nitrogen) [4, 11]. The reason for the formation of the colossal interstitial supersaturation is the presence of the high content of elements, like Cr and Mo, which can mutually reduce the activities of Cr and interstitials in solid solution [12]. This has successfully modeled by CALPHAD with the assumption of paraequilibrium condition [11]. Carbon surface concentration as high as 12 at.% is predicted, which matches well with the experimental result [4, 11]. A much higher supersaturation of nitrogen, as high as 30 at.%, was achieved in expanded austenite after low-temperature nitridation [13, 14].

A typical low-temperature treated austenitic stainless steel shows intact uniform etch-resistant layer on the surface, as shown in Fig. 1.3 [15], which clearly displays a uniform etch-resistant intact top layer (“case”). Grain boundaries (GBs) and twin boundaries in the bulk material were revealed after etching, while the case stayed uniform in appearance. There is a gap between the case and bulk material, implying the case depth in
the sample. The exact reason of its formation is not clearly understood, but it is believed to be due to an electrochemical reaction between the case and the bulk material during the etching because of their different electrochemical potentials.

![Microstructure of 316L stainless steel nitrided at 703 K for 20 h](image)

Figure 1.3 Microstructure of 316L stainless steel nitrided at 703 K for 20 h [15].

A good indication of the case formation in X-ray diffraction (XRD) is that all original austenite peaks shift to lower diffraction angles, due to an expansion of lattice parameter after surface treatments induced by interstitial atoms.

It is reasonable to expect residual stresses in the case region due to a lattice mismatch between the expanded austenite in the case and the original austenite in the bulk material. Due to the lattice mismatch, the original austenite in the bulk material restrains the austenite in the case region from free expansion and therefore biaxial residual stresses
can be expected in the case. The residual stresses measured from carburized 316L can be as high as 3.4 GPa [16]. As compared to carburization, residual stresses after nitridation can be even higher, due to the fact that the concentration of the interstitial nitrogen introduced by nitridation (≈ 25 at.%) is much higher than that of interstitial carbon introduced by carburization (12 at.%). The highest residual stresses reported on nitrided samples is 7 ~ 8 GPa [17]. Due to this high level of residual stresses, there are always cracks at the free surface after high nitriding-potential runs. Therefore, the highest stresses measured after nitriding are not at the very surface but at a certain depth. This can be detrimental to material performance like in tension or fatigue cycles, since these surface cracks can readily serve as the crack initiation sites during loading.

Dilation of austenite lattice from interstitial carbon and nitrogen was studied, which also contributes to the residual stress difference. It is predicted by Pauling’s rule, that the radius of nitrogen is smaller than that of carbon. In a FCC lattice, based on a rigid sphere model, the largest interstitial site in austenitic 316L is an octahedral site, which is estimated to be 0.0525 nm. Both carbon and nitrogen would expand the lattice when dissolved as interstitials. Empirically, a linear relationship, being defined in eqn. 1.1 below, is sufficiently accurate to describe the FCC lattice dilation by interstitials as carbon and nitrogen,

\[
a_{N/C} = a_0 + \alpha \times X_{N/C}
\]  

(1.1)
where $a_0$ and $a_{N/C}$ are original and dilated lattice parameters, respectively, and $\alpha$ is the fitting parameter and $X_{N/C}$ is the atomic fraction of the interstitial atoms. The available data for the fitting parameter of expanded austenite shows that nitrogen can more efficiently expand FCC lattice than carbon at the same concentration as illustrated in Fig. 1.4 [18].
Figure 1.4 Lattice parameter $a$ of expanded austenite as a function of (a) numbers of interstitial nitrogen or carbon atoms per metal atom ($y_N$ or $y_C$) and (b) concentration of interstitial nitrogen or carbon ($X_N$ or $X_C$) [18].

Though the essence of the low-temperature carburization and nitridation is the same, the results can be significantly different, due to their different interstitial concentrations and resulting residual compressive stresses.

Concentration-dependent carbon diffusivity was proposed to explain the observation of concave carbon diffusion profile in the case [19]. The local lattice expansion due to the uptake of carbon interstitials is believed to lower the diffusion barrier of carbon interstitials and the biaxial stress gradient and diffusion short circuit dislocations also promote the carbon diffusion.

However, compared to a smooth concave carbon profile, nitrogen profile obtained after low-temperature nitridation is significantly different as illustrated in Fig. 1.5 [20]. There are apparently two regions in a nitrogen profile, a “plateau” region and a “tail” region. In the plateau region, nitrogen concentration is more or less the same, while in the trailing tail region, the nitrogen concentration abruptly drops to zero. This was successfully explained by concentration-dependent diffusivity model as well [21], but with a larger concentration-dependent factor for nitrogen compared to that of carbon.
An alternative model proposed for nitrogen diffusion in austenitic stainless steels is the “trapping-detrapping” model [22]. It relates nitrogen with the concentration of Cr in the alloy, based on the fact that the nitrogen affinity to Cr is higher than any other elements in the common stainless steel and thus serves as trapping sites for nitrogen. It was observed that nitrogen prefers to stay around Cr atoms, got “trapped” and formed so-called “short-range ordering” [23]. Therefore, a 1:1 ratio of nitrogen to Cr was proposed to explain the nitrogen plateau with an assumption that nitrogen cannot diffuse deeper before all traps available have been filled. A trapping energy barrier (1.1 eV) was calculated from the experimental data and it is higher than the lattice diffusion barrier (0.8 eV) [22]. Further, a dynamic detrapping process was proposed to better explain the diffusion of nitrogen. The validation of this model needs to be scrutinized by careful denitridation experiment or two-step nitridation with nitrogen isotopes. However, this
model cannot explain that the surface nitrogen concentration varies depending on the nitriding parameters employed during gas-phase nitridation [20].

Due to a higher stress and strain after low-temperature nitridation, there are unique phenomenon observed which is absent from carburization, i.e. orientation-dependent diffusion, a room-temperature ferromagnetism, and cracking in the case.

A non-uniform case was observed after ion-implanted nitridation in AISI 304 stainless steel, in which nitrogen diffused deeper in a <100> oriented grain as compared to the one in a <111> orientation [24]. Similar orientation-dependent diffusion was observed in Ni-based alloy Inconel 690 [25], as shown in Fig. 1.6. Nitriding study on single crystal 316L austenitic stainless steels showed that nitrogen diffuses preferentially along a [100] direction, as compared to a [011] direction [26]. A tentative model [27] based on anisotropy in elasticity of FCC lattice was proposed. In expanded austenitic grains, due to the anisotropy, the stresses along each direction are different and thus the corresponding diffusion activation energies, which gives rise to this orientation-dependent diffusion. The possible reason for the absence of orientation-dependent diffusion in carburized sample is the low stress level achieved after carburization compared to that of nitridation as mentioned before. Moreover, the high concentration-dependence factor of nitrogen diffusion compared to that of carbon diffusion also contributes to the observable difference in the orientation-dependent diffusion.
The influence of external stresses on carbon diffusion has been investigated on plasma-carburized 316L ribbons [28]. A dead weight was applied on the ribbons during the carburization and the equivalent tensile stresses on the sample ranging from 20 to 80 MPa. It is shown in Fig. 1.7 that the case depth is almost doubled after 10 h with 80 MPa external tensile stresses. The formation of carbides was also promoted by the external stresses. However, this cannot be explained thermodynamically [29], which predicts no observable case depth difference under 0 or 80 MPa external stresses. The only explanation is some “mysterious” properties related to the ribbon samples. One possible reason is the presence of tensile stresses, instead of compressive stress, as observed in carburized thin foils by our group previously [29].
A room-temperature ferromagnetism was induced by low-temperature nitridation at a critical nitrogen concentration, i. e. a critical lattice expansion [30, 31]. Ferromagnetic domains were detected on the sample surface by magnetic force microscopy (MFM) after nitridation with paramagnetic material beneath them. Auger electron spectroscopy (AES) confirmed that 15 at.% nitrogen was the critical nitrogen concentration to introduce the ferromagnetism, which correlates this transition to a $\approx 5 \%$ critical lattice expansion. Compared to nitridation, a low-temperature carburization-induced ferromagnetism has never been observed, because that the lattice expansion after carburization is lower than the critical lattice expansion required ($\approx 3 \%$) [4].
Though low-temperature surface treatments can effectively inhibit carbide or nitride formation, in some aggressive or prolonged treatments, the formation of the carbides and nitrides is still a big concern [12, 28, 32]. In 316L, it has been reported that after low-temperature gas-phase carburization, both $M_5C_2$ (dominant) and $M_7C_3$ paraequilibrium carbide were identified [12, 32]. After the plasma carburization, carbide precipitation occurred as well [28], which is proposed to be the same structure of CrN, i.e. CrC.

In low-temperature gas-phase nitrided 316L, $M_4N$ is the first precipitate formed [20], as the nitrogen concentration in the austenite reaches a critical value then the ordering of nitrogen occurs. It is difficult to differentiate the $M_4N$ from expanded austenite with the same level of nitrogen, except the forbidden reflections of the simple-cubic-structured $M_4N$. However, the high Cr content in 316L makes the situation more complicated, because of its higher affinity to nitrogen than that of Fe. Chromium nitride may occur as first precipitation during nitridation.

Expanded austenite is a metastable phase, which decomposes at prolonged isothermal annealing at higher temperatures. The decomposition product is CrN for 316L. The orientation relationship (OR) between CrN and FCC lattice is cube-to-cube as defined as follows,

$$<111>_{\text{FCC}} // <111>_{\text{CrN}} \quad \text{(1.2)}$$

$$\langle 220 \rangle_{\text{FCC}} // \langle 110 \rangle_{\text{CrN}} \quad \text{(1.3)}$$
The splitting of reflections from expanded austenite has been observed in the diffraction patterns (DPs) during in situ TEM annealing at high temperatures [8, 33]. A larger lattice spacing due to CrN formation appears during annealing at 713 K and becomes distinct at 873 K annealing, as shown in Fig. 1.8.

Figure 1.8 Selected-area diffraction (SAD) patterns required from an expanded austenite region during in situ annealing at (a) 273 K, (b) 713 K, (c) 773 K and (d) 873 K [33].

1.4 Low-temperature carburization and nitridation on ferrite in stainless steels
After both low-temperature carburization and nitridation have been proved a great success on austenitic stainless steels, studies of their applications to other families of stainless steels, e. g. ferritic, martensitic, duplex, and PH grades, are attached great
importance. It is interesting to investigate the possible response of these alloys to surface treatments.

Previous studies showed that the formation of carbides and nitrides is much easier in stainless steels other than austenitic stainless steel [34-44]. Consequently, the processing temperature required for a precipitate-free hardened case in other stainless steels is much lower than that of austenitic stainless steels, because of a very limited solubility of interstitials in ferrite. According to CALPHAD modeling, by assuming paraequilibrium conditions, solubility of interstitials in austenite is above 10 at.%, but it is well below 1 at.% in ferrite. At the temperatures where carburization is performed, the diffusivities of substitutional solutes are sufficiently low for them to be considered “frozen”, whereas carbon atoms have reasonable mobilities [11]; paraequilibrium conditions thus pertain. Therefore, during the carburization or nitridation, ferrite can be easily saturated and tends to form precipitates. For example, low-temperature carburization of 316L is usually carried out at temperatures above 673 K [4, 12], while for 17-7 PH stainless steel, carburization at 653 K is high enough for carbide formation [45]. A precipitate-free hardened case can be achieved at 623 K for 17-7 PH stainless steel. On the other hand, a much thicker hardened layer can be achieved for the same time and temperature compared to austenitic stainless steel, due to a much higher interstitial diffusivity in BCC/body-centered tetragonal (BCT) structure, owing to a more open structure compared to FCC structure.
Lattice expansion of ferrite and martensite after treatment is usually $\approx 1\%$ or even less [36, 38, 39], which is much smaller than that in expanded austenite. Significantly broadened ferrite peaks were observed after nitrided 17-4 PH stainless steel in XRD patterns [34, 39], suggesting a worse crystallinity of ferrite after treatment, as shown in Fig. 1.9. The only ferrite peak visible after nitridation is $[011]_{\text{BCC}}$, which is severely broadened and shows much less intensity.

Figure 1.9 XRD pattern of 17-4 PH stainless steel treated at 653 – 773 K for 10 h.

There are usually at least two layers after low-temperature nitridation on PH stainless steels, i.e. a compound layer and a diffusion layer. A compound layer (sometimes called “white” layer) is usually comprised of nitrides [39, 42, 43], as shown in Fig. 1.10 [43]. This compound layer can be etching resistant and extremely hard [39] and correspondingly significantly improved wear resistance [39, 44]. Beneath the compound layer, there is a diffusion layer, where interstitials stay in the solid solution. The
hardening effect from interstitials can be significant but the interstitial concentration is low due to the limited solubility in the ferrite.

Figure 1.10 Cross-section of nitrided (683 K/6 h) layer on 17-4 PH steel after solution treatment and aging at 873 K before nitriding SEI.

Instead of a compound layer after nitridation, carburized surface usually yields a uniform carbide layer. In carburized 2205 duplex stainless steel, nano-crystalline paraequilibrium carbides were observed on the ferritic portion of the alloy, as shown in Fig. 1.11 [37]. A 2 μm thick carbide layer was formed on the carburized PH 13-8 Mo stainless steel as well [36]. Similar to a nitried compound surface, the surface hardness, mechanical properties of these carburized surface were enhanced significantly [36, 37]. Even corrosion resistance can be improved after carburization, but it is sensitive to the carburization temperature [36, 37].
Figure 1.11 (a) TEM cross-sectional image of ferrite grain carburized at 653 K and DPs acquired from (b) near interior and (c) near surface of grain.

Carburization has been done on duplex 301 [38] and 2205 (Fig. 1.12) [37] stainless steels. It is interesting to see that the surface concentration of carbon in the ferrite is always higher than that in austenite due to the carbide formation. However, the carbon diffusion depth is always larger in austenite than that in ferrite.

Figure 1.12 (a) Auger electron spectroscopy (AES) depth profile of wrought 2205 specimen carburized at 653 K and (b) carbon AES profile from wrought specimen compared with carbon profiles from cast specimen.
Compared with nitridation on ferritic stainless steels, there are more literatures investigated into nitridation on Fe-based alloys, like Fe-Cr [46-51], Fe-Si [52], Fe-Al [53, 54], Fe-V [55], Fe-Cr-Al [56, 57]. Various precipitates in different morphologies were observed. Due to the dominated Fe content, the most common nitride is Fe₄N. However, as Cr concentration increases, the Cr-enriched precipitates formed in the alloy [51]. As Cr content increases to several weight percent, finely dispersed CrN was formed in the grain, which can be verified by the increase of hardness. The fine CrN precipitates coarsen during continuous nitridation and the hardening effect disappeared [48]. Cr₂N was also observed in the nitried microstructure [51]. With addition of Al (usually for carbide inhibition or grain refinement), e. g. an Fe-Cr-Al alloy, a new kind of nitride, Cr₁₋ₓAlₓN, was formed [56]. This rocksalt-structured nitride is coherent and obeys a Bain OR with ferrite matrix. The concentration of high carbon/nitrogen affinity elements, like Cr, can effectively affect the nitried layer thickness and surface interstitial concentration [46]. This seems to agree with trapping-detrapping model, since the alloys with higher Cr concentrations yield deeper nitried zone and higher surface nitrogen concentration, as shown in Fig. 1.13. [46].
Figure 1.13 (a) Thickness of the nitrided zone depending on the nitriding time and the Cr content and (b) Nitrogen-concentration profiles of nitrided Fe-7Cr and Fe-20Cr alloys, as measured with EPMA (black dots) and as calculated profiles (full lines) [46].

“Excess” nitrogen was predicted and observed at GBs in Fe-Cr alloys [46, 48, 56], which is shown in Fig. 1.14 [56]. Besides nitrogen necessary for the nitride formation and dissolved in ferrite matrix, there is an amount of nitrogen in the nitrided microstructure depending on the nitriding potential. The excess nitrogen in the alloy is due to the presence of large area of coherent interfaces between ferrite matrix and precipitates. In
addition, pronounced misfit-strain fields between the ferrite matrix and the precipitates can also facilitate the dissolution of excess nitrogen.

Figure 1.14 (a) Summary of the prenitriding (24 h at 853 K, \( r_N = 0.104 \text{ atm}^{-1/2} \)) and denitriding (48 h at 743 K in pure \( \text{H}_2 \)) experiments performed with an Fe-Cr-Al alloy, (b) nitrogen-absorption isotherm of the pre- and denitried alloy determined at 833 K for different nitriding potentials [56].
The lack of capacity to take excess inward nitrogen leads to the formation of cellular precipitation. It was observed that the lamella structure nucleated from the near GB regions and finally take up the entire grain, as shown in Fig. 1.15 [48] and Fig. 1.16 [46], respectively. Similar observation was reported in 17-4 PH stainless steel as well [40], in which a “dark phase” was observed along the grain boundaries. Lamellae structure after cellular phase transformation is very coarse, inevitably leading to a hardness decrease [48]. There are different orientated colonies of lamellae within one transformed grain, implying the presence of different orientational invariants. The amount of cellular transformed areas increases with the Cr content in the alloy [46]. A fully cellular transformed layer was observed in Fe-13Cr and Fe-20Cr alloys, while it only partially occurred on Fe-4Cr and Fe-7Cr alloys after the same treatment.

Figure 1.15 (a) Optical micrograph of a cross-section of a through-nitrided (202 h; 10 vol. % NH₃/90 vol. % H₂; 833 K) Fe-Cr specimen [48].
Figure 1.16 An original grain of the Fe-4Cr alloy after nitriding transformed by the discontinuous coarsening reaction; (a) optical micrograph; and (b) SEM micrograph reveals the occurrence of many differently oriented colonies of lamellae [46].

In the present study, a cellular precipitation reaction in 17-7 PH stainless steel was observed after low temperature nitridation. The characteristic feature of this reaction is that decomposition occurs at an internal interface, which then begins to function as a migrating phase transformation front, leaving behind a lamellar-structured "cell".
Cellular precipitation has been extensively studied in gas-phase-nitrided Fe–Cr alloys [48-51]. With regard to stainless steels, there are only limited studies of cellular precipitation reactions. Discontinuous precipitations of Cr$_2$N nitride lamellae were observed in high-nitrogen Cr–Mn austenitic stainless steel after aging [58-60]. Similarly, lamellar M$_{23}$C$_6$ carbide was observed in Cr–Ni austenitic stainless steel [61]. In interstitially hardened stainless steels, there are only scant reports of cellular precipitation [62]. In AISI 304 austenitic stainless steel, after nitriding at high temperature (> 1073 K), a coarse lamellar structure of austenite and Cr$_2$N developed in front of fine lamellae composed of austenite and CrN.

While compared to “normal” layer-type precipitation occurred on the free surface during nitriding process, some “abnormal” nitride morphologies upon nitriding Fe-based alloys were observed, e. g. Fe-Al [53], Fe-Si [52] alloys. Instead of forming a uniform nitride layer on the free surface (Fig. 1.17 [63]), “abnormal” needle-shape nitride was observed in these Fe-based alloys, as shown in Fig. 1.18.
Figure 1.17 Optical micrograph recorded from cross-section of nitrided (a) pure iron, (b) Fe-4 at. % Cr, and (c) Fe-4 at. % V specimens, respectively [63].

Figure 1.18 Optical micrographs recorded from the cross-sections of nitrided iron-based alloys. (a) Fe-4.7 at. % Al alloy (b) Fe-1 at. % Mo alloy, and Fe-4.5 at. % Si alloy [63].

A model based on metal-nitrogen interaction was proposed to explain this. M-nitrogen interaction parameter can be defined as the ratio (per unit volume of precipitate) of the (chemical) Gibbs formation energy of precipitate and the (mechanical) misfit-strain energy induced in the precipitate/matrix system. “Strong” interaction, as a result of
strong/moderate M-nitrogen affinity and a moderate/small volume misfit is associated with establishment of a (semi)coherent interface. Otherwise, it is a “weak” interaction.

Alloying elements having “strong” M-N interaction, such as Cr, V and Ti, precipitate instantaneously as internal M-nitrides, i.e. inward-diffusing nitrogen atoms can be consumed instantaneously by forming nitride and no nitrogen supersaturation would be expected in the ferrite. Once the nitrogen solubility limit of ferrite is reached, Fe₄N can readily nucleate at the surface and grow laterally leading to a “normal” uniform layer-type nitride.

However, alloying elements having “weak” M-nitrogen interaction, such as Al, Si and Mo, though have a relatively strong to moderate affinity, the nitride volume misfit with the ferrite matrix is large. They also simultaneously have low solubilities in Fe-nitride. Therefore, nitride formation requires either partitioning of “weak”-interaction elements out of the nitride to form M-free nitride or incorporating into the nitride “unwillingly”. Consequently, this leads to a low driving force and kinetics for the nitride formation, delaying the nucleation of such Fe-nitrides at the surface. Therefore, a nitrogen supersaturation over an extended depth range from the surface can be achieved. But when the nitrogen supersaturation reaches a critical point, it forces the formation of nitride incorporating these “weak”-interaction elements over a large depth and thus forms plate-like nitrides. These ferrite-dissolved “weak”-interaction elements near the plate-like nitrides can precipitate out in a more favorable form, like AlN, Mo₂N, and Si₃N₄, by nucleating on dislocations generated to accommodate the misfit of Fe₄N with the ferrite.
In a sum, carburization and nitridation on ferrite generally induce carbides or nitrides formation, which also significantly improves surface hardness, wear resistance and even corrosion resistance. A discontinuous precipitation reaction was observed during nitridation due to the excess nitrogen. The alloying elements play an important role in controlling the nitride formation and morphology.

1.5 Carbon-Supersaturated Ferrite in Steels

The classic Fe-C phase diagram predicts a limited carbon solubility in ferrite at 1000 K, which gets diminishingly smaller when approaching room temperature. Due to the addition of Cr (≈ 17 at.%) in 17-7 PH stainless steel, the ferrite-stabilized region expands and a corresponding carbon solubility increase can be expected. At carburization temperature (653 K), the calculated carbon solubility is around 0.003 at.% [64]. This is far from experimental observations after carburization of this study, and in reported pearlitic [65-68] and bainitic [69-72] steels.
Figure 1.19 Fe-C paraequilibrium phase diagram calculated for 17-7 PH stainless steel [64].

Due to such limited carbon solubility in the ferrite, carbide formation is expected once ferrite is supersaturated by carbon. Cementite is the stable carbide predicted by an Fe-C phase diagram, as the pearlite formation. As a stable carbide, cementite is unstable under extreme deformation condition. Cementite, as a constitute of pearlitic steels, was dissolved during high-deformation process. A commercial carbon steel experienced several cycles of 7 GPa torsion (up to true strain of 6.0), applied by high pressure torsion [65], which is a common method to introduce high deformation. The microstructures of sample surfaces as-received and after 3, 5, and 7 cycles are shown in Fig. 1.20 [65]. High torsion deformed equiaxed grains, forming fibrous structure along the torsion direction.

Figure 1.20 Optical micrographs of the surface of the samples of UIC 860 steel in initial state and after the HPT deformation: (a) as-received, (b)-(d) after 3, 5, and 7 cycles. The arrow shows the shear direction [65].
Under transmission electron microscopy (TEM), cellular ferrite grains were formed after two cycles. A diffuse contrast at the ferrite-cementite interface is observed and probably due to a high dislocation density in that area. After 5 cycles, a homogeneous nanostructure was obtained and confirmed by ring patterns in SAD, in which cementite reflections disappear, implying the dissolution of cementite during the deformation.

XRD patterns acquired from as-received and deformed samples are shown in Fig. 1.21, which clearly confirms cementite dissolution. Thermomagnetic method used to quantify the relative dissolution of cementite based on its ferromagnetic to paramagnetic transformation shows that the cementite is completely dissolved after 5 cycles. Another thing worth noting is that the ferrite peak broadens as more plastic deformation applied. This is similar to the observation in carburized and nitrided ferritic and martensitic stainless steels, being attributed to the strain and worse crystallinity.
Figure 1.21 XRD patterns taken at initial stage and after certain torsion cycles [65].

Similar high-deformation study was carried out in other pealitic steels as well [66]. It was shown that carbon concentration in ferrite increases with strain applied and saturates at a true strain of 3.47. In addition, the carbon concentration in the cementite is inversely correlated with cementite lamellae thickness (well below cementite stoichiometry), as shown in Fig. 1.22. However, since cementite is known as a linear compound, the nonstoichiometric cementite observed by local electrode atom probe (LEAP) can be due to the insufficient instrument resolution.
Figure 1.22 Atom maps of cold-drawn pearlitic steel wires at $\varepsilon = 2$ (a) and $\varepsilon = 5$ (b). The yellow dots and blue dots represent carbon (100 % shown) and Fe (50 % shown), respectively. (c) 1D carbon concentration profiles along the direction perpendicular to lamellar interfaces and the error bars are marked in grey [66].

The distribution of carbon atoms in the microstructure after cementite dissolution is critical. Figure 1.23 [66] clearly shows that carbon atoms segregated to some internal boundaries between cementite lamellae and the carbon concentration at segregated region is quite high. These internal boundaries can be dislocation-related cell structure or subgrains formed during deformation. Therefore, a carbon-supersaturated ferrite can be achieved after cementite dissolution.
Figure 1.23 (a) Part of the three-dimensional (3D) carbon atom map with an isoconcentration surface at 7 at.% carbon for wires at $\varepsilon = 5.4$. (b) and (c) Front and side views, respectively of the atom maps for the region of interest (ROI) extracted from (a). The yellow, red, and grey dots represent carbon, Mn, and Si atoms, respectively. (d) One-dimensional (1D) concentration profiles for the three elements shown in (b) and (c) along the direction (marked with black arrows) perpendicular to the carbon-enriched boundary [66].

Another series of studies on bainitic ferrite was investigated by local-electrode atom probe (LEAP) as well [69-71]. A significant amount of carbon was detected in solid solution of ferrite, about 10 times higher than that expected from paraequilibrium between austenite and ferrite. There was no significant segregation of either substitutional elements or carbon to austenite—ferrite interface.
Linear features of carbon segregation (probably dislocations) were observed at austenite—ferrite phase boundary (PB) as shown in Fig. 1.24 [69]. Isoconcentration surfaces of 8 at.% carbon isolated carbon-enriched region around one dislocation. Proximity histogram shows no other elemental segregation except carbon. This is consistent with theories proposed by Kalish and Cohen [73] that dislocations trap carbon atoms at its core due to a more favorable binding energy.

Figure 1.24 (a) Carbon isoconcentration surfaces at 8 at.% carbon superimposed with the carbon atom map, and proximity histograms across (b) a carbon cluster, (c) a ferrite—austenite interface, and (d) a dislocation network in the vicinity of the ferrite—austenite interface in bainitic ferrite.
Clusters with significant amount of carbon were observed as well, as shown in Fig. 1.24 (a) and Fig. 1.25 (a) [71]. The alloying elements in the clusters are too low to be identified as carbides. These clusters are $\approx 6$ nm thick with a maximum carbon concentration of $\approx 14$ at.%, which is possibly due to the redistribution of carbon atoms along the dislocations in the ferrite.

![Figure 1.25 Carbon atom map and concentration profile along the marked y-direction across a carbon cluster in bainitic ferrite.](image)

Therefore, carbon-supersaturated ferrite in pearlitic and bainitic steels has been drawn attention and well studied in details. However, there are scarce reports about carbon-supersaturated ferrite after low temperature carburization and nitridation. For most carburized (nitrided) ferrite, extensive carbide (nitride) formation was observed, being completely different from this study, where carbide-free carbon-supersaturated ferrite was observed. In this study, interstitial-supersaturated ferrite was observed and investigated and a mechanism was proposed for its formation.
2. Experiments

2.1 Design of low-temperature gas-phase carburizing/nitriding process

Low-temperature gas-phase double-activation carburizing (nitriding) process is patented by the Swagelok Company, using HCl gas *in situ* in the activation step to remove the spontaneously formed Cr₂O₃-rich passive film [74]. Compared with other carburizing (nitriding) methods, e.g. ion-implantation and plasma, gas-phase carburizing (nitriding) has several advantages, as follows. The case formation on the treated surface is uniform, it could cover specimen with complex geometries, and most importantly, especially for nitriding, the activity of the process can be well controlled.

Specimens used in this study were 3 mm thick plates of 17-7 PH stainless steel (condition A [2]). 17-7 PH stainless steel in condition A is semiaustenitic and contains austenite, martensite and residual delta ferrite (formed during solidification). All samples were electropolished (EP) before carburization and nitridation. Gas-phase double-activation low-temperature carburization was carried out by the Swagelok Company. Two activations were applied at different temperatures and the total carburization time is 150 h; CO was used as carbon source during carburization. The time-temperature carburization “recipe” for the sample is shown in Fig. 2.1.
A similar gas-phase double-activation nitriding process was applied on 17-7 PH stainless steel condition A as well. All nitridation treatments were carried out at Case Western Reserve University with a customized chemical vapor deposition furnace. Samples were nitrided at different temperatures (623, 653, 713 K) and activities (3000, 7400, 144000) by a gaseous mixture of NH₃ and H₂ for 20 h. Activation temperature for all nitriding process is 598 K.

The nitriding potential \( a_{N_2} \) during the process can be defined as,

\[
a_{N_2} = (K \times \frac{P_{NH_3}}{P_{H_2}^{3/2}})^2
\]  

In eqn. (2.1), \( K \) is the reaction constant for NH₃ dissociation at nitriding temperature, and \( P_{NH_3} \) and \( P_{H_2} \) are the partial pressures of ammonia and hydrogen, respectively. The reaction constant for each temperature can be calculated by following the ammonia dissociation reaction (eqn. 2.2),
\[ \text{NH}_3 \rightarrow \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \] (2.2)

In order to conform to the conventional nitriding process, only NH\textsubscript{3} and H\textsubscript{2} were used during the nitridation. Different nitriding activities were achieved by varying the gas mixture composition during the nitridation (controlled by gas flow), as summarized in Table 2.1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Nitriding activity</th>
<th>N\textsubscript{2} (vol.%</th>
<th>H\textsubscript{2} (vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>623</td>
<td>144000</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>653</td>
<td>3000</td>
<td>43</td>
<td>57</td>
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<td>7400</td>
<td>52</td>
<td>48</td>
</tr>
<tr>
<td>713</td>
<td>7400</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td>713</td>
<td>144000</td>
<td>65</td>
<td>35</td>
</tr>
</tbody>
</table>

2.2 Characterization methods
Carburized and nitrided samples of 17-7 PH stainless steel were investigated by various instruments, both chemically and structurally, including X-ray diffraction (XRD), scanning electron microscopy/focused ion beam (SEM/FIB), transmission electron microscopy (TEM), Auger electron spectroscopy (AES), atom probe tomography (APT), and magnetic force microscopy (MFM).
2.2.1 X-ray diffraction

XRD was widely used for phase identification, and measurements of lattice parameter and residual stress. A Scintag X-1 advanced X-ray diffractometer with Cu radiation ($\lambda_{\text{CuK}\alpha_1} = 0.154056 \text{ nm}$) was used, which was mainly employed to reveal the different phases and measure the lattice expansion before and after low-temperature carburization or nitridation.

Usually, Bragg-Brentano (0-2θ) geometry was employed on a flat surface with a beam size on the order of mm. The X-ray penetration depth of such geometry is $\approx 5 \mu\text{m}$ and thus this setup is a macroscopic view of the samples, since the grain size of samples used in this study is on the order of micrometers. All samples were scanned from 35° to 100° with a step size of 0.04°/step and scan rate of 1 s/step. Before acquiring any spectrum from samples of interest, a peak from a flat piece of standard Al$_2$O$_3$ is acquired to ensure the machine is running properly.

For an as-scanned spectrum, noise background was corrected from the raw data by subtracting an average over neighbors and then peak fitting was performed by a software in the system according to Pearson VII equation. The plane spacing was then determined according to Bragg’s law defined as,

$$2d_{hkl}\sin\theta_{hkl} = \lambda \quad (2.3)$$
Then according to the crystallography of the sample of interest (FCC or BCC in this study), the lattice parameter of the unit cell can be deduced according to the Nelson-Riley method.

As compared to Bragg-Brentano geometry, grazing incidence (1°-3°) diffraction was used as a complimentary method for surface-sensitive measurement, which is of great importance for the surface measurement, like the thin carburized layer or carbidic layer on the free surface. The typical penetration depth of such geometry (1°) is about 200 nm.

2.2.2 Scanning electron microscopy/focused ion beam (SEM/FIB)

SEM was used to characterize the material microstructure, such as determining the case depth and distinguishing different phases (usually after etching). Cross-sectioned samples were usually polished to mirror-like surfaces and then etched by Kane’s etchant. In addition to imaging with secondary electrons, with a backscatter (BS) detector, sample can be imaged with BS electrons, which is closely related with atomic mass, also known as Z-contrast. This is helpful to reveal ferrite from austenite, and case from bulk material due to compositional differences between them.

Nowadays, most scanning electron microscopes are equipped with an X-ray energy dispersive spectrometry (XEDS) detector, which allows chemical analysis on the samples. XEDS is useful to differentiate the ferrite from austenite due to the Cr and Ni partitioning between the two phases during solidification. However, it is not ideal for
light-element quantitative analysis, like carbon and nitrogen, due to severe peak overlap at low energies. Qualitatively, XEDS works well for determining if the carbon or the nitrogen is present in the alloys. In addition to acquiring chemical information from one position, XEDS mapping is another convenient tool to show the chemical information from a much broader area. In this study, XEDS mapping was mainly used to determine the position of ferrite grain in the case for further sample preparation. A FEI Quanta 3D environmental dual beam SEM/FIB instrument and a FEI Nova Nanolab 200 dual beam SEM/FIB instrument were used to acquire images and chemical information.

FIB is a site-specific tool for sample preparation by using a focused Ga beam. Both TEM and APT samples were prepared by using a FEI Nova Nanolab 200 and a FEI Helios nanolab 650 dual beam FIB/SEM instruments from finely polished cross sections of carburized and nitrided 17-7 PH stainless steels.

Prior to lift-out procedure, samples were coated by Pd to mitigate the charging problem (not applied on samples need XEDS detection). Pt was deposited on the region of interest (ROI), which is usually ferrite grains identified by XEDS mapping and then trenches were made at the front and back sides of the deposited Pt strip. Foils were welded to an Omni-probe micromanipulator and cut free from the bulk samples and then lifted out. Final thinning was usually performed on the Helios SEM/FIB instrument to a proper thickness, at least electron-transparent under TEM. Most TEM applications require thin samples, preferably less than half of electron free path. The lift-out procedure of APT
samples is similar [75]. The final tip thinning was carried out on the Helios SEM/FIB by circular patterns and a customized pattern.

As a final step, some of TEM foils were cleaned by Fischione NanoMill 1040, in order to remove the amorphous layer (damage layer from Ga sputtering and redeposition of milled material). The nanomill uses Ar sputtering and operates only at 900 V to minimize the damage.

2.2.3 Transmission electron microscopy (TEM)

TEM was used to characterize the microstructure, crystal structure, and chemical composition of carburized and nitrided 17-7 PH stainless steels. A FEI Tecnai F30 (300 kV) and a Zeiss Libra 200EF (200 kV) were used to acquire TEM data. They are both equipped with field-emission guns. Tecnai is equipped with a post-column energy filter, while Libra has an in-column Ω energy filter. Tecnai was used mostly to acquire DPs, bright-field (BF) and dark-field (DF) images, and high-resolution TEM (HRTEM) images. Libra was employed to record DPs, BF and DF images, scanning TEM (STEM) images, and chemical analysis, including XEDS and electron energy loss spectroscopy (EELS). The in-column energy filter on Libra is a convenient tool to acquire convergent beam electron diffraction (CBED) patterns.

In software Digital Micrograph*, HRTEM images were filtered by applying masks with five pixels on the edge smoothed by a Gaussian function, in order to avoid a step function

* Digital Micrograph is a software developed by Gatan Inc.,
at the edge. An alternative Wiener filtering method was carried out by loading a pre-written script in Digital Micrograph [76]. The Wiener filtering can effectively eliminate the background noise due to amorphous layer. Java electron microscope simulator (JEMS) was used to simulate DPs, stereograms of different structures, and CBED patterns.

XEDS mapping in TEM was employed to acquire chemical composition information of the microstructure. EELS is good to analyze light elements, because they are well separated on a spectrum. Carbon peak (core loss) is around 283 eV, while that of nitrogen is about 405 eV. EELS line scan was performed in order to acquire interstitial concentration variation across boundaries in carburized and nitrided 17-7 PH stainless steels. Three-window electron spectroscopic imaging (ESI) was also performed to acquire carbon and nitrogen distribution in the microstructure.

2.2.4 Auger electron spectroscopy (AES)

In order to obtain more accurate carbon and nitrogen concentration measurements in 17-7 PH stainless steels, a PHI 680 scanning Auger microprobe (SAM) was employed. Line scans perpendicular to free surfaces on cross-sectioned samples were acquired. AES is surface sensitive, because only the Auger electrons within 10 nm from the surface can escape and be detected. Besides, a line scan on cross section is more efficient than sputtering through from plan view.
The AES samples were polished to mirror-like surface as well. In order to remove any hydrocarbon on the sample surface, all samples were Ar sputtered prior to any data acquisition. A continuous Ar sputtering was applied simultaneously, in order to make sure that there is no oxygen or carbon redeposition during the data acquisition.

The carbon measurement of the AES system was calibrated by alloys with known amount of carbon previously [77]. A similar calibration on nitrogen measurement was carried out as well. It was shown that the error of nitrogen measurement is about 1 at.%, but the presence oxygen can be problematic [20].

2.2.5 Atom probe tomography (APT)

APT was used in order to confirm the extraordinary carbon and nitrogen concentrations in the ferrite grains. APT is a destructive testing method.

APT was developed from field-ion microscopy and then being equipped with a time of flight (TOF) mass spectrometer with the ability to detect single evaporation event and finally a position-sensitive atom probe was developed [78]. LEAP tomography is a more recent invention [78]. By installing a local electrode (LE) in the vicinity of a sharp microtip (∼ 30 µm away from the sample), the voltage (Vex) needed to achieve evaporation voltage (E) is reduced. As illustrated in Fig. 2.2 [78], the conductive substrate is maintained at a positive potential (Vex) and a negative pulse is applied on the LE to achieve required E field for atom evaporation. Behind the LE, there is a position-
sensitive detector, consisting of a microchannel plate (MCP) and a delay-line detector behind it. The MCP measures the TOF of an ion, while the delay-line detector measures the position of such ion. The information of mass-to-charge ratio and the corresponding ion position is processed by computers and a 3D atom column can be reconstructed.

![Figure 2.2 Schematic drawing of a 3D LEAP tomography [78].](image)

The limitation of APT also arises from such configuration [78, 79]. First, the total ion detection efficiency is about 60 %, due to the open area of MCP. Secondly, the delay-line detector is designed to differentiate hitting events separated by some time and distance. But in reality, multiple hitting events occur all the time. Especially, for some species, like carbon, multiple hitting events occur more often than others, which can significantly influence the measurement accuracy [80].

LEAP can work in two different modes, i.e. voltage-pulse and laser-pulse modes. In voltage-pulse mode, only voltage applies on the tip that atoms are pulled out of the tip by
electric field only, which usually gives better spatial resolution. But the stress resulted from the electric field is also large, usually leading to an early fracture. On the other hand, the laser-pulse mode is more benign. By applying a laser beam with certain energy (0 ~ 100 pJ), the atoms on the tip can be evaporated at a relatively low voltage, compared with that of voltage-pulse mode. This yields a lower electric stress on the tip enabling a larger data set under the same voltage. Due to the laser pulse, the atom evaporation is more discrete and therefore offering a better mass resolution. The drawback of the laser-pulse mode is a lower spatial resolution, resulting from the possible atom migration on the tip surface before evaporation. All tips used in the present study are tested under laser-pulse mode, with a laser energy of 20 pJ.

Atom-probe tomographic data of the carburized and nitrided samples was acquired on a Cameca LEAP 4000 HR Atom Probe (School of Engineering, University of Michigan), in laser mode at a temperature of 50 K. The pulse rate is 250 kHz and the detection rates used are 0.5 % and 1 %. The temperature is empirically optimized for metals, which is related with spatial resolution and as well as possible data set size. The detection rate basically controls the acquisition time, i.e. the higher it is, the faster the acquisition is.

Regarding to nitrided samples, the $^{28}\text{Si}^{2+}$ peak overlaps with $^{14}\text{N}^+$ at 14 Da (mass-to-charge ratio) severely. In this study, peak at 14 Da is assigned as $^{14}\text{N}^+$ for nitrided tips, due to a limited Si content in the alloy. The accurate concentration of Si can be deduced from its stable isotopes, $^{29}\text{Si}$ and $^{30}\text{Si}$. 
Samples for APT were all prepared by FIB lift-out procedure from ferrite grains, located by XEDS mapping. All tips were cleaned under 5 kV ion beam to minimize the damage layer induced previously. The final tip radius is less than 50 nm and usually tips fracture at about 150 nm radius. A sample with 100 ~ 150 nm in length between the apex and 150 nm radius position is good. Any sharp side tips should be removed, or at least 5 μm under the main tip.

2.2.6 MFM

A Dimension 3100 scanning probe microscope (Veeco Digital Instruments) was utilized to reveal any magnetic phases from finely polished cross sections after nitridation. The Co-coated Si tip (ferromagnetic) worked at a non-contact mode and both topography and phase image (magnetism) were acquired at the same time.

A force between the Si tip mounted at the end of the cantilever and the sample surface was measured by the magnitude of the deflection of the cantilever, which yields topographic data. When the tip interacts with magnetic field from the sample, the phase of tip oscillation is changed, which is translated into the phase contrast observed in the MFM image.

2.2.7 Hardness

Hardness of nitrided samples was obtained from two different hardness machines. Plan-view hardness was obtained from a Buehler Micromet microhardness tester with a
Vickers diamond pyramid indenter. The load used on as-nitrided samples was 50 gf. On some extremely hard surfaces, like as-nitrided samples of condition T, 100 gf was used to minimize the measurement error.

Cross-sectional hardness values were acquired from an Agilent G200 nanoindentor. Samples were finely polished before any hardness measurement, in order to minimize any measurement error due to sample topography. The load used was 5 or 10 gf. A cross-sectional hardness profile was obtained along a line intersecting with the free surface at 30°, avoiding measurement error due to closely-spaced indents. In addition to hardness profile, the nanoindentation can also measure other useful properties, like material modulus.

2.2.8 Cyclic potentiodynamic polarization

The cyclic potentiodynamic polarization measurement according to the ASTM G61 protocol was conducted by our collaborators at Naval Research Laboratory to determine the corrosion resistance of the carburized materials to localized corrosion in form of pitting corrosion (and crevice corrosion, not shown here). Cyclic polarization curves were recorded for non-treated and carburized 17-7 PH stainless steel.

Cyclic potentiodynamic polarization experiments were conducted on carburized samples, using a PAR flat cell (Ametek Instruments, Oak Ridge, TN). The configuration used comprises a sample compressed between a backing plate and a knife-edge O-ring made
of polytetrafluoroethylene, exposing 1 cm² of specimen area to the test solution. Samples were allowed to establish open-circuit potential for 12 h prior to the cyclic polarization tests, which used Gamry PCI4–750 potentiostats (Gamry Instruments, Willow Grove, PA). Cyclic potentiodynamic polarization scans began 20 mV below (negative to) open-circuit potential, and specimens were anodically polarized in the positive direction at a scan rate of 0.6 V/h until a current-limiting reversal criteria was reached. Current reversal occurred at 1 mA/cm². Reference electrodes were seawater-immersed saturated calomel electrode (SCE) and all potentials reported are in reference to the SCE electrode. Counter electrodes were platinum.
3. Carburized 17-7 PH Stainless steel

3.1 General characterization of austenite in carburized 17-7 PH stainless steel

Fig. 3.1 (a) is a typical cross-sectional metallographic image of non-treated 17-7 PH stainless steel [45]. Stringer-featured grains are residual delta ferrite grains, which are formed during alloy solidification and preferentially etched during etching. XEDS quantitative analysis was performed on one of the stringer grain (areas 1) in order to compare with that of the matrix (areas 2) and results are summarized in Table 3.1. The stringer grains are higher in Cr and lower in Ni concentrations than those of the matrix, which demonstrates that the stringers are residual delta ferrite grains. During the alloy solidification, austenite precipitated out of the delta ferrite matrix. Since Cr is a ferrite-stabilizer and Ni is an austenite-stabilizer, element partitions between ferrite and austenite, resulting in Cr-enriched ferrite and Ni-enriched austenite. At last, delta ferrite is stabilized by high Cr content and remains in the alloy microstructure. The volume fraction of delta ferrite was estimated as $\approx 5\%$ based on the area fraction of the stringer features from SEM images like Fig. 3.1 (a).

Fig. 3.1 (b) is a typical cross-sectional metallographic image of carburized 17-7 PH stainless steel. An etch-resistant layer was observed at free surface, showing a hardened case with a thickness of $\approx 18\ \mu\text{m}$. The needle features extend from the free surface are due to the formation of paraequilibrium carbides. The hardness was improved by a factor of 3 on the free surface (not shown here).
Figure 3.1 SEM images of (a) an etched cross section of a non-treated 17-7 PH stainless steel with two areas analyzed with XEDS and (b) cross section of carburized 17-7 PH stainless steel.

Table 3.1 The compositions of different regions obtained by XEDS on the non-treated 17-7 PH stainless steel

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area 1</td>
<td>22</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>bal.</td>
</tr>
<tr>
<td>Area 2</td>
<td>17</td>
<td>7</td>
<td>2</td>
<td>1</td>
<td>0.6</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Two AES line scans were acquired from a cross section of carburized 17-7 PH stainless steel, as shown in Fig. 3.2 (a). Line 1 encountered three delta ferrite grains at different depths in the case, and line 2 came across austenite grains only. The carbon profiles extended $\approx 17 \mu m$ into the sample, agreeing with previous metallographic image. The delta ferrite grains (at the 6 and 10 $\mu m$ markers) near the interface between the case and the bulk material have lower carbon concentrations than those of their neighboring austenite grains. Especially, the grain at 10 $\mu m$ marker has a minimum carbon...
concentration as predicted by CALPHAD modeling. However, delta ferrite grain close to the free surface possesses an astonishingly high carbon concentration (18 at.%) and it is even higher than that of its neighboring austenite grain (at the 2 μm marker). This surprising behavior of ferrite grains in the interstitially-hardened case will be discussed in details in the following section. Line 2, which does not encounter any delta ferrite grain, shows a smooth concave carbon profile similar to the one observed in carburized austenitic 316L stainless steel, attributed to a strong carbon-concentration dependent diffusion process [19]. The steady increase of Fe concentration on the profiles is artificial, which is due to the composition normalization of all elements including interstitial carbon.

Hägg carbides were identified in the expanded austenite by XRD and TEM diffraction study and a carburization-induced isothermal martensite-to-austenite phase transformation was also observed as well [45]. A typical interface between the case and the bulk material is shown in Fig. 3.3 [45], i. e. equiaxed austenite grains in the case and lath martensite in the bulk material. Delta ferrite grains in the microstructure showed an unusual uniform, so-called “featureless”, contrast under TEM.
Figure 3.2 (a) AES line scan acquired on the carburized 17-7 PH stainless steel and the corresponding composition profiles along line 1 (b) and line 2 (c). The arrows indicate ferrite grains.
In order to verify this martensite-to-austenite phase transformation from thermodynamic perspective, a simple calculation based on CALPHAD model was carried out, aiming at obtaining the austenite start temperature ($A_s$) for 17-7 PH stainless steel. Only the major elements, like Fe, Cr, and Ni, were considered in the calculation. Since this phase transformation is carbon concentration-induced, the criterion to trigger the transformation is the equalization of the Gibbs free energies of the martensite and the austenite ($G_C^\gamma = G_C^\alpha$). The Gibbs free energy considered in the austenite includes the reference state, ideal mixing entropy and excess mixing enthalpy. Besides those terms considered in the austenite, a magnetic term was included in the ferrite calculation due to its ferromagnetism [81].
Four lines from different alloy compositions (Fe-C, Fe-17 wt.%Cr-C, Fe-7 wt.%Ni-C, and nominal composition of 17-7 PH stainless steel) were obtained as shown in Fig. 3.4. It is surprising that the addition of 17 wt.% Cr in the alloy can reduce the $A_s$ temperature, since Cr is a ferrite stabilizer. It is shown that the addition of 7 wt.% Ni is more effective in reducing the $A_s$ temperature, since it is a strong austenite stabilizer. In the quaternary Fe-Cr-Ni-C alloy, the $A_s$ temperature is the lowest. At the carburization temperature (653 K), the carbon content required to trigger the martensite-to-austenite phase transformation is less than 3 at.%. Even though this is relatively lower than that acquired by other alloy compositions, it is still larger than the experimental observation that a small carbon amount (< 1 at.%) is sufficient to induce the phase transformation. This discrepancy may arise from the other minor elements in the alloy, like Mn, which may be strong austenite stabilizer. This preliminary calculation result demonstrates that a small amount of carbon in the microstructure can significantly reduce the $A_s$ temperature and facilitate this martensite-to-austenite phase transformation.
Figure 3.4 Four Aₜ temperature lines calculated based on the pseudo compositions. From right to left are Fe-C binary, Fe-Cr-C and Fe-Ni-C ternary, and Fe-Cr-Ni-C quaternary alloys.

3.2 Carbon-supersaturated delta ferrite after low-temperature carburization

One TEM sample from plan view of as-carburized 17-7 PH stainless steels was prepared to reveal the microstructure of carburized ferrite grains. The ferrite grains display substantially different morphologies. Besides the featureless grains and non-carburized ferrite grains shown in the Fig. 3.3, ferrite grains with plates were observed in the lower ferrite grains near the interface, which are shown in Fig. 3.5 (b) and (c), respectively. Fig. 3.5 (d) shows a carburized ferrite grain with plates perpendicular to each other, which is similar to the ferrite grain on the right in Fig. 3.5 (b). In Fig. 3.5 (e), there is an almost fully-transformed featureless grain magnified from the lower part of the left ferrite stringer shown in Fig. 3.3. This supports a hypothesis that the plates initiated at PBs in the non-carburized ferrite grain at an early stage. Then with the nucleation of new needles, the first-formed plates grew laterally and expanded into the whole grain, forming the featureless grain observed near the free surface. As shown in Fig. 3.5 (c), even in a single grain, plates did not nucleate at the same time, but rather sequentially. It is tentatively proposed that the initiation of the plates is related to the stress induced by the concentration of interstitial carbon in the ferrite-neighboring austenite grains.
Figure 3.5 STEM images from carburized 17-7 PH stainless steel demonstrate the evolution of delta ferrite during carburization. (a) is an overview of plan-view sample, (b) and (c) are magnified ferrite grains located at deeper case regions with plate in them, (d) is a ferrite grain showing plates perpendicular to each other and (e) is a featureless-region-dominated former ferrite grain from Fig. 3.3.
3.2.1 Chemical analysis of carbon-supersaturated ferrite

Besides the carbon concentrations of carburized ferrite grains acquired by AES, as shown in Fig. 3.2, APT data was acquired to determine the carbon concentration and its distribution in the carburized ferrite grains.

In a 3D carbon atom map from a featureless grain shown in Fig. 3.6 (a), carbon appears homogeneously distributed in the volume, with a bulk carbon concentration ≈ 9 at.%, suggesting the absence of any carbide precipitates, in accordance with TEM diffraction observations to be shown later. However, this 9 at.% carbon concentration is much lower than the SAM data shown in Fig. 3.3. One possibility is that the ferrite grain analyzed by APT is in a different location, ≈ 5 µm from the free surface, compared with the specific ferrite grain measured by SAM containing 18 at.% carbon, and located ≈ 1.5 µm from the free surface; lower carbon contents can be certainly expected in grains located deeper in the material, although because of the marked concentration dependence of the carbon diffusivity [19], the carbon depth profiles are quite flat. A second possibility is that the measurement of carbon concentration by APT is low, due to an analytical artifact, which has been reported previously in APT carbon analyses of bainitic steels and different carbides [69, 80]. In any event, 9 at.% carbon in ferrite is a significant and totally unexpected carbon concentration for ferrite. The carbon nearest-neighbor distribution analysis (Fig. 3.6 (b)) confirms that the carbon distribution in the volume does not significantly deviate from a randomized distribution, indicating a homogeneous distribution of carbon atoms in the featureless grain.
Figure 3.6 (a) 3D carbon atom map reconstructed from a featureless ferrite grain, and (b) the carbon nearest neighbor distribution of APT data.

APT was also successfully acquired from a plate-containing ferrite grain. Fig. 3.7 shows 3D Ni and carbon atom maps of such a grain and its neighboring austenite grain. Fig. 3.7 clearly shows that both Ni and carbon partition between the two phases, being enriched in the austenite and depleted in the ferrite. A cylindrical ROI was drawn perpendicular to the austenite—ferrite PB and a concentration profile (Fig. 3.6 (c)) was obtained along the
cylindrical axis by averaging over atom fractions in slices of 0.1 nm thickness perpendicular to the axis of the cylinder. The concentration profiles show a similar result – both Ni and carbon are enriched in austenite. The carbon concentration, while being ≈ 8 at.% in austenite, is ≈ 4 at.% in the ferrite, which is orders of magnitude higher than the paraequilibrium prediction, indicating a notable increase of carbon solubility in the ferrite. In addition, there is no obvious carbon segregation at the PB, which is quite different from what has been observed at a similar PB after nitridation [82], where significant cellular precipitation occurred.

The plate-containing ferrite was separated from the whole volume and is shown in Fig. 3.8 (a); the higher concentration of carbon atoms in the plates can be clearly observed. The concentration profile across the plates obtained from another cylindrical ROI is shown in Fig. 3.8 (b). Only the carbon concentration varies between the plates, while all substitutional elements stay the same, clearly a result of paraequilibrium conditions existing during carburization. The carbon concentrations in the plates are lower than that of the featureless grains, and moreover, the carbon concentrations are different in each plate, indicating these plates most likely form sequentially, after which carbon diffusion to the plates allows plate thickening. Besides the high carbon concentration in the plates, the carbon concentration in the ferrite between the plates is also rather high (≈ 3 at.%), although lower than 4 at.% value shown in Fig. 3.7; both concentrations are well beyond the paraequilibrium prediction. In addition, NiAl-enriched clusters were identified within the volume with a Ni to Al ratio close to 1:1 (data to be shown in section 5.2). Similar analysis for NiAl clusters yielded the same result in the featureless grains.
Figure 3.7 3D Ni (a) and carbon (b) atom maps and (c) the concentration profile across the austenite–ferrite phase boundary from a cylindrical ROI shown in (b).
A plate-containing delta ferrite grain was investigated by XEDS. A STEM image (Fig. 3.9 (a)) shows plates (bright regions) in the ferrite grain and a corresponding BF image of the same grain in Fig. 3.9 (b) shows dark plates in the ferrite, indicating a diffraction contribution from the plates under these two imaging conditions. Figure 3.10 confirms that these two grains are ferrite grains, by revealing Cr enrichment and Ni depletion in the...
grains compared with those in neighboring austenite grains. XEDS quantification results summarized in Table 3.2 qualitatively show a higher carbon concentration in the plate (point 1) than that in matrix (point 2), in agreement with the atom-probe data presented earlier.

Figure 3.9 Delta ferrite near the case-core interface with plates in it. (a) STEM image and (b) BF image. XEDS was acquired from the two areas.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
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<td>31.8</td>
<td>1.5</td>
<td>0.9</td>
<td>16.5</td>
<td>2.4</td>
<td>46.9</td>
</tr>
<tr>
<td>Point 2</td>
<td>20.4</td>
<td>1.6</td>
<td>1.2</td>
<td>19.6</td>
<td>2.6</td>
<td>54.7</td>
</tr>
</tbody>
</table>

Table 3.2 XEDS results of different areas marked in Fig. 3.9 (a).
One TEM foil containing one carburized ferrite grain was prepared by Helios FIB milling and further cleaned by Nanomill for 20 min on each side. ESI elemental mapping and EELS line scan were carried out on the carburized ferrite grains.

An overview STEM image of the carburized ferrite grain is shown in Fig. 3.11. The needles in the grain are clearly revealed and shown under higher magnification in Fig. 3.12 (a). The high contrast image of the same region (Fig. 3.12 (b)) shows the sample is thin that can be imaged by 250 eV energy loss electrons. The corresponding ESI 3-window carbon mapping is shown in Fig. 3.12 (c), using a jump ratio function. It is surprising that the needles in the ferrite grain are carbon-poor compared with carbon-rich “matrix”, agreeing with the featureless-region-dominated grain observation in Fig. 3.5 (d). This supports the hypothesis that the carbon-enriched plates grew laterally and fulfilled the whole ferrite grain eventually during the carburization.
Figure 3.11 An overview of a carburized ferrite grain.

Figure 3.12 (a) BF image of carburized ferrite grain, (b) high contrast image acquired at 250 eV energy loss and (c) ESI carbon map of the same region as (a).

These carbon-poor plates were confirmed by EELS line scan. The positions of the line scan and drift control box are shown in Fig. 3.13 (a). The line was drawn across one plate with both ends in the neighboring “matrix”. One typical spectrum of carbon peak along the line scan is shown in the Fig. 3.13 (b) along with signal and background assignments of the carbon peak. The carbon counts along the line (Fig. 3.13 (c)) are consistent with
ESI carbon mapping that the carbon concentration in the plate is lower than that of its neighboring “matrix”.

Figure 3.13 (a) EELS line scan position, (b) typical carbon spectrum on the line scan, and (c) carbon counts along the line scan.
Electron energy-loss near-edge structure (ELNES) of carbon peak was acquired in order to compare the carbon valences in the plate and the matrix. The spectra were acquired from a plate and its neighboring “matrix”, respectively, as shown in Fig. 3.14 (a). The ELNES spectra (Fig. 3.14 (b) and (c)) show that the carbon valences in both regions are the same, i.e. the peak positions are the same, though the relative counts are different, indicating the carbon in the carbon-supersaturated ferrite is the same.

Figure 3.14 (a) positions of ELNES acquisition, (b) and (c) are spectra acquired near carbon edge from plate and “matrix”, respectively.
3.2.2 Structure of carbon-supersaturated ferrite

DPs were obtained from these carburized ferrite grains in order to identify their crystal structure. DPs acquired from featureless grains are shown in Fig. 3.15. All DPs conform to a BCC ferrite structure, with no sign of carbide formation and no appreciable tetragonality. The only DP showing a slight deviation from a standard BCC pattern is the pattern obtained from a <011>_BCC zone axis, displaying diffuse streaks along a [001]_BCC direction towards smaller reciprocal lattice spacing, indicating possible local lattice expansion, since [001]_BCC is the elastic soft direction of BCC-Fe [83]. The streaking along [001] ferrite direction has been observed in ion-nitrided ferritic (430 grade) and martensitic (410 grade) stainless steels [41], which was attributed to the formation of extremely small coherent nitride in the grain. However, APT data acquired from the featureless ferrite grain shows a uniform carbon distribution in the grain. Therefore, in the carburized ferrite grain, this streaking is probably due to local lattice expansion. The tetragonality estimated from the DPs was less than 5%. There is no diffraction evidence for the presence of NiAl in the DPs, but compositionally (the APT data), the clusters are still present.

An energy-filtered HRTEM image from a featureless ferrite grain along a <011>_BCC direction is shown in Fig. 3.16 (a), with a corresponding power spectrum in the inset, similar to the DP shown in Fig. 3.15 (d). A filtered inverse Fast Fourier Transform (FFT) image from the rectangle region in Fig. 3.16 (a) is shown in the Fig. 3.16 (b) and the inset is the correspondingly masked FFT. In Fig. 3.16 (b), there are at least three edge dislocations that can be identified within very small area. The dislocation density
estimated based on images like this is $10^{13}$/cm$^2$, which is above the dislocation density of a regular heavily cold-worked steel (dislocation density saturated at $10^{12}$/cm$^2$ [84]).

Figure 3.15 DPs acquired from featureless former ferrite grains, (a) to (d) are from bcc zone axes $<111>$, $<\bar{1}33>$, $<\bar{1}12>$ and $<011>$, respectively.

Besides the dislocations observed, severe local lattice fringe distortion was observed on (001)$_{BCC}$ planes, which probably gives rise to the diffuse streaks along [001]$_{BCC}$ in the DP shown in Fig. 3.15 (d). Lattice fringe spacing measured by a line drawn in Fig. 3.16 (b) is 0.203 nm, agreeing with ferrite (011) plane spacing, indicating no significant lattice expansion along $<011>_{BCC}$ direction in the featureless grains.
Figure 3.16 (a) HRTEM image of a featureless ferrite grain with the corresponding FFT in the inset, (b) is a filtered inverse FFT image from the rectangle region in (a), and (c) is the lattice fringe spacing along the line drawn in (b).
One complication of HRTEM images needed to be considered in this study is the spatial resolution of Tecnai F30, which is 0.19 nm (the information resolution is 0.14 nm). The ferrite lattice parameter is 0.2881 nm. The plane spacings of interest are \{011\}_BCC and \{002\}_BCC, which 0.204 and 0.144 nm, respectively. For plane (011)_BCC, the plane spacing is very close to the instrument point resolution. But for plane (002)_BCC, the plane spacing is beyond the point resolution limit -- actually close to information resolution limit. Therefore, the HRTEM image of the carburized featureless ferrite grain along \langle011\rangle_BCC zone axis is not directly interpretable in terms of projected atomistic structure. For the Tecnai F30, at “optimum” defocus, i. e. 1.2 * Scherzer defocus (- 58 nm*), the first contrast-reverse point of the transfer function is 5 nm\(^{-1}\) (calculated by Dr. Frank Ernst), and therefore while the plane spacings can be imaged, the imaging conditions will be sensitive to thickness, focus, etc. and the image may not be interpretable in terms of projected atom columns.

In order to observe one particular spatial frequency beyond the point resolution limit, a passband can be generated at that particular spatial frequency [85]. In this case, 0.204 and 0.144 nm are of interest. By changing the defocus value, the passband can be optimized for imaging the higher one of these two specific spatial frequency. This technique can be problematic, since contrast reversals are generated in low frequency regime, which could lead the image uninterpretable, particularly for non-periodic structural components -- i.e. defects such as dislocations -- in terms of projected atomistic structure.

* Calculated based on Eqns. 28.35 and 28.37 in Transmission Electron Microscopy [85], given the electron wave length of 0.00197 nm at 300 kV, and spherical aberration (Cₐ) of 1.2 mm for Tecnai F30.
Such passband imaging technique required a (nearly) flat phase-distortion function at the frequency, which can be estimated by setting its differentiating equation to be 0 [85]. For ferrite plane (002)_{BCC}, the defocus value of its optimum imaging is -224 nm. With the presence of such passband, the contrast from ferrite plane (002)_{BCC} can be observed in the HRTEM image. But the contrast in the image is uninterpretable, due to multiple contrast-reverse points in low spatial frequency regime. The image -- and in particular its non-periodic parts, i.e. defects -- may not be interpretable in terms of projected atomistic structure.

Moreover, the lattice fringes in the HRTEM is also sensitive to defocus value, i.e. the lattice fringes shift under different defocus values (true for slight misfit and local thickness fluctuations, which are expected in the TEM foil). Therefore, in order to confirm these “apparent” dislocations in the ferrite microstructure, a series of images should be recorded at different defocus settings. At last, Bragg filtering is also a problematic technique for HRTEM image processing. Artifacts can be introduced by the filtering, depending on the mask size and shape. Since these “apparent” edge dislocations observed in filtered image were all originated from heavily distorted regions in the original image, these “apparent” dislocations in the microstructure were dubious. Nevertheless, in this study, these “apparent” dislocations were considered as a plausible explanation to our observation.

The situation is more complicated in plate-containing ferrite grains. Major reflections in the DP are similar to those obtained from featureless grains, in agreement with a BCC
structure. Further, faint tails were also observed along a [001] BCC direction towards smaller reciprocal lattice spacings, which signals the appearance of the diffuse streaks observed in the featureless grain. This indicates that the larger lattice spacing is related to the formation of the featureless grain, which is probably due to the carbon-induced lattice distortion. However, extra reflections were observed in the <011> BCC zone axis, as shown in Fig. 3.17 (a). Because 17-7 is a PH stainless steel, the possibility of aging and conventional precipitate formation during carburization must be considered. Although the aging temperature for this alloy is above 773 K [2], the long time exposure during carburization could induce the formation of NiAl. A sample from the bulk material (deep in the material) was prepared, which experienced the carburization heat treatment without carbon species being available. The sample was tilted to the same <011> BCC zone axis, as shown in Fig. 3.17 (b). Similar extra spots were observed, indicating that the presence of the extra spots in Fig. 3.17 (a) is not due to the carburization but rather to aging and formation of precipitates during carburization. NiAl, as the precipitation hardening phase in this alloy, is the best candidate for these extra spots. Clusters of this composition were positively identified by APT, as mentioned previously. Extra reflections observed were also consistent with B2-structured NiAl as shown in Fig. 3.17 (c).
Figure 3.17 (a) is DP of a <011> bcc zone axis from a ferrite grain with plates, (b) is the same zone axis from a ferrite grain in bulk material, (c) is DP simulated from B2 structure along <011> zone axis, (d) and (e) are BF and DF images from plate-containing ferrite grain, respectively (spot used in DF is circled in (a)), (f) is the defocused DP from the same region and.
A BF TEM image from a plate-containing ferrite grain shows dark plates, while a DF TEM image from the extra reflection shows massive and uniform distribution of fine particles (possibly NiAl) within the matrix, but not in the plate regions. A defocused DP (Fig. 3.17 (f)) was obtained from the same region, showing that the plates grew parallel to a $[011]_{\text{BCC}}$ direction, but perpendicular to a $[001]_{\text{BCC}}$ direction.

A HRTEM image from a plate-containing ferrite along a $<011>_{\text{BCC}}$ direction is shown in the Fig. 3.18 (a), one featureless plate in between ferrite matrix. The power spectrum of the image is similar to the DP shown in Fig. 3.17 (a), with extra spots attributed to NiAl precipitates. An inverse FFT filtered image, from the interface between a plate and ferrite matrix (from the rectangle region in Fig. 3.18 (a)) is shown in Fig. 3.18 (b). Only the ferrite spots were used to form the filtered image, as shown in the inset of Fig. 3.18 (b). It clearly shows that the lattice of the carbon-poor region ferrite is almost dislocation-free, while edge dislocations (as encircled) appear at the interface and also can be observed within the carbon-rich region. Therefore, it is concluded that the enrichment of carbon both in the plates and the featureless grains is related with the formation of a massive dislocation network.
Figure 3.18 (a) A HRTEM image from a plate-containing ferrite grain with its corresponding FFT and (b) is an inverse FFT filtered image of (a), with BCC ferrite spots only as shown in the inset.
Convergent beam analysis was performed on the plate-containing ferrite grains in order to get local lattice information. The ferrite grain identified in Fig. 3.9 was tilted to a \( <315>_{\text{BCC}} \) zone axis and the corresponding energy-filtered CBED pattern is shown in Fig. 3.19 (a). The pattern was acquired from a carbon-poor region with 90 mm camera length (CL). The pattern clearly shows first-order Laue zone (FOLZ) ring and zero-order Laue zone (ZOLZ) kikuchi line (KL) bands and high-order Laue zone (HOLZ) deficient lines. A simulated \( <315>_{\text{BCC}} \) pattern is consistent with the experimental observation regarding to the FOLZ ring, KL band and disk intensity. A more detailed analysis was summarized in Table 3.3. All ZOLZ KL band widths are significantly expanded, implying local lattice expansion. However, the simulated HOLZ deficient lines cannot match with experimental observation, which is probably because of local strain in the grain. One more possible reason for the discrepancy between experimental observation and simulation is the instrumental artifacts, because Libra has not been calibrated for the CL used to acquire the pattern and may introduce the distortion.
Table 3.3 Summary of experimental and simulation results of a zone axis $<315>_{BCC}$

<table>
<thead>
<tr>
<th>Kikuchi band</th>
<th>Angle with respect to $(\bar{1} \bar{2} 1)$</th>
<th>Theoretical angle (°)</th>
<th>Band width (nm)</th>
<th>Theoretical width* (nm)</th>
<th>Expansion* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\bar{1} \bar{2} 1)$</td>
<td>--</td>
<td>--</td>
<td>1</td>
<td>1</td>
<td>6.9</td>
</tr>
<tr>
<td>$(2 \bar{1} \bar{1})$</td>
<td>80.8</td>
<td>80.4</td>
<td>1.02</td>
<td>1</td>
<td>9.2</td>
</tr>
<tr>
<td>$(1 \bar{3} 0)$</td>
<td>49.9</td>
<td>49.8</td>
<td>1.27</td>
<td>1.29</td>
<td>9.0</td>
</tr>
<tr>
<td>$(\bar{3} \bar{1} 2)$</td>
<td>40.6</td>
<td>40.2</td>
<td>1.52</td>
<td>1.53</td>
<td>7.7</td>
</tr>
</tbody>
</table>

* Calculated based on body-centered cubic original ferrite $a=0.2881$ nm. Band width of $(\bar{1} \bar{2} 1)$ calculated based on CBED pattern is 0.1261 nm.
** FOLZ ring radius is $56 \text{ nm}^{-1} = 0.01786$ nm.

In order to reveal the detailed HOLZ deficient line structure in the center disk, CBED patterns were acquired with CLs of 720 and 1440 mm, respectively, as shown in Fig. 3.20 (a) and (b). The dynamical fringes in the center disk were used to identify the local foil thickness. By comparing the dynamical fringes to simulations, the local foil thickness can be identified as 108 nm. In Fig. 3.20 (b), the HOLZ deficient lines are revealed and the
line splitting can be clearly observed. The HOLZ deficient lines are known to be very sensitive to local lattice parameter [85]. The splitting of the HOLZ deficient lines indicates local strain in the grain [86], which is probably due to the residual stress introduced by low-temperature carburization. It has been reported that the presence of dislocation in the microstructure could also be due to the presence of dislocations near the probe [87-89]. The surface relaxation at foil surface can introduce HOLZ line splitting [86, 90, 91]. A potential good simulation match for the center disk (Fig. 3.20 (d)) is from a slight BCT structure with a lattice parameter of $a = 0.2849$ nm and $c = 0.2827$ nm, suggesting a modest lattice compression. This is consistent with our previous speculation that the ferrite became tetragonal after uptake of carbon before the plate formation [82].
Figure 3.20 CEBD patterns acquired with 720 mm CL (a) and 1440 mm (b), (c) simulated fringes with the thickness of 108 nm, and (d) simulation with a lattice parameter of $a=0.2849$ nm and $c=0.2827$ nm with a BCT structure.

A similar pattern was acquired from a carbon-rich plate in the ferrite grain (Fig. 3.12), displaying significant differences. All features in the disks were smeared out possibly due to the strain induced by high carbon concentration. Nevertheless, the ZOLZ KL bands and FOLZ ring were still visible, despite of severe splitting, indicating a severe lattice distortion induced by carburization. By comparing with Fig. 3.19, positions of visible
HOLZ deficient lines are the same, indicating the similarity of the lattices of the two regions. But the splitting of the FOLZ rings indicating the presence of the severe lattice distortion induced by the high carbon concentration. Since it gives the lattice spacing along the viewing direction, the ring splitting implies the spacing variation along the view direction, which can be attributed to the local strain in the grain. By comparing the two CBED patterns from two regions, the ring splitting of high-carbon region is clearly due to the lattice distort, but beyond the effect of surface relaxation.

![Figure 3.21 CBED pattern from carbon-rich region.](image)

CBED patterns were also acquired from another zone axis, \(<123>_{\text{BCC}}\), as shown in Fig. 3.22. The general features of the patterns from carbon-poor region are similar to that acquired from the \(<315>_{\text{BCC}}\) zone axis (Fig. 3.19 and 3.20), e.g. ZOLZ KL bands, FOLZ ring and HOLZ deficient lines. The splitting of the HOLZ deficient lines can be clearly observed as well. As summarized in Table 3.4, there is still significant local lattice expansion measured from the ZOLZ KL band width.
Figure 3.22 CBED pattern taken from a \(<123>_{\text{BCC}}\) direction, with 90 (a), 720 (b) and 1440 (c) mm CL, and (d) the simulation of the same zone axis.

<table>
<thead>
<tr>
<th>Kikuchi band</th>
<th>Angle with respect to ((2\bar{1}1))</th>
<th>Theoretical angle</th>
<th>Width</th>
<th>Theoretical width (nm)</th>
<th>Expansion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((211))</td>
<td>--</td>
<td>0.1253</td>
<td>0.118</td>
<td></td>
<td>6.2</td>
</tr>
<tr>
<td>((22\bar{2}))</td>
<td>65</td>
<td>61.9</td>
<td>0.0868</td>
<td>0.0832</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Table 3.3 Zone axis \(<123>\) summary of experimental and theoretical simulation results
To sum up, the carbon-supersaturated ferrite grains possess a significant amount of carbon, well exceeding its equilibrium solubility and showing uniform contrast under TEM, which had been confirmed by both AES and APT. However, structure analysis indicated neither carbide formation nor significant tetragonality, but BCC structure of the ferrite grains. HRTEM images revealed an extremely high dislocation density in the featureless ferrite and plates in plate-containing ferrite, implying the carbon-supersaturation in the ferrite is associated with the presence of the high dislocation density. CBED analysis shows a localized strain in the carburized ferrite grain.

### 3.2.3 Cyclic Potentiodynamic Polarization

It has been reported that the low-temperature carburization process can significantly improve the localized corrosion resistance of 316L stainless steel in ambient-temperature seawater compared to nontreated materials [92-94]. Therefore, it is of interest to investigate the effect of low-temperature carburization on the corrosion resistance of 17-7 PH stainless steel.

Two cyclic polarization runs were carried out, as shown in Fig. 3.23. The abscissa of the plot is the current density (dependent) and vertical axis is electric potential difference (independent) measured versus saturated calomel electrode. The open-circuit potentials of...
the nontreated and carburized samples are almost the same. However, the pitting potentials of these two are significantly different. The passivity of nontreated materials breaks down at a potential of above 320 mV, which is lower than that of 316L stainless steel ($\approx 450$ mV [92]). The passivity breakdown potential of carburized 17-7 PH stainless steel is $\approx 1000$ mV, which is probably not due to pitting but rather the transpassive dissolution of the solution, indicating a significant increase of pitting corrosion resistance of carburized 17-7 PH stainless steel.

Figure 3.23 Anodic potentiodynamic cyclic polarization curves of nontreated (blue) and low-temperature carburized (red) 17-7 PH stainless steels.
4. Nitrided 17-7 PH stainless steel

4.1 Macroscopic view of nitridation on 17-7 PH stainless steel

In the present study, different nitriding parameters were applied on the 17-7 PH stainless steel, i.e. temperatures and nitriding activities. Three different temperatures (623, 653, and 713 K) and three nitriding activities (3000, 7400, and 144000) were employed for nitridations, in order to investigate their effects on the microstructure of the 17-7 PH stainless steel.

XRD patterns from all nitrided samples were summarized in Fig. 4.1. Peaks from bulk material are still visible in samples treated at 623 K and 653 K, due to shallow cases at the surface. All peaks belonging to austenite show a significant peak shift to lower diffraction angles, indicating lattice expansions induced by low-temperature nitridation. Accompanying with lattice expansion, peak broadening was also observed in expanded austenite. The full-width-at-half-maximum (FWHM) was much larger in expanded austenite than that of non-treated one. For example, the FWHM of austenite peak (111) in non-treated sample is about 0.2 °, but it is about 0.6 ° for the same peak of expanded austenite after nitridation at 713 K with a nitriding activity of 144000. This can be ascribed to two reasons. One is the defects induced by nitridation in the austenite, which leads to low intensity of high angle peaks. The other one is the nitrogen concentration gradient within the penetration depth of X-ray, which also gives rise to asymmetricity of the peaks. This can be particularly true for the samples with shallow cases (treated at 623 K and 653 K), in which X-ray penetrates from the high-concentration-nitrogen surface...
region to non-treated bulk material. However, all peaks belong to BCC structure disappeared after low-temperature nitridation, indicating a nitridation-induced martensite-to-austenite phase transformation, similar to the observation of carburization-induced martensite-to-austenite phase transformation previously mentioned [45]. Detailed studies of this phase transformation will be presented in next section.

Lattice parameters of all samples were estimated by Neilson-Riley theory. As shown in Fig. 4.2, the lattice parameters calculated based on each plane spacing vary significantly after nitridation, compared with non-treated one. This was postulated to be due to a
ferromagnetism induced by nitridation in FCC austenite [30], i. e. larger lattice variations observed in magnetic expanded austenite. However, possibility of an anomalous anisotropy of nitrided expanded austenite cannot be ruled out that (100)_{FCC} is the elastic soft direction for austenite. Due to the large variation of plane spacings, the error of calculated lattice parameters is large for expanded austenite.

The lattice parameters of the expanded austenite of all nitrided samples are summarized in Table 4.1. Generally, higher temperatures and higher nitriding activities give rise to larger lattice expansion. The lattice expansion can be as high as 8 %, which is comparable to nitrided 316L [20] and much larger than carburized 316L [4] and 17-7 PH stainless steels [45]. Residual stresses in the nitrided case were not measured, which is positively correlated with nitrogen concentration in the case. The residual stresses are on the order of several GPa, generally higher than that achieved after carburization. Except at high-nitriding-activity treatments, most residual stresses were released due to extensive crack formation on the free surface.
Table 4.1 Processing parameters of nitridation on 17-7 PH stainless steel

<table>
<thead>
<tr>
<th>Temperature (K) / Activity</th>
<th>623</th>
<th>653</th>
<th>713</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>--</td>
<td>0.376 nm (4.2 %)</td>
<td>--</td>
</tr>
<tr>
<td>7400</td>
<td>--</td>
<td>0.377 nm (4.69 %)</td>
<td>0.388 nm (7.6 %)</td>
</tr>
<tr>
<td>144000</td>
<td>0.384 nm (6.5 %)</td>
<td>--</td>
<td>0.390 nm (8.3 %)</td>
</tr>
</tbody>
</table>

* a = 0.3600 nm for non-treated austenite.

In the XRD patterns, in addition to peaks belong to austenite after nitridation, there is one peak at 45 °, which is very close to the position of ferrite (110). It cannot be a BCC peak, because all BCC peaks disappeared due to the martensite-to-austenite phase transformation. This peak becomes stronger as the nitriding activity increases, which is most clear in the two treatments at 713 K. In the sample treated with 7400 nitriding activity, this peak is practically a “hump”, but it becomes much sharper in the sample...
treated with 144000 nitriding activity. It is also very sharp in the sample treated at 623 K and 144000 activity. Undesired surface nitride (ε-M$_2$N, mainly Fe$_2$N) layer was observed in the nitried 316L austenitic stainless steel [20], which could possibly explain the presence of the extra peak.

A STEM image from a surface particle after nitridation at 653 K with 3000 activity is shown in Fig. 4.3 (a), clearly showing that the particles are porous. Chemical information was acquired from these particles by XEDS. One typical energy dispersive spectrum is shown in Fig. 4.3 (b). Quantification results (Table 4.2) show that these particles are basically iron oxide, almost without Cr, Ni and nitrogen, which is similar to ε-M$_2$N observation in nitried 316L austenitic stainless steel. Some residual Cl was also detected in the oxide, possibly inherited from HCl in the activation steps reacted with NH$_3$ during nitridation. Based on the Fe to oxygen ratio, the oxide must be highly Fe-deficient. DP acquired from it (not shown here) is a complex ring pattern, suggesting the surface particles are polycrystal. Possible source of oxygen during the nitridation is the contamination from the gases used in nitridation, like NH$_3$ and H$_2$. 
Figure 4.3 (a) STEM image of surface oxide particle after nitrided at 653 K with 3000 activity and (b) is the XEDS spectrum of point 2.

Table 4.2 XEDS quantification results of the two point shown in Fig. 4.3 (a)

<table>
<thead>
<tr>
<th>At. %</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>Cl</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>68.4</td>
<td>1.0</td>
<td>0.6</td>
<td>--</td>
<td>1.7</td>
<td>1.6</td>
<td>25.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Point 2</td>
<td>69.6</td>
<td>--</td>
<td>0.7</td>
<td>1.1</td>
<td>1.7</td>
<td>1.5</td>
<td>24.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Metallographic images from all nitriding treatments are shown in Fig. 4.4. All images were acquired by confocal microscopy, except the image of sample nitrided at 653 K with 3000 nitriding activity was recorded by SEM. In order to expose thin nitrided layers better, samples treated at 623 K with 144000 activity and 653 K with 7400 activity were
imaged with Nomarski interference contrast (also known as differential interference contrast) by confocal microscope, which shows interface best.

Figure 4.4 Cross-sectional images of all nitrided 17-7 PH stainless steel, (a) 623 K with 144000 activity, (b) and (c) 653 K with 3800 and 7400 activities, (d) and (e) 713 K with 7400 and 144000 activities.
The reason that case can be revealed by etching is that the case is more etching-resistant than the bulk non-treated material. The case depth of each treatment was summarized in Table 4.3. The nitrided case becomes thicker at higher temperature and nitriding activity, in agreement with what has been studied previously [20] in nitrided 316L austenitic stainless steel, indicating that the austenite in 17-7 PH stainless steel behaves similar to that in 316L. When samples were treated at low temperatures, like 623 and 653 K, cases are thin (< 5 µm) but intact. At higher nitriding temperature (713 K), crack formation was observed in the case in order to release the strain energy, which is correlated to the lattice expansion due to the nitrogen uptake of austenite.

<table>
<thead>
<tr>
<th>Temperature (K) / Activity</th>
<th>623</th>
<th>653</th>
<th>713</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>--</td>
<td>2 µm</td>
<td>--</td>
</tr>
<tr>
<td>7400</td>
<td>--</td>
<td>3.5 µm</td>
<td>11 µm</td>
</tr>
<tr>
<td>144000</td>
<td>1.5 µm</td>
<td>--</td>
<td>12-15 µm</td>
</tr>
</tbody>
</table>

Ferrite stringers in the bulk material, running parallel to the free surface is the first phase revealed by the etchant, as observed in Fig. 4.4. However, it is interesting to see that the ferrite grains in the case stand out, as shown in Fig. 4.4 (b). This is more clearly demonstrated in Fig. 4.5 that stringers of ferrite grains protrude out of the case, suggesting that it is more etching-resistant than its neighboring austenite. XEDS analysis (Fig. 4.5 (b)) shows that the ferrite grains possess significant amount of nitrogen. If the etching resistance of a phase is positively correlated with the interstitial (carbon or
nitrogen) concentration in it, the greatly improved etching resistance of ferrite can be reasonably ascribed to the high nitrogen concentration.

Microhardness with 50 gf was measured from plan view of all nitrided samples as summarized in Fig. 4.6. The non-treated EP sample yields lowest hardness, ≈ 350. The highest hardness value also comes with the largest variation, as obtained from the treatment of 713 K with 7400 nitriding activity, ≈ 1200. The surface hardness was effectively increased at least by a factor of 3 compared with bulk material. It is even higher than the material treated at a higher activity (144000) of the same temperature.
One possible explanation is the crack formation on the sample surface that cracks form more extensively on the sample surface after the treatment of 713 K with 144000 activity compared to that of 7400 activity of the same temperature. The low surface hardness values of the three samples treated at relatively low temperatures (623 and 653 K) are due to the thin case that the indenter penetrates the case and thus the measured hardness value is an average of the case and the bulk material.

![Figure 4.6](image)

Figure 4.6 Summary of microhardness values of non-treated and all nitrided samples from plan view with 50 gf load.

Nitrogen concentration profile was acquired from a finely-polished cross section of sample nitrided at 713 K with 7400 nitriding activity. The nitrogen profile agrees with that obtained from a nitrided austenitic stainless steel, like 316L [20]. There is a plateau in the case region and a sharp interface between the case and the bulk material. The nitrogen concentration in the case region is ≈ 18 at.%, comparable to the surface concentration obtained in 316L austenitic stainless steel nitrided at the same condition [20]. However, it is very interesting that the case thickness obtained in 17-7 PH stainless
steel is \( \approx 13 \) \( \mu \text{m} \) after nitriding at 713 K with 144000 activity, defined by both AES nitrogen profile and metallography, which is much thicker than that obtained in 316L austenitic stainless steel (\( \approx 9 \mu \text{m} \)) after the same nitridation. One possible explanation is the presence of martensite in as-received material, as revealed by XRD. It is well-known that the interstitial (carbon and nitrogen) diffusion in BCC ferrite or BCT martensite is orders of magnitude higher than that in FCC austenite [3]. Therefore, before reaching the critical interstitial concentration in the martensite required by martensite-to-austenite phase transformation, interstitial atoms can diffuse in a BCC/BCT structure rather than FCC structure, leading to a case in 17-7 PH stainless steel much deeper compared to a fully austenitic stainless steel. The diffusion occurs after the martensite-to-austenite phase transformation is similar to that in 316L alloy, but gets enhanced initially due to a concentration-dependent diffusion by carbon inherited from martensite.

Due to a different sputtering rate between ferrite and austenite, the ferrite grains can be differentiated from austenite based on its stringer morphology. As can be seen in Fig. 4.7 (a), the AES line scan goes through two delta ferrite grains near the interface region, which can also be confirmed by Cr and Ni concentration profiles where Cr is enriched and correspondingly Ni is depleted. The most interesting observation in the case is that the nitrogen concentrations in the ferrite grains are \( \approx 20 \) at.%. The high nitrogen concentration may be due to the nitride formation or interstitial nitrogen segregation to defects, similar to carburized ferrite grains. Detailed microstructure characterization will be provided in the following sections.
4.2 Nitridation-induced martensite-to-austenite phase transformation

Similar to the carburization-induced martensite-to-austenite phase transformation, there is an isothermal nitridation-induced martensite-to-austenite phase transformation in 17-7 PH stainless steel.
XRD patterns in Fig. 4.1 shows that all peaks related with BCC/BCT structure disappeared after nitridation, indicating the occurrence of such phase transformation in all nitriding treatments.

In addition, MFM was used in order to confirm this phase transformation, because that austenite is paramagnetic but both ferrite and martensite are ferromagnetic. Therefore, a contrast-free layer would be expected if this phase transformation occurred. A MFM image acquired from a finely-polished cross-sectioned 17-7 PH stainless steel nitrided at 713 K with 7400 activity is shown in Fig. 4.8. With the free surface on the left, the bulk material on the right is dominated by magnetic domains, which is due to the formation of strain-induced martensite during polishing. It is clear that there is a contrast-free band next to the bulk material, suggesting the existence of a paramagnetic layer in the nitrided layer. This paramagnetic layer becomes ferromagnetic as it approaches the free surface. This has been reported as low-temperature nitriding-induced ferromagnetism in austenitic stainless steel after reaching a critical nitrogen concentration of 14 at.% and a critical lattice expansion of 5 % [30, 31]. On the other hand, phase contrast in the nitried ferrite grains is very strong, compared with a rather low magnetization of expanded austenite and also much stronger than that of the martensite in the bulk material, implying possible formation of magnetic nitride, as CrN [95].
This martensite-to-austenite phase transformation can also be verified by its microstructure. The microstructure of heat-treated 17-7 PH stainless steel is dominated by lath martensite, as shown in Fig. 4.9 (a). In Fig. 4.9 (b), nitrided microstructure is dominated by equiaxed austenite grains and stringers of ferrite grains. With free surface on the right, there are laths deeper in the sample, indicating that the lath martensite in the bulk material has not transformed to austenite. The mechanism of this martensite-to-austenite phase transformation has been discussed elsewhere [38]. The thermodynamic principle behind it is that both carbon and nitrogen are strong austenite stabilizers. With addition of these two interstitials, the eutectoid temperature of the alloy is effectively reduced to the temperature lower than the carburizing or nitriding temperature, which enables this phase transformation. However, this phase transformation has to compete with kinetics. If the martensite transforms to carbide or nitride instead of austenite due to
kinetic reasons, this phase transform cannot occur, even though the eutectoid temperature is lower than the treating temperature, as observed in 2205 [37] and 13-8 [36].

Figure 4.9 STEM images from a finely-polished cross-sectioned piece of 17-7 PH stainless steel nitriding at 713 K with 7400 activity, (a) heat-treated bulk material and (b) interface between nitrided layer and bulk material.
4.3 Expanded austenite in nitried 17-7 PH stainless steel

Though there is no obvious precipitate in the expanded austenite in the XRD patterns (Fig. 4.1), under TEM, extra reflections were observed in the DPs of austenite after nitriding at 653 K with 3000 activity (also in some of other nitriding treatments, e. g. 653 K with 7400 activity).

A clear DP along an austenite zone axis $<001>_{\text{FCC}}$ is shown in Fig. 4.10. Lattice parameter of the expanded austenite was estimated based on the spacings of (002) and (220) planes, yielding 0.380 and 0.382 nm, respectively, which is about 1 % higher than the XRD measurement (4.2 %).

![Figure 4.10 DP from a surface expanded austenite in a $<001>_{\text{FCC}}$ zone axis.](image-url)
However, in the other zone axes obtained from the same grain, extra reflections appear between some original FCC matrix reflections. The matrix reflections in Fig. 4.11 were identified as a $<\overline{1}14>_{\text{FCC}}$ zone axis. In Fig. 4.11 (a), a $\frac{1}{3}g_{(511)}$ and a $\frac{1}{3}g_{(442)}$ vectors are strongly excited, while $\frac{1}{2}g_{(511)}$ and $\frac{1}{2}g_{(311)}$ vectors are faint. In Fig. 4.11 (b), the relative excitation is reversed between extra reflections. The $\frac{1}{3}g_{(511)}$ vector can be rationalized as triple $g_{(111)}$ vector in original FCC structure. Likewise, the $\frac{1}{3}g_{(442)}$ vector can be rationalized as triple $g_{(200)}$ vector. Therefore, this is a twinning mechanism in austenite, that a $<011>_{\text{FCC}}$ zone axis overlaps with a $<\overline{1}14>_{\text{FCC}}$ zone axis and the $g_{(511)}$ vector overlaps with triple $g_{(111)}$ vector. The twinning behavior of austenite has been studied in details [96, 97].

However, $\frac{1}{2}g_{(511)}$ and $\frac{1}{2}g_{(311)}$ vectors are curious, which are strongly excited in Fig. 4.12 (b). Half of these all-odd-indexed $g$ vectors suggest a possible superlattice structure in the nitrided austenite. This can arise from the ordering of interstitial nitrogen atoms in the FCC expanded austenite, making eight original FCC unit cell into one new unit cell with four extra interstitial nitrogen atoms sitting on the octahedral sites at body centers of original FCC unit cell on a (011) plane of the new unit cell. These half of (511) and (311) $g$ vectors can be explained, which belongs to the (511) and (311) planes of the new unit cell. This ordering can occur as a precursor of nitride formation, if there is any. The atom ratio of Fe to nitrogen is 32:4. However, this nitrogen-ordered structure (maintaining FCC structure) is different from a BCT $\text{Fe}_{16}\text{N}_2$ structure, which can be treated as a distorted $\gamma'$-$\text{Fe}_4\text{N}$ structure (simple cubic) with alternate nitrogen atom missing [98].
Figure 4.11 Extra reflections in $\langle 1\bar{1}4 \rangle_{\text{FCC}}$ zone axis. (a) $\frac{1}{3} g_{(511)}$ and $\frac{1}{3} g_{(442)}$ vectors are strongly excited and (b) $\frac{1}{2} g_{(511)}$ and $\frac{1}{2} g_{(311)}$ are excited.

Austenite twinning was observed in other zone axes as well. Fig. 4.12 (a) shows that a $\langle 2\bar{1}5 \rangle_{\text{FCC}}$ zone axis overlaps with a $\langle 110 \rangle_{\text{FCC}}$ zone axis. The simulation is consistent with the DPs from the microtwin. A DF image acquired from a twin reflection is shown in Fig. 4.12 (c). The microtwins are parallel thick plates ($\approx 100$ nm) in the austenite matrix.
Figure 4.12 (a) DP acquired from a microtwin in austenite matrix, (b) simulated DP for microtwin, a DP from a $<215>_{\text{FCC}}$ zone axis overlapped with a DP from a $<110>_{\text{FCC}}$ zone axis, and (c) DF image from a (111) reflection in twinning pattern, as encircled in the inset DP.

On a $<013>_{\text{FCC}}$ zone axis (Fig. 4.13), where two different $g_{(311)}$ vectors are present ($g_{(13\bar{1})}$ and $g_{(13\bar{1})}$), extra reflections at half reciprocal spacing were observed with different excitations. DF image from one of the strong extra reflections (encircled in the inset DP) showed a band structure in FCC matrix. The band structure was observed from the same
grain under STEM as well, as shown in Fig. 4.13 (c), implying the presence of such nitrogen-ordered domain structure in the austenite.

Figure 4.13 (a) DP of a superlattice FCC structure in a zone axis <013>, (b) DF image from extra reflection at $\frac{1}{2} g_{(\overline{1}3\overline{1})}$ and (c) STEM image of the same grain.

After nitriding at 713 K with 7400 nitriding activity, needles in the austenite grain were observed as shown in Fig. 4.14. The DP recorded from this area closely matches with
pattern from a $<112>_{\text{FCC}}$ zone axis, but with extra reflections at $\frac{1}{2}g_{(311)}$. In a BF image, the austenite matrix is bright and the needles are dark, indicating that only needles were tilted in a zone axis. Both DF images from a matrix reflection and an inner sharp reflection (as encircled in the inset DPs of both DF images) showed needles in the matrix, being consistent with previous observations of expanded austenite with superlattice reflections (Fig. 4.13 (b)). But the needle structure revealed by DF images is more well-defined structure compared with Fig. 4.13 (b), which is probably due to a different nitriding condition, i.e. higher nitriding temperature. It is worth noting that there are diffuse reflections in the outer region of the DP, which are probably from the austenite matrix.
4.4 Delta ferrite nitrided at high temperature

Delta ferrite grains respond differently at different nitriding temperatures. At relatively high temperature, delta ferrite grains transformed to featureless grains as what had been observed in carburized ferrite. However, plate-containing ferrite grains were observed only in samples treated at low temperature.
A plan-view TEM foil was prepared from sample nitrided at 713 K with 7400 activity. The overview of this foil is shown in Fig. 4.15 (a) and the ROI is the rectangular region, where several delta ferrite grains are enclosed. Magnified ROI (Fig. 4.15 (b)) shows four ferrite grains, all showing uniform contrast. The encircled grain is studied by DPs in details. Straight lines perpendicular to the foil surface are due to curtaining effect generated during the FIB sample preparation.
Figure 4.15 (a) Overview of a plan view TEM sample nitrided at 713 K with 7400 activity, and (b) magnified rectangular region in (a).

Fig. 4.16 shows a DP along a ferrite zone axis $<011>_{\text{BCC}}$ obtained from the encircled ferrite grain (Fig. 4.15 (b)). Compared with DP acquired from carburized featureless delta ferrite grain of the same zone axis, extra reflections were observed at the end of diffuse
streak tails after low temperature nitridation, indicating possible nitride formation in the nitrided ferrite grain. DF images shown in Fig. 4.17 indicate that there is no difference between DF images acquired from different reflections, other than uniform contrast. DF images acquired from a $<133>_{\text{BCC}}$ zone axis show similar contrast (Fig. 4.18). However, in the $<133>_{\text{BCC}}$ zone axis, extra reflections were observed in half reciprocal spacing of the possible nitride reflections, indicating a possible superlattice structure in the nitride. Nonetheless, all DF images display uniform contrast in the grain, i.e. no obvious contrast in the grain after nitridation.

Figure 4.16 DP acquired from the encircled ferrite grain showing a $<011>_{\text{BCC}}$ pattern with extra reflections.
Figure 4.17 (a) BF image of the ferrite grain of interest, (b) and (c) DF images from two BCC matrix reflections, and (d) and (e) DF images from two extra reflections. Reflections used to form DF images are encircled in the inset DPs.
Figure 4.18 (a) DP from the same delta ferrite grain tilted to a $<133>_{\text{BCC}}$ zone axis. (b) BF image, and (c) to (e) are DF images from matrix reflection, reflection of nitride and extra reflection at half reciprocal spacing of the nitride reflection, respectively, as encircled in the inset DPs.

A series of DPs recorded within one delta ferrite grain are shown in Fig. 4.19. DPs were acquired from the regions within a grain where is closest to the free surface (b) and farthest from it (d). This set of DPs was acquired due to the fact that a nitrogen concentration profile can be very steep at its tail so the corresponding lattice parameter can vary significantly within one grain. However, the measurements from this particular grain suggest that the lattice parameter of this grain is uniform, demonstrating that a uniform lattice expansion was achieved within one ferrite grain in the plateau region of nitrogen concentration profile.
Figure 4.19 (a) STEM image shows where all four DPs were acquired, and (b) to (e) are the corresponding DPs acquired from a $<011>_{\text{BCC}}$ zone axis.

DPs from other major BCC zone axes $<111>_{\text{BCC}}$ and $<001>_{\text{BCC}}$ were also obtained, as shown in Fig. 4.20. The observation is that matrix reflections are much more diffused after nitridation, implying the crystallinity of the nitrided ferrite grains is deteriorated.
There are no streaks observed along the $<111>_{\text{BCC}}$ zone axis, which are clearly shown in other zone axes like, $<001>_{\text{BCC}}$ and $<011>_{\text{BCC}}$.

If the possible nitride is assumed to have a FCC lattice, based on the ferrite-nitride-shared reflections in DP (Fig. 4.16), the lattice parameter of the nitride is $\approx 0.406$ nm. This is much larger than that of expanded austenite, and thus it is reasonable to assume nitride formation within this grain. In addition, using the same reflection, the lattice parameter of ferrite is estimated to be 0.287 nm, which is in good agreement with ferrite lattice parameter measure by XRD from nontreated material.

Among not too many available nitrides, rocksalt-structured MN is the most promising candidate (M being Fe, Cr, Ni, and Al) because of its lattice parameter (CrN -- 0.415 nm)
and known OR. It has been reported that CrN exhibits a Bain OR with ferrite [56], which is shown as follows,

\[
\begin{align*}
<001>_{MN} & \parallel <011>_{BCC} \
\{001\}_{MN} & \parallel \{001\}_{BCC}
\end{align*}
\] (4.1) (4.2)

It is the same as our observation shown in Fig. 4.16. The Bain OR is a 45° \( <001> \) rotation versus cube-on-cube OR, which also have been observed after nitriding in other alloys like Fe-Cr-Al alloys [56].

Simulation based on the Bain OR was carried out by JEMS and the results are shown in Fig. 4.21. Stereograms of BCC and FCC structures were obtained first, centered by \( <011>_{BCC} \) and \( <001>_{FCC} \) zone axes, respectively, as shown in Figs. 4.21 (a) and (b). Two stereograms were overlapped so as to see the possible orientations between the two phases along other directions. Besides OR shown in eqns. 4.1 and 4.2, BCC and FCC lattices were orientated in other zone axes as well, as follows,

\[
\begin{align*}
<103>_{MN} & \parallel <102>_{BCC} \
<103>_{MN} & \parallel <133>_{BCC}
\end{align*}
\] (4.3) (4.4)

where eqn. 4.3 can be obtained by tilting along \( g_{[001]_{MN}} \) and \( g_{[001]_{BCC}} \) vectors and eqn. 4.4 can be obtained by tilting along \( g_{[001]_{MN}} \) and \( g_{[011]_{BCC}} \) vectors. However, there is no major FCC zone axes overlap with a \( <111>_{BCC} \) zone axis, which can explain...
the absence of extra reflections in the DP of a $<111>_{\text{BCC}}$ zone axis, as shown in Fig. 4.20 (a).

![Figure 4.21 Stereograms of (a) BCC and (b) FCC structure.](image)

In order to verify these ORs in other zone axes, DPs were acquired in one grain under different tilting conditions. Sample was tilted to a $<011>_{\text{BCC}}$ zone axis, by tilting along certain $g$ vector, next zone axis along this $g$ vector can be obtained and compared with the simulation.

A big advantage of this foil is that the sample is in a $<011>_{\text{BCC}}$ zone axis when put in the microscope. The tilting axes of alpha and beta are aligned with two vectors in the pattern of $<011>_{\text{BCC}}$ zone axis, namely $g_{[001]_{\text{BCC}}}$ and $g_{[011]_{\text{BCC}}}$. Equation 4.3 should be observed by tilting along a $g_{[001]_{\text{BCC}}}$ vector. Similarly, by tilting along a $g_{[011]_{\text{BCC}}}$ vector, eqn. 4.4 can be obtained.
Fig. 4.22 (a) shows a DP acquired from a \(<011>_{\text{BCC}}\) zone axis. The simulation of overlapped a \(<011>_{\text{BCC}}\) and a \(<001>_{\text{FCC}}\) zone axes is illustrated by Fig. 4.22 (b) (Note: a lattice parameter of 0.288 nm and 0.405 nm were used in the simulation for BCC and FCC lattice, respectively). The experimental observation agrees with simulation, except the absence of diffuse streaks between the FCC and the BCC reflections along a \([001]_{\text{BCC}}\) direction, which confirms the Bain OR between the ferrite and possible rocksalt-structured MN nitride.

![Figure 4.22](image)

Figure 4.22 (a) DP obtained in a sample with 0 deg. tilting and (b) simulation of OR shown in eqn. 4.1.

By tilting along alpha for 17.2 deg., next zone axis is obtained and shown in Fig. 4.23. In a \(<133>_{\text{BCC}}\) zone axis, \(g_{[011]_{\text{BCC}}}\) vector was kept strongly excited. The corresponding FCC zone axis is \(<103>_{\text{FCC}}\). The simulation resembles experimental result, but the same
set of extra reflections appear in the pattern as observed in Fig. 4.18, which is possibly due to a superlattice structure resulting from a nitrogen interstitial ordering in the nitride. The streaks between BCC and FCC reflections were observed as well. The same pattern was observed at an angle of alpha -17.2 deg..

Figure 4.23 (a) a <133>\text{BCC} zone axis with a <103>\text{FCC} zone axis, and (b) a simulation of these two zone axes.

By tilting along another vector, \(g_{[001]_{\text{BCC}}}\), a <102>\text{BCC} zone axis was reached after a 23 deg. tilting (Fig. 4.24 (a)). In the <102>\text{BCC} zone axis, \(g_{[001]_{\text{BCC}}}\) vector was strongly excited. The outer reflections of the two phases are closely spaced as illustrated in the simulation, and thus difficult to separate. In the experimental DP, due to the presence of the diffuse streaks, as observed in the previous DPs, the closely-spaced outer reflections are like an arch at the corresponding position.
The great importance of the tilting experiments is the verification of BCC structure of ferrite matrix after low-temperature nitridation. A possible rocksalt-structured MN nitride is formed in the BCC matrix, which can explain the extremely high nitrogen concentration detected in the nitrided delta ferrite grains. Though the ferrite matrix still behaves as BCC structure, the BCC reflections are diffuse and no longer as sharp as original ferrite, implying the crystallinity of ferrite grains deteriorates during nitridation, which probably can also be ascribed to the formation of coherent nitride.

In the effort of trying to observe the possible nitride in the nitrided ferrite, ferrite grain was tilted to achieve a two-beam condition. Ferrite grain was tilted to a $<011>_{\text{BCC}}$ zone axis first. After further tilting, $g_{[001]_{\text{BCC}}}$ vectors were strongly excited compared with other $g$ vectors as shown in Fig. 4.25.
The DF images acquired from reflections of ferrite and nitride are shown in Fig. 4.26. DF images recorded from different reflections are essentially the same, i.e. speckles distributed uniformly within the grain, which is similar to the observation under lower magnifications (Figs. 4.17 and 4.18). This can be interpreted as the nitrides in the ferrite grains are extremely small particles ($\approx 1$ nm). In addition, there are dark lines within the ferrite grain, which are evident in the DF images under 100 k magnification. The dark lines are almost parallel to $g_{[001]_{BCC}}$ vector. This is similar to the features observed in a so-called “tweet” structure [99-101], which was ascribed to the strain-field-induced atom displacement, which can be applicable to the nitride phase in the ferrite as well. Given the OR (eqn. 4.1), the extremely small nitride particles can be coherent with the ferrite matrix and the coherent strain field gives rise to the dark lines in the DF images. The uniform distribution of these coherent nitride particles probably contributes to the featureless appearance of the ferrite.
Figure 4.26 DF images from ferrite reflection under magnifications of 50 k (a) and 100 k (b), and DF images from nitride reflection under the same magnifications (c) and (d).

Sample was further tilted in order to excite $g_{[001]}^{BCC}$ vectors. Fig. 4.27 (a) shows the corresponding DP and DF image was acquired from a (011)$_{BCC}$ reflection and shown in (b). Uniformly distributed speckles were observed, as well as the dark lines within the grain being perpendicular to the vector, which confirms the presence of the nitride particles in the ferrite grain after nitridation.
Figure 4.27 DP from a ferrite grain tilted to a \( <011>_{\text{BCC}} \) zone axis with \( g_{[011]_{\text{BCC}}} \) vectors excited (a), and (b) DF image from an excited reflection under magnifications 100 k.

HRTEM images were acquired from the featureless ferrite grains in order to reveal the ferrite microstructure and identify the possible nitride. HRTEM images were recorded from two BCC zone axes, \( <111>_{\text{BCC}} \) and \( <011>_{\text{BCC}} \).

Fig. 4.28 shows a HRTEM image viewing along a \( <111>_{\text{BCC}} \) direction. The power spectrum of this image is shown in the inset, which is similar to the DP acquired from the same direction presented earlier (Fig. 4.20 (a)). The image background is not uniform, which may be due to the sample thickness local variation. The lattice fringes of the ferrite are clear and no indication of any nitride. Nevertheless, the lattice distortion is visible in the image, similarly to the observation in carburized ferrite grains, which probably gives rise to diffuse reflections in the nitrided ferrite.
Figure 4.28 HRTEM image of ferrite grain after nitridation viewing along a $<111>_{\text{BCC}}$ direction and the inset is the power spectrum of the image.

HRTEM image was also recorded from a $[011]_{\text{BCC}}$ viewing direction shown in Fig. 4.29. The power spectrum of the image is shown in the inset, where extra spots were observed, in addition to the ones arising from ferrite matrix and nitride. The extra spots are believed to be due to in situ formation of spinel $\text{Fe}_3\text{O}_4$ during electron beam exposure. More details will be discussed in the appendix II.

The original image (Fig. 4.29 (a)) from a $<011>_{\text{BCC}}$ viewing direction reveals grain microstructure similarly to the previous observation along $<111>_{\text{BCC}}$ viewing direction (Fig. 4.28). In order to differentiate the nitride from the ferrite, the original image was “filtered” by putting selective masks in the power spectrum without transmitted beam.
BCC ferrite reflections in the power spectrum were used to form an inverse FFT “filtered” image first, which is shown in the inset of Fig. 4.29 (b). The ferrite lattice fringes are severely distorted and apparently the ferrite microstructure is full of dislocations, which is similar to the observation in the carburized ferrite grain, implying that the ferrite was heavily deformed during nitridation. An inverse FFT image from nitride reflections in the power spectrum shows extremely small nitride particles being coherent with the ferrite. However, given the presence of extra spots in the power spectrum, this image cannot be fully understood and thus nitride particles revealed in the image is not fully reliable, although it is consistent with the DF images.
Figure 4.29 (a) HR image from a $<011>_{\text{BCC}}$ viewing direction in a ferrite grain and the inset is the power spectrum of the image. (b) and (c) The inverse FFT filtered HRTEM images formed by ferrite and nitride reflections, respectively. The insets are the masked power spectrum.

Foil thickness from which the HRTEM images were acquired was estimated by EELS thickness map, which is shown in Fig. 4.30 (a). The curved line feature is due to bending induced during sample preparation and dark spots are due to beam damage during image acquisition. A thickness profile was extracted along a line drawn in (a) showing the foil is relatively thin (only $\approx 0.65 \lambda$). However, the sample thickness is not uniform. The maximum sample thickness estimated along the line was $\approx 0.8 \lambda$, while the minimum is only $\approx 0.55 \lambda$. The sample thickness can easily vary 30 nm within a short distance. However, this problem is mitigated by the fact that the field of view in a HRTEM image is only $\approx 10$ nm, which is much smaller than scale of the sample thickness topography.
This foil thickness variation could explain the black-and-white background in each HRTEM image acquired. A further complication of this local thickness variation is the discontinuity of the phases of the plane waves, which may distort the lattice fringes and gives the apparently dislocations observed in the HRTEM images.

Figure 4.30 (a) Thickness map of the sample nitrided at 713 K with 7400 activity and (b) thickness profile along the line drawn in (a).

Chemical analysis was performed on nitrided ferrite grains in a plan-view foil, in order to confirm the high nitrogen content. Spectra were acquired from four points shown by the
markers in Fig. 4.31. XEDS quantification results from an austenite (point 1) and a ferrite (point 2) of a similar depth from the free surface (on top of the image) show the nitrogen concentration in the ferrite grain is qualitatively higher than its neighboring austenite grain, which is in agreement with AES line scan results shown earlier (Fig. 4.7). Even ferrite at point 4, which is deeper in the case, shows a higher nitrogen concentration than that of austenite at point 3.

![Figure 4.31 STEM image showing where XEDS was acquired, areas 1 and 3 are from austenite and areas 2 and 4 are from ferrite. The free surface is on the top.](image)

Figure 4.31 STEM image showing where XEDS was acquired, areas 1 and 3 are from austenite and areas 2 and 4 are from ferrite. The free surface is on the top.

<table>
<thead>
<tr>
<th>Point</th>
<th>N</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.3</td>
<td>1.8</td>
<td>0.9</td>
<td>13.0</td>
<td>-</td>
<td>5.0</td>
<td>Bal.</td>
</tr>
<tr>
<td>2</td>
<td>30.6</td>
<td>2.3</td>
<td>1.1</td>
<td>14.3</td>
<td>0.5</td>
<td>2.3</td>
<td>Bal.</td>
</tr>
<tr>
<td>3</td>
<td>17.7</td>
<td>1.9</td>
<td>1.3</td>
<td>14.0</td>
<td>-</td>
<td>5.2</td>
<td>Bal.</td>
</tr>
<tr>
<td>4</td>
<td>22.9</td>
<td>2.6</td>
<td>1.1</td>
<td>15.7</td>
<td>-</td>
<td>2.8</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

XEDS spectra were acquired from another ROI, which is near the case-core interface. In a cross-sectional TEM foil (Fig. 4.32), with free surface on the right, two ferrite grains in different case depths were included. The quantification results are summarized in Table
4.5. Both points 1 and 2 from the near-surface ferrite and austenite grains give a significant amount of nitrogen, while points 3 and 4 only show marginal nitrogen contents. This is in accordance with a typical nitrogen concentration profile, a sharp nitrogen concentration profile at the interface. Even with a relatively low nitrogen concentration, the ferrite grain still shows featureless appearance, indicating the featureless appearance occurs at a low nitrogen concentration. This is totally different from carburized ferrite grain, where only featureless plates were observed in the ferrite grains near the case-core interface (Fig. 3.5).

Figure 4.32 Areas where XEDS spectra were acquired, 1, 3, and 4 are from ferrite and 2 is from austenite. This is a cross-sectional sample and free surface is on the right.

<table>
<thead>
<tr>
<th>At.%</th>
<th>N</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>25.6</td>
<td>2.7</td>
<td>1.2</td>
<td>16.1</td>
<td>-</td>
<td>51.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Point 2</td>
<td>22.4</td>
<td>2.7</td>
<td>1.2</td>
<td>13.6</td>
<td>0.7</td>
<td>54.6</td>
<td>4.9</td>
</tr>
<tr>
<td>Point 3</td>
<td>4.6</td>
<td>3.7</td>
<td>1.5</td>
<td>21.2</td>
<td>-</td>
<td>65.4</td>
<td>3.6</td>
</tr>
</tbody>
</table>
In another cross-sectional foil shown in Fig. 4.33, there are at least three ferrite grains identified in the foil, with equiaxed austenite grains in between. The two ferrite grains near the free surface (on the right) show featureless appearance. However, conventional TEM features were still observed in the lower part of the ferrite grain close to the case-core material interface. The top part has transformed to a featureless appearance, suggesting a direct transition from original ferrite grain to featureless grain, which is different from the observation in carburized ferrite grains. The DPs recorded from these two parts do not show a significant difference. Extra reflections from NiAl particles were observed in both DPs, which is the same as DP acquired from plate-containing carburized ferrite grains. However, there are still noticeable differences between the two DPs. The reflections from the featureless region (b) are slightly elongated along a [001]_{BCC} direction compared to the ones in original ferrite (c), signaling the appearance of the diffuse streaks as observed in plate-containing carburized ferrite grain. In addition, there is no nitride reflection observed in either DP, implying the featureless appearance of ferrite under the microscope is not related to the nitride formation but some other reasons. This agrees with the fact that carbide is absent in carburized featureless grains as well and thus it is other factors that induce the featureless appearance to the nitrided (carburized) ferrite grains.
Figure 4.33 (a) Cross-sectional foil from nitrided sample at 713 K 7400 activity, with free surface on the right, showing three ferrite grains. DPs acquired from the transforming ferrite grain (b) from top featureless part and (c) from lower original grain, as marked in (a).

Fig. 4.34 (a) is an elastically filtered image containing a PB between ferrite (on the left) and austenite (on the right), which clearly testifies that the featureless ferrite grain shows no contrast. The neighboring austenite shows different features, due to the microtwins, defects and possible nitride formation.
The nitrogen peak in the energy-loss spectrum was clearly identified (Fig. 4.34 (b)), confirming the presence of nitrogen in the ROI. ESI mapping of nitrogen by three-window method from the same area was acquired, as shown in Fig. 4.34 (c). The nitrogen map vaguely shows nitrogen enrichment along the austenite—ferrite PB, which will be discussed in details in section 5.1. The mapping suggests, though not clearly, a higher nitrogen concentration in the ferrite grain compared with neighboring austenite grain, which is consistent with XEDS results shown early.
Figure 4.34 (a) Elastic image from a PB between featureless ferrite and austenite, (b) EELS nitrogen spectrum, and (c) is the ESI nitrogen mapping.
In order to investigate the nitrogen content and possible nitride formation in the ferrite grains, APT was acquired from the featureless ferrite grains. The APT samples were prepared from a finely-polished cross section of a sample nitrided at 713 K with 7400 activity. Three stringers of ferrite grains can be clearly identified in the BS image, due to the elemental partitioning between ferrite and austenite, as well as the uptake of nitrogen atoms in both phases. The case extends from the free surface and stops before entering the innermost ferrite stringer. The Pt strip was deposited on all three ferrite stringers, as shown in Fig. 4.35 (b). Three samples were prepared in order to see the nitrogen concentrations at different depths.

Figure 4.35 BS image of a cross-sectional sample after nitridation at 713 K with 7400 activity. (a) Before and (b) after Pt deposition.

An atom probe sample including an austenite–ferrite interface region was successfully prepared from the middle ferrite stringer (≈ 7.5 µm away from the free surface) in Fig. 4.35. 3D nitrogen and Cr atom maps are shown in Fig. 4.36. The nitrogen atom map
4.36 (a)) shows significant nitrogen segregations in the volume and similar segregations are observed in the Cr map as well. By superimposing 15 at.% nitrogen isoconcentration surfaces, Fig. 4.36 (b) clearly shows that isoconcentration surfaces are mostly distributed on the interface in the original austenite grain next to the ferrite grain, indicating a high nitrogen concentration on the austenite–ferrite interface. Moreover, the nitrogen isoconcentration surfaces in the shape of clusters also scatter in the ferrite grain, suggesting possible nitride particle formation.

![Figure 4.36 3D nitrogen (a) and Cr map (b) with nitrogen isoconcentration surfaces (green) showing 15 at.% nitrogen. A ferrite grain is on the right and lamellar-structured nitride (a former austenite grain) is on the left.](image)

The ferrite part of the sample was extracted from the whole volume and shown in Fig. 4.37 (a). The nitrogen distribution in the ferrite is uniform. The clusters defined by 15 at.% nitrogen isoconcentration surfaces distribute uniformly in the volume. A proxigram was obtained from all enclosed nitrogen clusters and shows that the clusters are about 1

161
nm in radius, which is in good agreement with the nitride particles revealed in DF images. But the nitrogen concentration in the clusters is only $\approx 20$ at.%, which is much lower than the stoichiometry required by the rocksalt-structured nitride MN, indicating a highly nitrogen-deficient structure. Within the clusters, both Cr and Al are enriched but Fe and Ni are rejected, being consistent with the fact that Cr and Al are strong nitride former. Nitrogen concentration in the bulk material is $\approx 12$ at.%, which is significantly higher than the nitrogen solubility in ferrite.

The nearest neighbor distribution analyses were carried out on Cr-nitrogen and nitrogen-nitrogen atom pairs in the ferrite. Both of them suggest a random distribution, indicating nitride-free interstitial nitrogen in solid solution of ferrite. However, this contradicts diffraction observations, which can be due to the fact that the size of the nitride particles in the ferrite is too small that it is even lower than the resolution of APT under the testing condition.
Concentration (at.%) vs Distance (nm)

- Cr
- N
- Ni
- Al
- Mn

20 nm scale bar
Figure 4.37 (a) Nitrided ferrite grain extracted from the whole volume, (b) proxigram of the 15 at.% nitrogen isoconcentration surfaces, (c) and (d) are nearest neighbor distribution of Cr-nitrogen and nitrogen-nitrogen, respectively.

A similar analysis was performed on the ferrite grain closest to the free surface (≈ 2.5 µm away) in Fig. 4.35. A 3D nitrogen atom map was shown in Fig. 4.38 (a), also suggesting a uniform distribution of nitrogen in the volume. Similarly, some nitrogen-enriched clusters were identified, as superimposed in the map. A proxigram was obtained from these clusters, suggesting a maximum nitrogen concentration over 30 at.% in the clusters with radius about 1 nm. Comparing to the ferrite grain deeper in the case (Fig. 4.37), the cluster size does not grow, but the maximum nitrogen concentration is much higher. Similar Cr and Al enrichment and Fe, Ni depletion are observed as well. In addition, the bulk nitrogen concentration around the clusters is also higher, ≈ 13.5 at.%, suggesting a
higher nitrogen concentration in the ferrite grain close to the free surface. Despite of these nitrogen-enriched clusters, the nearest neighboring analyses on both Cr-nitrogen and nitrogen-nitrogen indicate the distribution of nitrogen in the ferrite grain is uniform without any nitride precipitation. This can be misleading -- the nitride particles in the ferrite are too small to be detected.
Figure 4.38 (a) 3D nitrogen atom map from the ferrite sample close to the free surface (≈ 2.5 µm away from free surface) superimposed by 17 at.% isoconcentration surfaces, (b) proxigram from all the clusters defined in (a), (c) and (d) are nearest neighbor distribution of Cr-nitrogen and nitrogen-nitrogen, respectively.

Two atom-probe samples were also successfully prepared from the austenite grains between the three ferrite stringers (Fig. 4.35). 3D nitrogen atom maps are shown in Fig. 4.39. Both maps suggest a homogeneous distribution of nitrogen in the austenite grains, confirming a random solid solution of nitrogen in the austenite grains. The bulk nitrogen concentrations in these two grains are 6.4 and 10.3 at.%, respectively, agreeing with the nitrogen concentrations expected according to a nitrogen concentration profile.
4.5 Delta ferrite nitrided at low temperature

Nitridation was also carried out at low temperatures, i.e. 623 K and 653 K, on 17-7 PH stainless steel. A very different morphology of nitrided ferrite grain was achieved, i.e. plate-containing ferrite grains. A different type of nitride was observed in the ferrite grain, the ferrite matrix between the plates is similar to the featureless ferrite grains observed after nitridation at high temperatures.

An overview of a lift-out sample treated at 653 K with 3000 activity is shown in Fig. 4.40. Most protective Pt and pre-coating Pd were lost during the ion milling. The microstructure of the case is similar to that achieved after high-temperature nitridation, i.e. large equiaxed austenite grains surrounding ferrite stringers, indicating a nitridation-
induced martensite-to-austenite phase transformation. Cursors in the image indicate the case depth of this sample revealed by metallography previously.

Figure 4.40 An overview of 17-7 PH stainless steel nitrided at 653 K with 3000 activity.

An elemental mapping by XEDS was performed on this sample (Fig. 4.41), verifying the delta ferrite grains in the microstructure by showing depletion of Ni and enrichment of Cr.

Figure 4.41 Elemental mapping by XEDS on 17-7 PH stainless steel nitrided at 653 K with 3000 activity.
Fig. 4.42 (a) shows several ferrite grains with or without plates in them. One ferrite grain
(Fig. 4.42 (b)), featureless on the top, shows parallel plates in its bottom half, separated
by possible defects across the grain. Thin lines can be clearly observed in the featureless
top part of the grain. There are two sets of lines, running perpendicular to each other,
which rules out milling damage and is possibly due to the strain in the grain.
The plate feature in the delta ferrite grain is interesting because it is similar to the plate-containing ferrite in carburized 17-7 PH stainless steel. The plates in the ferrite grains grow in two orientations. The plates in each orientation are parallel to each other. Two
sets of plates are connected at a “node” on a boundary (PB between austenite and ferrite or internal boundary between defect and ferrite), indicating they share the same habit plane and are two orientational variants of a possible nitride. A similar observation has been reported in the precipitation of Fe₄N in Fe-nitrogen system [102].

An XEDS line scan was acquired across one plate and results are shown in Fig. 4.43 (b). There is no compositional variation between the plate and ferrite matrix, suggesting the substitutional elements are under paraequilibrium condition. In order to have a better estimation of nitrogen content in the plates and matrix, EELS line scan was carried out, as shown in Fig. 4.44. Due to the thickness of the sample (≈ 1.2 λ), the result cannot be conclusive, but it suggests a higher nitrogen concentration in the plate than that of ferrite matrix.
Figure 4.43 (a) Delta ferrite grain containing plates, showing the position of a XEDS line scan, and (b) signals of the line scan.

Figure 4.44 EELS line scan across one plate in a ferrite grain, (a) the original image and the position of EELS line scan and (b) nitrogen signal collected along the line.
DPs were acquired from the plate-containing ferrite grains so as to study the nitride structure in the ferrite matrix. The DP was acquired from the top precipitate-free area of the grain, as shown in Fig. 4.45 (a). The DP is clear, i.e. no extra spots in the pattern. However, the DP cannot match perfectly with any ferrite zone axes, but close to a zone axis $<\bar{1}13>_{BCC}$. Except the reflections correspond to $\{011\}_{BCC}$ planes, all other reflections are not sharp spots, but stretched into arches, which can possibly be ascribed to the grain rotation introduced by interstitial nitrogen atoms, which has been observed previously [103]. DF images (Figs. 4.45 (b) and (c)) confirm that the whole grain is in zone and all the reflections in the DP are from the ferrite matrix.
Figure 4.45 DP recorded from the top of delta ferrite grain (a) and DF images acquired with the matrix spots (b) and (c), the reflections used are encircled in the insets.

After confirming the ferrite grain in zone, the area-selection aperture was moved to the plate-containing region and sharp extra reflections were present in the DP, as shown in Fig. 4.46 (a). While the matrix reflections are diffuse as previously observed, extra reflections are present and sharp. There is no extra reflection present along \([011]_{\text{BCC}}\)
directions, indicating a possible OR between the ferrite matrix and nitride. DF image recorded from the extra reflection (Fig. 4.46 (b)) clearly reveals the plates in the ferrite grain. When DF image was acquired from a (011)_{BCC} reflection (Fig. 4.46 (c)), both ferrite matrix and plates are bright, indicating the ferrite and nitride share the same lattice plane spacing and direction.

Figure 4.46 DP acquired from the plate-containing region of delta ferrite grain (a) and DF images acquired from sharp extra reflection (b) and matrix (011)_{BCC} reflection (c).
DP acquired from another region, where two variants of plates are present, gives another set of extra reflections, as shown in Fig. 4.47 (a). However, one set of the reflections is stronger than the other, indicating that one set of the plates dominates, which is confirmed by DF images in Figs. 4.47 (b) and (c) that plates in one direction are much larger in size and population than its variants.

Figure 4.47 (a) DP acquired from orientational variant-containing region. (b) and (c) DF images from two variants reflections in (a). The aperture is the area-selecting aperture.
DPs from a $<111>_{\text{BCC}}$ zone axis were also obtained with and without the plates. Fig. 4.48 (a) is a DP recorded from a $<111>_{\text{BCC}}$ zone axis and the reflections are diffuse, agreeing with previous observation. When plates were included in the aperture, sharp extra spots appear in the DP. The OR between the ferrite and plates is confirmed as they share a [011]$_{\text{BCC}}$ plane spacing and direction, but not on the other [011]$_{\text{BCC}}$ directions.

Figure 4.48 DPs acquired from (a) plate-free region and (b) plate-containing region.

One foil was tilted to a zone axis $<011>_{\text{BCC}}$, as shown in Fig. 4.49. Similar features were observed in this BCC pattern, i.e. diffuse streaks along a [001]$_{\text{BCC}}$ direction and an overlap of (011)$_{\text{BCC}}$ reflection with sharp extra reflections from the plates. The spacing and estimated ferrite lattice are summarized in Table 4.6 and all the angles and lattice spacings from the pattern match with a $<011>_{\text{BCC}}$ zone axis.
Table 4.6 Angles and lattice spacings of a $<011>_{\text{BCC}}$ zone axis in Fig. 4.49

<table>
<thead>
<tr>
<th>Plane</th>
<th>Theoretical Angle (deg.)</th>
<th>Experimental Angle (deg.)</th>
<th>Experimental Spacing (nm)</th>
<th>Equivalent Lattice Parameter (nm)</th>
<th>Lattice Expansion* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(01\overline{1})</td>
<td>--</td>
<td>--</td>
<td>0.219</td>
<td>0.310</td>
<td>8.0</td>
</tr>
<tr>
<td>(200)</td>
<td>90</td>
<td>90.3</td>
<td>0.145</td>
<td>0.290</td>
<td>1.0</td>
</tr>
<tr>
<td>(21\overline{1})</td>
<td>54.7</td>
<td>55.3</td>
<td>0.120</td>
<td>0.293</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*The non-treated lattice parameter is 0.288 nm.
The spacing of sharp reflections from the plates is 0.235 nm. If it is a $<111>_{\text{FCC}}$ zone axis, the corresponding lattice parameter is 0.665 nm, which is much larger than any known nitride structure. Therefore, a HCP-structured nitride, $M_2N$, would be a more promising candidate. If it is HCP structure, the planes on a $<0001>_{\text{HCP}}$ zone axis are ($\overline{1}100$), (01$\overline{1}0$), and (10$\overline{1}0$), which only depends on lattice parameter $a$. The estimated lattice parameter $a$ equals to 0.470 nm, which is very close to the lattice parameter of a Cr$_2$N nitride from ASM standard ($a = 0.4752$, nm and $c = 0.4429$) [104]. The corresponding OR is defined by eqns. 4.5 and 4.6,

$$<011>_{\text{BCC}} // <0001>_{\text{HCP}} \quad (4.5)$$

$$ (112)_{\text{BCC}} // (10\overline{1}0)_{\text{HCP}} \quad (4.6)$$

This OR was observed in other studies of high temperature aging of high-Cr stainless steel [105, 106]. One thing worth noting is a nitride $(01\overline{1}0)_{\text{HCP}}$ direction is very close to the $a (011)_{\text{BCC}}$ direction (Fig. 4.49), which was actually observed overlapped in Fig. 4.46 and Fig. 4.48. In addition, there is no superlattice reflections observed in the experimental DPs, indicating the disordering of such nitride or nitrogen is in solid solution of such nitride structure.

Figure 4.50 (a) is a STEM image of a ferrite grain with plates of different orientational variants. BF image (Fig. 4.50 (b)) shows plates in the ferrite grain. Areas where two DPs were acquired are encircled in the image. Previous DP (Fig. 4.49) is from DP1 area and
DP from DP2 area is shown in Fig. 4.51. DF images from a nitride reflection are shown in Fig. 4.50 (c) and (d) of different magnifications, both showing parallel nitride plates.

Figure 4.50 (a) STEM image of a ferrite grain with plates, (b) BF image, (c) and (d) DF images from a nitride reflection with different magnifications. The reflections used for DF images were encircled in the inset.
In addition, Fig. 4.51 is a DP that reveals a twin pattern along a (112)$_{\text{BCC}}$ plane, a common twinning mechanism of ferrite. But the twin reflections are much weaker than the matrix reflections. Because of the OR (eqn. 4.6), (112)$_{\text{BCC}}$ plane can serve as a twinning plane of the nitride plate, and therefore may be the habit plane for the orientational variants.

![Figure 4.51 DP acquired from a plate-containing ferrite, showing ferrite twins.](image)

In order to obtain a $c$ value for the HCP M$_2$N unit cell, at least one more zone axis is needed. According to the OR, stereogram of M$_2$N was centered by a <0001> zone axis and it is rotated and overlapped with a stereogram of ferrite centered by a <011> zone axis, as shown in Fig. 4.52. This can be used to predict orientations between the two phases on other zone axes. It is shown and encircled in Fig. 4.52 (b), as follows,

$$<111>_{\text{BCC}} // <01\bar{1}3>_{\text{HCP}}$$  \hspace{2cm} (4.7)
\[ <001>_{\text{BCC}} // <2\overline{1}\overline{3}>_{\text{HCP}} \]  \hspace{1cm} (4.8)

\[ <113>_{\text{BCC}} // <10\overline{1}3>_{\text{HCP}} \]  \hspace{1cm} (4.9)

Figure 4.52 (a) Stereogram of HCP-structured M$_2$N and (b) overlapped stereograms of M$_2$N and ferrite.
One pattern from a $<111>_{\text{BCC}}$ zone axis was obtained and shown in Fig. 4.53 (a). The extra reflections in the DP was measured carefully and labeled in Fig. 4.53 (b). According to eqn. 4.7, a DP of a $<01\bar{1}3>_{\text{HCP}}$ zone axis was simulated. By applying a lattice parameter $a = 0.470$ nm, lattice parameter $c$ was finely tuned, in order to obtain a good match. The DP with $c = 0.400$ nm gives the best match and spacings and angles were summarized in Table 4.7. In a narrow range, $c = 0.425$ nm is also a reasonable good match. Nevertheless, a significantly smaller $c$ value than standard structure suggests a nitrogen-deficient nitride structure, namely M$_2$N$_{1-x}$. 
Figure 4.53 (a) DP from ferrite in a $<111>_{\text{BCC}}$ zone axis, (b) measured DP, (c) and (d) are simulated DPs of a $<01\bar{1}3>_{\text{HCP}}$ zone axis and overlapped DP based on the OR of eqn. 4.7.

Table 4.7 Experimental DP comparison with a DP simulated with a nitride structure $a = 0.470$ nm and $c = 0.400$ nm

<table>
<thead>
<tr>
<th>Plane</th>
<th>Theoretical Angle (deg.)</th>
<th>Experimental Angle (deg.)</th>
<th>Theoretical Spacing (nm)</th>
<th>Experimental Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;2\bar{3}10&gt;$</td>
<td>--</td>
<td>--</td>
<td>0.235</td>
<td>0.233</td>
</tr>
</tbody>
</table>
Figure 4.54 (a) shows another DP from a zone axis <001>_{BCC}, in which sharp extra reflections were observed and matrix reflections are severely stretched, suggesting a possible grain rotation during nitridation. According to eqn. 4.8, a <2\bar{1}\bar{3}>_{HCP} zone axis is close to a <001>_{BCC} zone axis. By using the same nitride lattice parameter, a DP along a <2\bar{1}\bar{3}>_{HCP} zone axis was simulated (Fig. 4.54 (b)). The overlapped HCP-nitride and BCC-ferrite DP (Fig. 5.54 (c)) shows good match with the experimental DP, confirming the OR predicted earlier.

<table>
<thead>
<tr>
<th></th>
<th>Value1</th>
<th>Value2</th>
<th>Value3</th>
<th>Value4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(11\bar{2}\bar{3})</td>
<td>64.5</td>
<td>64.7</td>
<td>0.203</td>
<td>0.203</td>
</tr>
<tr>
<td>(10\bar{1}\bar{1})</td>
<td>51.1</td>
<td>51.8</td>
<td>0.203</td>
<td>0.204</td>
</tr>
</tbody>
</table>
Figure 4.54 (a) DP from a $\langle 001 \rangle_{\text{BCC}}$ zone axis, (b) a simulated DP along a $\langle 2\bar{1}13 \rangle_{\text{HCP}}$ zone axis, and (c) an overlapped simulated DP of $\langle 001 \rangle_{\text{BCC}}$ and $\langle 2\bar{1}13 \rangle_{\text{HCP}}$.

However, experimental DP obtained from some zone axes, like a $\langle 113 \rangle_{\text{BCC}}$ zone axis, cannot agree with simulation very well. This is probably because that the nitride has a very defective structure, implied by a much smaller nitride lattice parameter ($c=0.400$ nm) than the ASM standard (0.4429 nm). It is well known that $c$-axis of HCP structure is sensitive to the defects (vacancies) in the structure, which probably could give a range of lattice parameter depending on the nitrogen content in the structure. In addition, the absence of superlattice reflections in the nitride DPs indicates that there is no ordering between nitrogen atoms and vacancies in the nitride structure, i.e. the nitrogen is in solid solution of such nitride structure.

Moreover, as shown in Fig. 4.52 (b), the same BCC zone axis can be close to different nitride zone axes, which makes the situation more complicated. Last but not least, the
diffuse BCC reflections also make it difficult to index the pattern and tilt the sample exactly on zone axis.

A DP from a \( <011>_{BCC} \) zone axis (Fig. 4.55) was obtained from plate-free region in a ferrite grain. Interestingly, the DP is similar to the one obtained from the featureless grains after nitridation at high temperature, except there are no discrete reflections. This DP suggests a possible transition from plate-containing ferrite to featureless ferrite, similar to the transition observed in carburized ferrite grains.

Figure 4.55 DP acquired along a \( <011>_{BCC} \) zone axis from a plate-free region. The inset shows where the DP was acquired.

In order to clarify either the nitriding temperature or the nitriding potential controls plate formation in nitrided ferrite grains, samples from the same 653 K nitriding temperature but with a higher nitriding activity (7400) was prepared. Because featureless ferrite grain
was observed in samples after 713 K nitriding with 7400 activity, so samples nitrided at
the same activity but a lower temperature would be a good comparison. Fig. 4.56 clearly
shows plates in ferrite grains, indicating that the nitriding temperature controls the ferrite
morphology in nitrided 17-7 PH stainless steels.

Finally, calculation has been carried out in order to predict any nitride formation in the
ferrite grain of 17-7 PH stainless steel during nitridation. A composition of 18.1 at.% Cr,
6.6 at.% Ni and 75.3 at.% Fe was used in the calculation, due to the inadequate data for
Al and Si. As predicted by Fig. 4.57 [64], at the nitriding temperature range utilized in
this study (623, 653, and 713 K), formation of $\text{M}_2\text{N}_{0.75}$ and $\text{M}_4\text{N}$ are very close. The
formation of $\text{M}_4\text{N}$ is even more favorable at lower temperature. As indicated in the plot,
nitrogen-deficient $\text{M}_2\text{N}_{0.75}$ nitride is more energetically favorable compared to
stoichiometric $\text{M}_2\text{N}$. Therefore, it is reasonable to assume that a higher nitrogen

Figure 4.56 17-7 PH stainless steel after nitridation at 653 K with 7400 activity, (a) and
(b) are two different ferrite grains.

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stoichiometric $\text{M}_2\text{N}$. Therefore, it is reasonable to assume that a higher nitrogen

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deficiency in the \( \text{M}_2\text{N} \) structure, e. g. HCP \( \text{M}_2\text{N}_{0.5} \), would further stabilize the structure and makes it even more energetically favorable than \( \text{M}_4\text{N} \) formation. This could explain the observation of nitrogen-deficient \( \text{M}_2\text{N}_{1-x} \) in nitrided ferrite at low temperature. Conversely, this implies that the \( \text{M}_2\text{N}_{1-x} \) nitride formed in the ferrite is highly nitrogen deficient.

Figure 4.57 Calculations on the nitride phase stability in the ferrite grain, considering \( \text{M}_2\text{N}_{0.75} \), \( \text{M}_4\text{N} \), \( \text{M}_2\text{N} \) and \( \text{MN} \) nitrides.
5. Microstructure of nitrided 17-7 PH stainless steel

5.1 Phase boundary engineering

A typical austenite–ferrite interface in 17-7 PH stainless steel after nitridation is shown in Fig. 5.1. A ferrite grain is at the bottom of the image and the region at the top of the image is austenite. Between the two grains, there is a region ≈ 100 nm wide showing a lamellar structure, apparently extending from the austenite–ferrite interface into the austenite. This is similar to recent observations in nitrided Fe–Cr alloys [46, 49], suggesting that a cellular precipitation reaction had occurred which had nucleated at the austenite–ferrite interface. Atom-probe tomography and TEM were used to fully characterize the cellular precipitation zone.
Figure 5.1 A scanning TEM image shows a cellular product in nitrided 17-7 PH stainless steel at an austenite (gamma)–ferrite (alpha) interface.

5.1.1 Atom-Probe Data

An atom probe sample including the desired austenite–ferrite interface region was successfully prepared by FIB. A three dimensional (3D) Cr atom map from this sample is shown in Fig. 5.2. (Only Cr atoms are included in the reconstruction in Fig. 5.2.) Each dot on the map represents a Cr atom. Isoconcentration surfaces of nitrogen were included in the Cr map, on which the local nitrogen concentration equals a preset value. Figure 5.2 (a) is the Cr map with 25 at.% nitrogen isoconcentration surfaces, and shows that these isoconcentration surfaces are almost exclusively on the interface in the original austenite grain next to the ferrite grain, indicating a high nitrogen concentration on the austenite–
ferrite interface, possibly due to nitride formation. Since the lamellar region extends about 100 nm from the original austenite–ferrite interface, as shown in Fig. 5.1, the region to the left of the ferrite grain in Fig. 5.2 is within the nitride region – i.e. it corresponds to (former) austenite that has undergone the cellular reactions. Besides a high Cr concentration at the interface, the Cr atom map with 25 at.% Cr isoconcentration surfaces in the original austenite region (Fig. 5.2 (b)) shows another Cr-enriched region at the top and a well-defined lamellar structure at the bottom at the interface.

Figure 5.2 3D Cr atom (pink dots) maps (a) with nitrogen isoconcentration surfaces (green) showing 25 at.% nitrogen and (b) with Cr isoconcentration surfaces (blue) showing 25 at.% Cr. A ferrite grain is on the right and lamellar-structured nitride (a former austenite grain) is on the left. The cylindrical region shows where the concentration profile (shown later) was obtained.

To analyze this further, a cylindrical ROI was drawn perpendicular to the original austenite–ferrite interface across the Cr-enriched region in the original austenite (as
shown in Fig. 5.2) and a concentration profile (Fig. 5.3) was constructed across the interface. The concentration profile was obtained along the cylindrical axis by averaging over atom fractions in slices of 0.1 nm thickness perpendicular to the axis of the cylinder. The original interface can be defined at the 22 nm marker, where the Fe-, Cr-, Ni-, Al-, and N- concentrations assume their values in the ferrite, as indicated by the vertical dashed line. The ferrite grain can be identified by its lower Ni content (4 at.%) compared to that in the austenite (6 at.%), which is due to element partitioning occurring during alloy solidification. This figure shows that Cr and nitrogen are enriched at the interface adjacent to the ferrite grain, while Fe and Ni are rejected into the neighboring region. There is also a modest Al enrichment at the interface. The plateau in the Cr- and N-profiles in the austenite region suggest this region is still austenitic; otherwise, it should be alternating peaks and valleys of both profiles in the lamellar nitride. In the ferritic region on the right of Fig. 5.3, a massive number density of finely-dispersed nitride precipitates has formed, the explanation for the significant nitrogen content in the ferrite ($\approx 12\,\text{at.\%}$) and will be discussed in a separate publication.
Figure 5.3 One dimensional concentration profile across an original austenite–ferrite PB. The nitride lamellae extends from $\approx 15$ nm to $\approx 22$ nm. The original PB is shown by the dotted line.

Another rectangular ROI was assigned to the lamellar nitride layer (left in Fig. 5.2 (b)), being parallel to the original austenite–ferrite interface. The lamellar spacing is $\approx 10$ nm in each elemental column, as shown in Fig. 5.4. The Cr-, Al-, and N-distributions strongly overlap, suggesting nitride formation. On the other hand, Fe- and Ni-enriched lamellae intertwine with Cr-Al nitrides in the reconstructions shown in Fig. 5.4. Besides the obvious lamellar structure in the lower part of the ROI, there are several lamellae at the top as well. Between these lamellae, there is no obvious lamellar structure, indicating the original austenite has not decomposed in this region and agreeing with the concentration profiles observed in Fig. 5.3. However, significant Cr, N, and Al
segregation has occurred in this region, which probably can be considered as a sign of nitride initiation.

Figure 5.4 Lamellar nitride region, (a) to (e) are Cr-, Al-, N-, Ni-, and Fe-reconstructions, respectively.

In order to identify the composition of the lamellar nitride formed at the austenite–ferrite interface, a proximity histogram (a proxigram) from a randomly chosen nitride (isoconcentration surface enclosed in the volume) within the lamellar structure is shown in Fig. 5.5. Such proxigrams involve local concentration profiles with respect to the proximity to an interface, the interface location being defined at 0 nm and the concentration being averaged from the same distance away from the interface. Besides the enrichment of Cr, Al, and nitrogen in the nitride, Fe and Ni were rejected into the neighboring region, which agrees with our previous observation. Major elements in the
nitride (between 0 nm and 1 nm markers) are Fe, Cr and nitrogen, whose concentrations are about 23, 36 and 23 at.%, respectively. Based on electron diffraction data to be shown later, the nitride phase at the interface is face-centered cubic, most likely rocksalt-structured (Cr, Al, Fe) N$_{1-x}$. The M:N ratio suggested by the atom-probe analysis is 1:0.4. Accordingly, if the nitride does have the rocksalt structure, there must be abundant nitrogen vacancies in the nitride. Non-stoichiometric CrN has been obtained under non-equilibrium processing conditions, e. g. physical vapor deposition [107] and reactive sputtering [108]. Metal-deficient transition-metal carbides and nitrides are known as well [109].

![Proxigram from a random nitride lamella](image)

**Figure 5.5** Proxigram from a random nitride lamella.

5.1.2 Transmission electron microscopy

A conventional TEM BF) image from a region including the austenite–ferrite interface is shown in Fig. 5.6 (a). The dark region is the ferrite grain in a $<001>_{\text{bcc}}$ zone axis
orientation, while the bright region is the austenite. There is a reaction zone between the two phases.

DF images of crystallographically equivalent orientational variants of nitride acquired from the encircled area in (a) are shown in Figs. 5.6 (b), (c) and (d). In Fig. 5.6 (b), both the ferrite grain on the left and the area extended (≈ 100 nm) from the original PB into the austenite grain are bright. This shows the region where cellular precipitation has occurred by the migration of the original PB. The DF images shown in Figs. 5.6 (c) and (d) unambiguously confirmed that the variants possessed a lamellar shape and are oriented perpendicular to one other. Besides the lamellar structure at the PB shown in Fig. 5.6 (c), a speckled contrast was obtained in the ferrite grain, which is ascribed to the formation of massive number density of finely-dispersed nitride precipitates within the grain.
Figure 5.6 (a) BF image of a region containing a section of austenite–ferrite interface, (b), (c), and (d) are DF images of different orientation variants obtained with the \{011\}_ferrite reflection and the other two variant reflections around it (as encircled in the inset DPs). The slightly different orientation of the $g_{MN(200)}$ vectors used for imaging reflect the slightly different positions of the $\{200\}_MN$ reflections in the diffraction pattern.

A nitried ferrite grain containing nitride precipitates was tilted to a $<011>_{bcc}$ zone axis, as shown in Fig. 5.7. The diffraction pattern (DP) in Fig. 5.7 (a) matches the Bain OR between the ferrite and the FCC lattice of the nitride,

\[
\{011\}_\text{ferrite} \parallel \{001\}_{MN_1-x} \tag{5.1}
\]

\[
<011>_{\text{ferrite}} \parallel <001>_{MN_1-x} \tag{5.2}
\]

The lattice parameter of the ferrite and the nitride can be estimated from this DP, since the ferrite and the nitride overlap at the $[011]_{BCC}$ reflection, which is the $[002]_{MN_1-x}$ reflection. With the spacing being 0.204 nm, the lattice parameter of the ferrite can be
calculated as 0.288 nm and the corresponding lattice parameter of the MN$_{1-x}$ nitride is 0.408 nm. The lattice parameter of the ferrite is about 0.5% larger than that of the BCC structure from the non-treated sample (0.2866 nm).

DF images obtained exclusively from nitride and ferrite reflections are shown in Figs. 5.7 (b) and (c), respectively. The lamellae in both DF images demonstrate the existence of alternating ferrite and nitride lamellae. The spacing between the lamellae is $\approx 10$ nm, in agreement with the atom-probe data. Fig. 5.7 (c) implies that the lamellar ferrite in the original austenite grain is in the same orientation as the original ferrite. Speckled contrast is observed in the ferrite grain in Fig. 5.7 (b), as previously observed in Fig. 5.6 (c), confirming the existence of uniformly-distributed small nitride particles within the ferrite grain.
Figure 5.7 (a) is a \(<011\>\) zone axis pattern of ferrite, (b) and (c) are conventional TEM DF images taken from the nitride reflection and the ferrite reflection, respectively, along the same \(<011>_{\text{bcc}}\) direction.

In order to confirm the crystal structure of the nitride formed at the austenite–ferrite interface, another ferrite grain was tilted to a \(<001>_{\text{bcc}}\) zone axis (Fig. 5.8 (a)). A DP acquired from the ferrite grain close to the interface show diffuse streaks along the ferrite \([001]\) direction. When the area-selecting aperture for the DP included the austenite–ferrite interface, in addition to the major reflections from the ferrite, streaks along and perpendicular to the ferrite \(<001>_{\text{bcc}}\) direction appeared, as shown in Fig. 5.8 (b). These streaks, if interpreted as arising from diffraction from a second phase, are consistent with the presence of a rocksalt-structured precipitate, MN_{1-x}, with M being Fe, Cr and Al, as shown earlier. This again indicates nitride formation on the austenite–ferrite interface. The streak positions with respect to the ferrite matrix spots agree with the Bain OR, which corresponds to a 45° \(<001>\) rotation versus a cube-on-cube OR and has been reported in gas-phase-nitrided Fe–Cr–Al alloys. The corresponding DP is drawn in Fig.
5.8 (c) [56]. There are three nitride orientation variants formed at the interface. The corresponding lattice parameters of the ferrite and the nitride can be estimated from the same [011]\textsubscript{BCC} reflection as well, which are 0.292 nm and 0.413 nm, respectively.

The rocksalt-structured MN nitride observed here is Cr-enrich, space group Fm\overline{3}m. AlN can exist as a metastable rocksalt phase [54, 110], and forms a solid solution with CrN. The lattice parameter of metastable cubic rocksalt-structured AlN (0.403 nm) is very close to that of CrN (0.415 nm). The rocksalt-structured FeN is not stable but should have a lattice parameter close to that of CrN. This agrees well with the lattice parameter we estimated for the nitride of Figs. 7 and 8 (0.408 nm and 0.413 nm). The slight deviation from standard CrN lattice can be ascribed to the defects (mainly vacancies) in the lattice, which was also observed in nitrogen-deficient CrN [108].
Figure 5.8 (a) and (b) are DPs that were recorded in regions close to and on the interface between ferrite and austenite, respectively. (c) illustrates the DP to be expected from ferrite in $<001>$ zone axis with three rocksalt-structured MN nitride orientation variants (the open circles indicate the positions of ferrite spots and the solid circles indicate the positions of nitride spots).

HRTEM image acquired from a colony of lamellae along a $<011>_{\text{BCC}}$ direction and the corresponding power spectrum with masks around the major reflections from the outlined area are shown in Fig. 5.9 (a). Within the outlined area, one ferrite lamella is sandwiched between two nitride lamellae. Fig. 5.9 (b) shows an image obtained by inverse FFT of Fig. 5.9 (a) after applying masks shown in the power spectrum in the inset. The lamellar nitride is orientated perpendicular to a $<001>$ direction of the ferrite, as observed in the DF images. The lamellae thickness ($\approx 6$ nm) in the HRTEM image agrees reasonably well with previous observations ($\approx 10$ nm). The nitride is partially coherent with the ferrite grain along (011) ferrite planes at the interface.
Figure 5.9 (a) is HRTEM image from a region featuring lamellar nitride. The inset shows the power spectrum of the image (on a logarithmic intensity scale), superimposed with masks and (b) is the inverse Fourier transformation image with all bcc and nitride spots.
5.2 NiAl formation & dissolution during carburizing/nitriding

5.2.1 NiAl formation

As shown in Fig. 4.35, one atom-probe sample was prepared from the bulk ferrite (innermost ferrite grain with no nitrogen present). The nitrogen detected within the volume is less than 0.1 at.% (data not shown here), indicating a practically nitrogen-free ferrite in the bulk material.

Fig. 5.10 shows 3D atom maps of Ni and Al with isoconcentration surfaces superimposed, implying possible Ni and Al segregations in the ferrite. It is confirmed by the cluster analyses (Fig. 5.10 (c) and (d)) that Ni and Al are not randomly distributed, but rather segregated in the volume. The actual cluster size detected in the ferrite is smaller than the random size.
Figure 5.10 3D Ni (a) and Al (b) atom maps, superimposed with 10 at.% Ni and 6 at.% Al isoconcentration surfaces. (c) and (d) Cluster size and count distributions of Ni, Al, respectively.

A proxigram (Fig. 5.11) obtained from enclosed 6 at.% Al isoconcentration surfaces clearly shows that clusters have a Ni to Al ratio of 1:1, but still possess significant amounts of Fe and Cr. The Ni and Al are ≈ 30 at.% each, and Fe and Cr are ≈ 25 at.% and ≈ 10 at.%, respectively. This strongly suggests formation of NiAl intermetallic particles during nitridation, which is the age-hardening phase of 17-7 PH stainless steel. Even though the optimum aging condition of this alloy is at ≈ 773 K for 1 h [2], nitriding temperatures used in this study (as high as 713 K) are high enough that with a prolonged exposure (20 h), NiAl particles can nucleate, but their size is limited by sluggish substitutional diffusion. As suggested by the proxigram, the particle size is ≈ 2 nm, implying an early stage of cluster formation. It has been reported that, at early stage of NiAl formation during aging, there is a significant amount of other elements in the clusters, which gradually decreases as aging proceeds [111, 112].
The ferrite grain in the bulk material was studied by TEM from a cross-sectioned foil (free surface on the right). Two different kinds of ferrite grains were revealed in Fig. 5.12, i.e. featureless ferrite grain in the case (rectangular region) and bulk material ferrite (circular region).

Figure 5.12 (a) STEM image of cross-sectioned 17-7 PH stainless steel foil (free surface on the right) nitrided at 713 K with 7400 activity. The circle and rectangle indicate where the DPs were acquired.
Due to a close lattice parameter of NiAl to ferrite, NiAl is on a cube-on-cube OR with respect to ferrite, which can be defined as follows,

\[
<001>_{\text{BCC}} // <001>_{\text{NiAl}} \tag{5.3}
\]

\[
(001)_{\text{BCC}} // (001)_{\text{NiAl}} \tag{5.4}
\]

The DPs acquired from a bulk ferrite grain are shown in Figs. 5.13 (a) and (b). The major reflections in the DPs match ferrite patterns of a \(<001>_{\text{BCC}}\) and a \(<011>_{\text{BCC}}\) zone axes, however, there are weak reflections in both DPs, indicating the presence of NiAl in the ferrite grain. In Fig. 5.13 (a), extra weak reflections are observed at half reciprocal spacings of \((002)_{\text{BCC}}\) reflections along a \(<001>_{\text{BCC}}\) zone axis, being consistent with B2-structured NiAl reflections. Reflections in agreement with the B2 structure were also observed in a \(<011>_{\text{BCC}}\) zone axis (Fig. 5.13 (b)), except many more weak reflections due to double diffraction were also present. Streaks were observed extending along two directions on the weak reflections, possibly due to some strain effect between the ferrite and NiAl. Figures 5.13 (c) and (d) are DF images from the encircled reflection of NiAl, which show a speckle contrast, suggesting a uniform distribution of extremely small NiAl particles in the ferrite grain.
Figure 5.13 (a) and (b) DPs along $<001>_{\text{BCC}}$ and $<011>_{\text{BCC}}$ recorded from the encircled area in Fig. 5.12 (a). (c) and (d) DF images of the same grain with different magnifications.
Similar contrast in the carburized ferrite grains was observed as presented earlier (Fig. 3.17 (e)). Therefore, both low-temperature carburization and nitridation processes can facilitate the formation of B2-structured NiAl particles in the ferrite grain.

5.2.2 NiAl disordering

Though NiAl forms in the ferrite grain in bulk material during low temperature carburization and nitridation, it is not stable in the carburized or nitrided ferrite grains, supported by the absence of NiAl reflections in all the DPs recorded from featureless grains after both carburization and nitridation.

In carburized featureless ferrite grains, all the DPs conform to a BCC structure, without any extra reflections. In the carburized plate-containing ferrite grains, the DF image (Fig. 3.17) indicates NiAl particles are absent in the plates but present in the matrix. In nitrided featureless ferrite grains, besides BCC reflections in the DPs, there are reflections belong to MN nitride, but no indication of the presence of NiAl particles.

A cross-sectional TEM foil including the case-core interface was prepared from nitrided 17-7 PH stainless steel with free surface on the right. There are several ferrite grains present in the foil, as shown in Fig. 5.14 (a). Featureless grains are observed in the case, while one ferrite grain with conventional electron contrast is observed near the case-core interface, the encircled region. Even though the ferrite grain is in the case (fully
surrounded by equiaxed austenite grains), it has not been transformed to featureless grain yet.

Two DPs were obtained from the two different ferrite grains, but from the same ferrite $<011>_{\text{BCC}}$ zone axis, as shown in Figs. 5.14 (b) and (c). The DP from the deeper ferrite grains shows diffuse streaks along $[001]_{\text{BCC}}$ directions, which is a primitive sign of featureless ferrite transformation as has been observed in both carburized and nitrided ferrite grains. Moreover, there is no sign of any MN formation in the DP, compared with Fig. 5.14 (c), suggesting this grain is at the early stage of transformation. However, this DP is significantly different from the one observed in bulk ferrite grain (Fig. 5.13 (b)) as well, i.e. the weak reflections from NiAl are much more diffuse, implying a possible disordering occurrence during ferrite uptake of nitrogen.
Figure 5.14 (a) STEM image of a cross-sectioned foil nitrided at 713 K with 7400 activity. (b) and (c) DPs acquired from encircled and rectangular region ferrite grains, respectively.

This was investigated in details by APT in samples of nitrided and carburized ferrite grains. Fig. 5.15 (a) shows a 3D Al atom map of the same sample shown in Fig. 4.37 (a),
superimposed with 4.5 at.% Al isoconcentration surfaces; the Al distribution in the ferrite
is not random. Proxigram of these clusters shows Al-enriched clusters with no
corresponding Ni enrichment, or even implying a Ni rejection in the cluster. NiAl cluster
analyses of nitrided ferrite grain (cluster size and count distribution in Fig. 5.16) show a
random Ni-Al distribution within the ferrite, indicating there is no NiAl cluster in the
nitrided featureless ferrite. This agrees with TEM data that extra reflections ascribed to
NiAl cluster formation in the ferrite grains from bulk material disappeared in featureless
ferrite grains, indicating NiAl clusters were dissolved during nitridation.
Figure 5.15 (a) 3D Al atom map of a nitried ferrite grain superimposed with 4.5 at.% Al isoconcentration surfaces, and (b) proxigram of these clusters.

![Figure 5.15](image)

Figure 5.16 (a) and (b) are NiAl cluster count and size distribution analyses, respectively.

The situation is a little bit different in the carburized ferrite grains. Though there is no evidence of NiAl presence in the featureless ferrite grain in the TEM diffraction, NiAl was positively identified in the proxigram (Fig. 5.17 (b)) and cluster analyses (Fig. 5.18). It is obvious in Fig. 5.17 (a) that the Al distribution in the ferrite is not random, which is
similar to the nitrided ferrite (Fig. 5.15 (a)). Within the Al-enriched clusters, there is a corresponding Ni enrichment but it is less than 1:1 ratio. Both Cr and carbon are rejected from NiAl clusters, implying a low solubility of Cr and carbon in NiAl.

Figure 5.17 (a) 3D Al atom map of a carburized featureless ferrite grain superimposed with 6 at.% Al isoconcentration surfaces and (b) proxigram of these isoconcentration surfaces.
Figure 5.18 NiAl cluster count (a) and size (b) distribution in carburized featureless ferrite grain.

Similar cluster analyses were performed on plate-containing ferrite (Fig. 3.8) grains as well. It clearly shows that NiAl cluster count and size distributions (Fig. 5.19) deviate from a random distribution, confirming the presence of NiAl clusters in the plate-containing ferrite. This can be explained as the matrix between the plates is still ferrite, which contributes to this result.
Figure 5.19 (a) and (b) are NiAl cluster count and size distribution analyses, respectively.

In sum, NiAl clusters, as an aging product, are present in the ferrite grain in the bulk material are both carburization and nitridation. However, diffraction evidence of NiAl clusters is absent after carburization and nitridation, suggesting NiAl dissolution during the process. APT data confirms the dissolution of NiAl during nitridation. On the other hand, NiAl clusters are positively identified by APT in carburized featureless ferrite, suggesting a different mechanism of disordering induced by carburization to that induced by nitridation.
6. Discussion

6.1 Mechanism of carburized featureless ferrite formation

6.1.1 Inhibition of cementite formation in the ferrite grains

The classic Fe-C phase diagram predicts a very limited carbon solubility (≈ 0.1 at.%) in ferrite at the eutectoid temperature (≈ 1000 K), which becomes much smaller at lower temperatures. Even with the assumption of paraequilibrium conditions [4], the predicted carbon solubility in ferrite with the composition of 17-7 PH stainless steel is only ≈ 0.15 at.% at processing temperature (713 K) [64]. Therefore, it is reasonable to expect carbide formation, once the carbon content in the ferrite exceeds this modest solubility limit. However, there is no evidence of carbide formation in carburized ferrite grains that we can observe. Apparently, carbide formation was inhibited during the low-temperature carburization process.

Cementite is the most likely carbide candidate phase, as cementite has been observed after carburization in martensitic stainless steels [34, 35]. However, cementite in pearlitic steels can decompose during high strain experiments [65-68], indicating that cementite is not stable in a high dislocation density environment. Conversely, the presence of an extremely high dislocation density can prevent the formation of cementite [69, 113]. The interaction between carbon and a dislocation core has been calculated; it was found that the binding energy between carbon atoms and the dislocation core is higher than the binding energy between carbon and iron in cementite [114-116]. Therefore, if carbon atoms in the ferrite were segregated at defects, e.g. the distorted regions or dislocations...
in both featureless ferrite grains and carbon-rich plates in plate-containing ferrite grains, the carbide formation would be effectively inhibited. It is reasonable then to expect that the presence of uniform carbon-supersaturated ferrite grains should be correlated with uniform distribution of defects in the grain.

Moreover, in 17-7 PH stainless steel, there are appreciable amounts of Al and Si in the ferrite, nominally ≈ 2 at.% of each element in the alloy. The APT results show ≈ 2 at.% Al and ≈ 1 at.% Si in ferrite (shown in Fig. 3.8 (b)) due to the element partitioning during solidification. The effect of Si on cementite formation is well studied [67, 113, 117]; Si is known to retard cementite formation, due to its limited solubility in this phase. A similar effect of Al was observed in Fe-Al-C alloys [118], i.e. the presence of Al increases the temperature at which cementite begins to precipitate during aging. Due to their limited solubility in cementite, the driving force for the formation of Al- and Si-containing cementite much be reduced. First-principle simulations predict both Al and Si to partition to ferrite with respect to cementite after long time tempering [119]. Therefore, the presence of both Al and Si can effectively delay or inhibit the formation of cementite in the ferrite.

Last but not least, as in carburized 316L stainless steel, significant compressive stresses can be achieved after carburization [4, 16], and is to be expected in the carburized layer of 17-7 PH stainless steel. This biaxial stress does not favor and indeed tends to inhibit any carbide formation, because the free volume per Fe atom of all carbides are much larger than the free volume per Fe atom of ferrite – 0.0118 nm³/Fe, compared to that of
cementite, 0.0129 nm³/Fe [120]. Therefore, if a given amount of Fe atoms transform into cementite, there must be a volume expansion of ≈ 9 %, which is unfavorable given the presence of large residual compressive stresses. As cementite has the most dense structure of known carbide phase, a larger expansion is required for all other carbides.

Therefore, under the circumstances of high defect density, the presence of Si and Al, and a large compressive stress in the carburized layer, the formation of cementite in the ferrite grain can be effectively delayed or even totally inhibited.

6.1.2 Carbon supersaturated ferrite

Carbon concentrations as high as 18 at.% in the delta ferrite grains were obtained by SAM (a more modest but still extraordinary value of 9 at.% was measured by APT), and can be attributed to carbide formation in the ferrite being inhibited. However, ferrite grains with supersaturated carbon contents have been reported in other steel systems [65-72]. In a bainitic steel, carbon segregated to linear defects (almost certainly dislocations) near the austenite–ferrite interface [69, 70]. A carbon concentration as high as 15 at.% was detected at the dislocation cores [69]. The carbon atoms at the dislocation cores were believed to be trapped and immobile, which would delay or even inhibit the nucleation of cementite. In addition to the clear carbon segregation at dislocations, there are clusters observed in the ferrite grains as well [69-71], with a maximum carbon content of ≈ 15 at.%. Although this is well above the equilibrium carbon concentration in the ferrite, it does not correspond to the carbon content of any known carbide. These clusters can be
due to the entangled dislocation network or to carbon-redistributed dislocation debris. However, the size and population of these high-carbon clusters are limited by the carbon content in the alloy. In the bainitic ferrite, the total carbon concentration is only ≈ 3 at.% [69]. Inasmuch as the carbon concentration in the carburized ferrite is 18 at.%, many more uniformly distributed high-carbon dislocations and clusters can be expected, whose local strain fields may overlap and cause uniform contrast in the ferrite grain, as we observed.

Carbon supersaturated ferrite was also observed in pearlitic steels that had experienced extremely high strain [65-68]. A carbon-enriched “cell” structure was observed in the ferrite grain between the cementite lamellae [66]. This was attributed to carbon segregation in the dislocation walls formed during deformation, which may be analogous to our observations of the plates formed in the carburized ferrite grains. This may also give rise to an inhomogeneous carbon distribution in the highly-deformed ferrite; the carbon concentration being much higher than the equilibrium predictions [65-67, 72].

Besides the extraordinary carbon concentration in the plates, the carbon concentration of ferrite in the matrix between the plates in the plate-containing ferrite is also quite high, > 2 at.% (Figs. 3.7 (c) and 3.8 (b)). A high carbon form of ferrite, with tetragonal symmetry – c/a of 1.07 – and containing about 2 at.% of carbon, has recently been postulated [121].

Finally, the carbon supersaturation observed in ferrite matrix may also be due to the inhibition of the carbide formation, resulting in carbon-rich clusters. It has been reported
that the delay of nitride nucleation leads to a high nitrogen supersaturation in ferrite [52, 53, 63], which lends credence to this notion. Presumably, as potential carbide nuclei, the presence of subcritical carbon-rich metastable clusters, could increase the average carbon concentration in the ferrite matrix significantly, but never grow to a critical nucleation size. We assume that such metastable clusters are too small (< 1 nm) to be detected by APT.

6.1.3 Segregation of carbon atoms to defects in ferrite

With no sign of carbide formation in the ferrite grain and no carbon segregation at the austenite–ferrite PBs, carbon atoms are present at an astonishingly high concentration in the ferrite. However, the estimated tetragonality from the DPs is below 5 %, which cannot explain the 18 at.% carbon concentration observed in this study. Further, visible tetragonality in DPs can be expected when carbon exceeds 0.25 at.% [122]. These factors all suggest that carbon atoms are in the grain but not in conventional interstitial sites, and the most probable sites to accommodate carbon atoms are defects in the ferrite.

It has been proposed [65, 123, 124] that, instead of carbon forming a solid solution in the ferrite grains, the most probable sites to accommodate carbon atoms during cementite decomposition in pearlitic steels are dislocations stored at the ferrite–cementite interface. It was further suggested [66] that dislocation walls can be formed in the ferrite to which the dissolved carbon atoms can segregate. These ideas seem applicable to our
observations. From the HRTEM images shown in Fig. 3.16 and 3.18, carburized ferrite grains are heavily dislocated and highly defective.

The capability of dislocation cores to accommodate carbon atoms has been addressed in the literature [125, 126]. Experimentally, more than 20 carbon atoms per plane perpendicular to the dislocation line can be absorbed in ferrite [125]. It was suggested that the Cottrell atmospheres extend to $\approx 7 \pm 1$ nm ($\approx 30 \, b$) with a maximum carbon concentration of $8 \pm 2$ at.%. A recent study [126] showed that about 90% of the carbon atoms in a Si-rich martensite steel were trapped in Cottrell atmospheres around dislocation cores in dislocation tangles in the matrix. Therefore, an overlapping Cottrell atmosphere could give rise to the carbon-supersaturated ferrite grains we have observed. The critical dislocation density for the Cottrell atmospheres to overlap in the ferrite can be predicted, considering the average spacing between dislocations ($\rho^{-0.5}$). With an averaging spacing of $7 \, \text{nm}$, the dislocation density in the material can be estimated as $10^{12}/\text{cm}^2$, which is on the same order of severely plastically deformed steels.

A detailed model of carbon segregation in dislocations during martensite tempering was proposed some time ago [73]. A reasonable assumption of carbon concentration in the featureless ferrite based on AES and APT results is $\approx 12$ at.%. Based on the BCC crystallography, there is one site (at a distance of $1b$) per dislocation (with half edge and half screw components) that is stable with respect to cementite, assuming the carbon binding energy in cementite is $\approx 0.5 \, \text{eV}$ [127]. Based on this model, the number of carbon atoms per iron plane as a function of dislocation density is plotted in Fig. 6.1. A
dislocation density of \(10^{14}/\text{cm}^2\) would be required in order to fully accommodate 12 at.% carbon. This is higher than the dislocation density estimated from HRTEM images along a \([011]_{\text{BCC}}\) direction, but still plausible by taking account of dislocations in all directions (i.e. dislocations on the other \([011]\) directions) and of different dislocation types (edge and screw).

Moreover, only one site being stable with respect to cementite is a very conservative assumption. Several studies [115, 116, 128] showed that the carbon binding energy with dislocations in ferrite (at a distance of 1\(\text{b}\)) is \(\approx 0.75\) eV instead of \(\approx 0.5\) eV. Furthermore, it has been shown that alloying elements can effectively change the binding energy between carbon and dislocations in ferrite – the high Cr content in the ferrite in particular can further increase the binding energy [128]. The combination of these factors can substantially increase the number of stable carbon sites around a dislocation core. If the
stable sites for carbon around a dislocation are 10 per plane (still less than the Cottrell atmosphere), then according to Fig. 6.1, a dislocation density of \( \approx 10^{13}/\text{cm}^2 \) is needed to accommodate 12 at.% carbon in the ferrite, close to the estimated dislocation density in this study and comparable to that in a severely plastically deformed alloy.

6.1.4 Microstructural evolution of carburized ferrite grains

Fig. 6.2 schematically illustrates the evolution of ferrite grains during the low-temperature carburization. At an early stage of carburization, martensite in the alloy transforms to austenite at low carbon concentration. Carbon partitions between the austenite and ferrite, and chemical potential equilibrium of carbon is established between the two phases. The carbon concentration would be as low as the paraequilibrium condition predictions, i.e. 0.15 at.%. Carbon concentration in this type of ferrite grain is almost zero – as observed in the innermost ferrite grain in Fig. 3.2.
Figure 6.2 A model shows the plate growth in the ferrite grain in 17-7 PH stainless steel during carburization. The dots in the ferrite grain are metastable carbide nuclei.

If the plates are treated as a pseudo phase, it is reasonable that this phase nucleates at PBs. Then the growth of such “phase” would depend on the interfacial energy and strain energy. Due to the plates being essentially BCC, the interfacial energy between these two phases are minimized and therefore the plate growth could be controlled by strain energy. It is expected that these plates should grow along a \([001]_{\text{BCC}}\) direction, which is the elastically soft direction in ferrite. This agrees with the observation that plates grow along a \([011]_{\text{BCC}}\) direction, as well as perpendicular to a \([001]_{\text{BCC}}\) direction (but along other \([001]_{\text{BCC}}\) directions in the family of \([100]_{\text{BCC}}\) or \([010]_{\text{BCC}}\) directions), as shown in the defocused DP (Fig. 3.17 (f)).

Another possibility is activation of deformation slip systems. As the interstitial carbon concentration in the austenite grains increases, it is accompanied by lattice expansion and a corresponding compressive strain applied to their neighboring ferrite grains. At some point, the shear component of this strain, will be high enough to cause yielding of the ferrite. The most easily activated slip system in ferrite (\([110] <10\overline{1}\>) would then be activated. At the same time, the very high carbon chemical potential in ferrite leads to a carbon-supersaturated ferrite, presumably containing metastable carbide nuclei.

Once slip is activated, carbon segregates to dislocations and due to the high binding energy between them, this segregation can be an exothermal process. It also results in a
depletion of the interstitial carbon in the solid solution in the “perfect”, i.e. dislocation-free lattice, which consequently reduces the chemical potential of carbon in the ferrite. Therefore, the higher carbon chemical potential in the austenite will drive the interstitial carbon into the ferrite. In order to accommodate the inward diffusion of carbon and lower the total free energy, more dislocations need to be generated. Eventually, an extremely high dislocation density is achieved in the ferrite.

The slip planes are not activated simultaneously and thus the time for carbon diffusion is different for each plate. That is the reason that plates in the ferrite grains are of different lengths and carbon concentrations, but parallel to one other. A typical morphology is shown in Figs. 3.5 (b) and (c). Especially, in Fig. 3.5 (b), two perpendicular sets of plates were observed in one grain, consistent with activation of different slip systems. Since the beam size of AES is larger than several nanometers, the composition measured from these plate-containing ferrite grains is an average carbon concentration of the plates and the intact matrix, which is the middle ferrite grain in Fig. 3.2.

Eventually, plates grow laterally into the whole grain and transform the ferrite grain such that it shows uniform contrast, the so-called “featureless” grains. This scenario is consistent with Fig. 3.1, in which the original ferrite region was almost completely consumed by the plates, as shown in the lower part of the left ferrite stringer.

Similar low-temperature carburization has been studied in 2205, 13-8 and E-Brite stainless steels [36-38]; however, all the ferrite in these alloys form carbides instead of
featureless grains containing enormous carbon supersaturation. This is probably due to the volume fraction of ferrite phase in these latter alloys being much higher (≥ 50 %) than that in 17-7 PH stainless steel (≈ 5 %), which substantially changes the stress state of the ferrite grains in the carburized layer. For 17-7 PH stainless steel, ferrite grains are fully surrounded by austenite grains, which effectively restricts the ferrite to a confined volume; yielding can occur under the stresses applied by the neighboring austenite grains due to their volume expansion. However, due to a much higher volume percent of ferrite in the other alloys, the ferrite grains can easily relax the strain before reaching a critical value and therefore carbides form before dislocations in the ferrite can be activated.

At last, besides dislocation-induced carbon supersaturation in the carburized ferrite grains, other possibilities were considered as well. Carbon clustering on ferrite (001) plane was predicted previously [114]. Even though such cluster configuration is not stable [114], it might be an alternative explanation for the carbon supersaturation observed in this study. Especially, such carbon clusters could be as thin as one or several atomic planes (in the form of graphene), making it “GP zone –like”. However, one thing cannot be explained is the effect of such zones on the DPs of the featureless ferrite grains, where pronounced sharp streaks were expected extending to both directions of the major ferrite reflections. One more possibility of carbon in the carburized featureless ferrite is the carbon segregation at the PBs between ferrite and austenite, which was ruled out by the APT data (Fig. 3.17).
The origin of dislocations in the ferrite grain is also still in discussion. The yielding mechanism discussed in this study is one of the most possible mechanisms. One other possible mechanism is prismatic loop formation in the ferrite with carbon segregated to it. The loop can be formed by “punching out” from some source at the PB. One common loop source is Frank-Read source, which is usually in the size of several micrometers, which is too big for the ferrite grain. In principle, the defect formation process with carbon segregation must be exothermic that could lower the system energy. Normally, in carbon-supersaturated ferrite, the Gibbs energy is reduced by carbide formation.

6.2 Low-temperature nitridation

6.2.1 Expanded austenite

A detailed CALPHAD modeling has performed to assess the effect of temperature and activity on the nitrogen concentration [20]. It is summarized as,

a. since nitridation is an exothermic process, for the same nitriding activity, the higher temperature gives a lower surface nitrogen;

b. for the same temperature, the higher nitriding activity gives a higher surface nitrogen concentration.

The experimental observations are that both the case depth and lattice expansion increase with nitriding temperature and activity. Besides, all CALPHAD predictions overestimated the surface nitrogen concentration at least by a factor of 2. The measured
nitrogen concentration for 713 K nitridation with 7400 is \( \approx 18 \) at.\%, and the corresponding calculation prediction is \( \approx 34 \) at.\%. This was explained by

a. The presence of compressive stress, which increases the chemical potential of nitrogen and decreases nitrogen solubility correspondingly;

b. A low mass transfer efficiency at metal/gas interface, which delays achieving local nitrogen equilibrium at the interface and therefore nitriding afterwards.

However, though the surface nitrogen concentration is comparable between 17-7 PH stainless steel and 316L grade, the lattice expansion and case depth achieved in 17-7 PH grade are larger than those in 316L grade after the same nitridation process, e. g. nitridation at 713 K with 7400 activity, as summarized in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>17-7 PH</th>
<th>316L [20]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface nitrogen content</td>
<td>( \approx 18 ) at.%</td>
<td>( \approx 17 ) at.%</td>
</tr>
<tr>
<td>Lattice expansion</td>
<td>7.6 %</td>
<td>6.4 %</td>
</tr>
<tr>
<td>Case depth</td>
<td>11 ( \mu m )</td>
<td>( \approx 8 ) ( \mu m )</td>
</tr>
</tbody>
</table>

The surface nitrogen concentration difference is negligible between the two alloys and a possible difference is due to the Cr content difference in the alloys, i. e. a higher Cr concentration gives a higher possible nitrogen interstitial concentration [19, 129, 130]. The larger lattice expansion observed in 17-7 PH stainless steel is probably due to the higher surface nitrogen content as well. As previous studies showed [18], the expanded austenite lattice as a function of nitrogen content is defined as,
Therefore, 1 at.% of nitrogen content difference can give a different lattice expansion of ≈ 0.3 %, which is not sufficient to explain the difference observed between the two alloys. Another possibility is experiment error, which is significant for expanded austenite, due to anomalous lattice expansion on (002)_{FCC} planes.

The case depth achieved in 17-7 PH stainless steel after the same nitridation is significantly larger than that of 316L. This can be explained by the presence of martensite in the as-received 17-7 PH stainless steel. The carbon/nitrogen diffusivity in BCC/BCT structure is much higher than that in FCC, due to a more open unit cell. Therefore, the interstitial atoms can diffuse much faster in the martensite in 17-7 PH stainless steel before it transforms to austenite.

A nitridation-induced martensite-to-austenite phase transformation was observed in 17-7 PH stainless steel, which is ascribed to the fact that nitrogen is a strong austenite stabilizer, similar to carbon. With a relatively low nitrogen concentration, the alloy eutectoid temperature is effectively reduced to a temperature lower than the nitridation temperature, facilitating this phase transformation [38]. The inward diffusion of nitrogen further stabilizes the austenite and makes it stable even at room temperature.

However, there is a competition between the phase transformation and carbide formation. This phase transformation does not occur in other stainless steels, like 13-8 [36], 2205...
[37] and E-Brite [38], but carbides and nitrides formed. This was considered as a kinetic reason, i.e. a lower treatment temperature would delay/inhibit carbide formation and favor martensite-to-austenite phase transformation.

Moreover, the same phase transformation does not occur in delta ferrite grains in the 17-7 PH stainless steel, contradicting the predictions and suggesting other factors that may control this phase transformation. It is possible that this phase transformation is ready to occur in martensite, which has a “memory” of being austenite. Besides one more possible reason is that the actual composition of delta ferrite is different than that of martensite in the bulk material, i.e. a higher Cr and lower Ni contents.

Several DPs with microtwins were acquired from the expanded austenite zone axes \(<114>_{\text{FCC}}\) and \(<215>_{\text{FCC}}\). The twinning plane for both zone axes is \((011)_{\text{FCC}}\), as expected. The microtwins in the austenite are thick plates.

Another band structure was observed in the austenite grains, showing \(\frac{1}{2}gv_{(\overline{1}3\overline{1})}\) and \(\frac{1}{2}gv_{(511)}\) in FCC DPs, suggesting a possible superlattice structure due to nitrogen ordering. This reflection also rules out the possibility of simple cubic structure, e.g. Fe₄N. The other FCC-like nitride is Fe₁₆N₂, which can be seen as a distorted Fe₄N with alternate nitrogen atom missing (Fe₄N₀.₅) [131]. However, if this is true, according to the simulation (data not shown here), many more superlattice reflections can be expected in DPs, such as \([001]_{\text{FCC}}\) reflections.
Therefore, a new unit cell structure is needed in order to interpret these observations. However, exact unit cell has not been figured out. But due to the nitrogen concentration on the surface (estimated as 15 at.%), there need to be sufficient number of nitrogen atoms in the new unit cell. One possible configuration is a unit cell comprised of $2 \times 2 \times 2$ original austenite unit cells with 4 nitrogen atoms on body-centered octahedral interstitial sites on (011) plane of the new unit cell. The band structure in the austenite grain can be ascribed to different domains of such unit cells.

6.2.2 Mechanism of nitrided featureless ferrite formation

Featureless ferrite grains were observed after low-temperature nitridation at 713 K, which is similar to the observation of carburized featureless ferrite grain.

First, all these featureless ferrite grains possess significant interstitial contents. The nitrogen concentration in a ferrite grain at a depth of $\approx 9 \, \mu m$ revealed by AES line scan is $\approx 20 \, \text{at.\%}$ (Fig. 4.7), which is higher than that of its neighboring austenite. This is comparable to the carbon concentration measured in near-free surface carburized ferrite grain (Fig. 3.2). However, the carbon concentration of carburized ferrite grain at a similar depth is much lower, and also lower than that of its neighboring austenite.

Secondly, both ferrite grains with significant amount of interstitials show negligible lattice expansion and tetragonality, but a significant lattice distortion along a $[001]_{\text{BCC}}$ direction. Moreover, an extremely high dislocation density was revealed in ferrite grains.
after both carburization and nitridation, which is even higher than that of heavily cold-worked steels.

Finally, both carbon and nitrogen distributions in the featureless ferrite are random and uniform, as suggested by APT. The uniform distribution of nitrogen and high dislocation density in the ferrite grain suggest a similar featureless ferrite formation mechanism, i.e. nitrogen-stabilized dislocation cores and the overlapped dislocation strain fields give a uniform contrast.

Nevertheless, the nitridation-induced featureless grains can be distinguished from carburization-induced featureless grains by the following features,

a. a rocksalt-structured MN nitride was identified in nitrided featureless grains,

b. the original ferrite grain transforms to featureless grain directly during nitridation, i.e. there is no transition stage like plate formation,

c. the critical nitrogen concentration to induce featureless appearance is lower than that required by carbon.

Therefore, the nitridation-induced featureless ferrite is probably due to the dislocation strain field overlap. But the nitrogen in the ferrite is also in the form of nitride. The nitride observed in the ferrite is rocksalt-structured MN, with a lattice parameter of 0.405 nm. It is probably nitrogen-deficient, i.e. MN\textsubscript{1-x}, because the stoichiometric lattice parameter of CrN is 0.415 nm. Though CrN is essentially a linear compound in a Cr-nitrogen phase diagram, it has been studied that the lattice parameter of CrN depends on
its stoichiometry for CrN prepared under non-equilibrium condition [108]. The nitrogen deficiency of the lattice gives a smaller lattice parameter of CrN.

A Bain OR was identified between the MN$_{1-x}$ nitride and the ferrite. This OR minimizes the possible misfit strain between them, as schematically illustrated in Fig. 6.3. With a lattice parameter of 0.405 nm, MN$_{1-x}$ along a <001> direction can match well with Fe atoms in ferrite along a <011>$_{BCC}$ direction. Since the nitride particle size observed under TEM is extremely small (< 2 nm), it is easy for these particles to keep coherency with ferrite matrix. Therefore, the coherent strain field due to the nitride formation could contribute to the uniform contrast as well.

![Figure 6.3 Schematic of Bain OR between ferrite and MN.](image)

This has been observed in nitrided Fe-Mo binary alloys, which was nitridated by a gas mixture of NH$_3$ and H$_2$ at a constant activity [132]. After nitridation, GP zone-like
“zones” formed on {001} planes in the ferrite grains and give streaks along a [001]_BCC direction due to soft elasticity, which is similar to our observation. Homogeneous nucleation of these metastable zones on {001} matrix ferrite plane was observed in the temperature range of 673 ~ 873 K. With 2.5 at.% nitrogen in the alloy, the zones are dense enough that the coherent strain fields from these zones dominate the contrast. Given the fact that a 20 at.% nitrogen concentration was achieved after nitridation, it is reasonable that the coherent strain fields overlap and give rise to the uniform contrast under the microscopes.

Besides, the overall nitrogen concentration in the ferrite measured by AES and APT is ≈ 20 at.%. According to rule of mixture, 40 vol.% of stoichiometric MN is enough to achieve an average of 20 at.% nitrogen concentration, assuming negligible nitrogen content in ferrite matrix. This is close to the phase fraction estimated based on speckle contrast in ferrite observed in DF images. But since the nitride is non-stoichiometric, it would require more nitride than it appears in the DF images in order to achieve 20 at.% nitrogen in the ferrite, and thus there is probably an appreciable amount of nitrogen in the ferrite.

Even though the nitride formation is positively identified by DPs in TEM, atom probe cannot distinguish it from interstitials in solid solution, which is probably because the nitride particle size is below the atom-probe resolution under the testing conditions. The possible nitrogen concentration in clusters implied by proxigram is ≈ 30 at.%, which is comparable to the nitrogen concentration measured from the cellular nitride at the
austenite—ferrite PBs, indicating that the nitride stoichiometry is about CrN_{0.5}. Again, according to rule of mixture, by assuming a 40 vol.% of nitride in ferrite matrix, the nitrogen concentration in the ferrite matrix should be $\approx 17$ at.%. This is close to the estimation of carbon concentration in a carburized ferrite grain, which we proposed that almost all carbon atoms are segregated to dislocation cores. Further, this suggests a possible saturation concentration of interstitials (carbon and nitrogen) in ferrite matrix by dislocation mechanism.

If two competitive mechanisms were considered in a ferrite during nitridation, i. e. nitrogen segregation to dislocation cores and nitride formation, nitrogen probably segregates to dislocation cores before the formation of any nitride. This is supported by the non-stoichiometry of nitride and as well as diffraction data (Figs. 4.33 and 5.14) showing lattice distortion (streaks) along a [001]_{BCC} direction before any nitride formation. Since if nitrides formed first, it should reach its stoichiometry before any segregation to dislocation cores occured. In this sense, the dislocation core is stable with respect to nitride formation, which can be due to similar reasons previously presented for carbide inhibition.

However, the reason for nitrogen saturation in ferrite matrix is due to the saturation of dislocations, which is limited by the interaction between dislocations. If the space between dislocations is too small, the stress (strain) field between them could cancel each other and even get destabilized.
The much higher nitrogen concentration in ferrite is driven by a high nitrogen concentration in its neighboring austenite. In a carburized stainless steel, like 316L, the highest carbon concentration can be achieved is 15 at.% [19], which is lower than that achieved after nitridation (≈ 18 at.%). Therefore, the driving force (chemical potential) for nitrogen to diffuse in ferrite is correspondingly higher, as shown in Fig. 6.4. As dislocations being generated, nitrogen segregates to dislocation cores. But after nitrogen saturation in dislocations, the nitrogen chemical potential drives nitride formation. The absence of carbide in carburized ferrite can be ascribed to a lower carbide formation driving force due to smaller carbide formation energy, compared to that of nitride [133].

Even though formation of rocksalt-structured nitride is not the first nitride expected according to the phase diagram, thermodynamically, precipitation of coherent rocksalt-structured nitride in ferrite can be justified. It has been shown that in a recrystallized Fe-Al alloy, incoherent hexagonal AlN nitride formation is favored [54]. With the presence of dislocations, the precipitation of metastable coherent rocksalt AlN can occur without
any energy barrier, but the growth of such nitride is controlled by volume diffusion of Al, which is analogous to the nucleation of rocksalt-structured nitride MN$_{1-x}$ in the ferrite.

Once the nitridation-induced dislocation cores are saturated by nitrogen, these dislocations can serve as heterogeneous nucleation sites for nitride nucleation. Because the dislocation density in the ferrite is so high that its distribution is uniform, resulting in a uniform nitride particle distribution. Even though the nucleation barrier can be effectively eliminated, the nitride growth is limited by the sluggish diffusion of substitutional elements under nitriding temperature.

The reason for no transition plate-containing ferrite in nitrided featureless ferrite grain is the shape of nitrogen concentration profile in the case, which exerts a significant influence on the ferrite transition. The nitrogen concentration profile in the case is comprised of two parts, i.e. a plateau region and a sharp tail. For a carburized case, the carbon concentration profile, with a maximum carbon solubility of 15 at.% at the free surface, decreases gradually across the case, as illustrated in Fig. 6.4. Further, the compressive residual stresses due to the lattice expansion induced by interstitial carbon changes gradually correspondingly and the maximum residual stress is 2 ~ 3 GPa [16], which is limited by maximum carbon solubility. However, for a nitrided case within a 1 ~ 2 µm range, the nitrogen concentration profile changes abruptly from a tail with a minimum nitrogen concentration to a plateau region, where the nitrogen concentration is ≈18 at.%. Due to the much higher surface nitrogen concentration, a compressive residual stress of 7 ~ 8 GPa can be achieved in the plateau region [18]. Consequently, the material
experiences an abrupt change from a stress-free state (or a negligible residual tensile stress) at the diffusion front to a highly-stressed state in the plateau region.

Therefore, as the nitrogen diffuses to a ferrite grain, which has a dimension of several µm in length (parallel to the free surface) by 1 ~ 2 µm in width (orthogonal to sample free surface), the compressive stress applied on such ferrite grain by its neighboring austenite grains changes from zero to several GPa in a distance of 1 ~ 2 µm, which could happen within a single grain. Under such high stresses, the yielding of ferrite grain is massive. Consequently, slip systems are activated simultaneously in a ferrite within a nitrided case, compared with a carburized case, where the slip bands were activated discretely and sequentially due to a gradual change of stress state. This is confirmed by the observation in a nitrided ferrite grain (Fig. 4.33) that the top of the ferrite has transformed to featureless, but its lower part still shows conventional electron contrast. The DP acquired from the newly-transformed featureless region shows no sign of MN$_{1-x}$ nitride formation, indicating the featureless appearance is due to the massive dislocations activated in slip systems. Furthermore, this could also explain the relatively low nitrogen content in featureless grains, compared to the carbon concentration in a carburized featureless grain.

6.2.3 Mechanism of plate-containing nitrided ferrite grain

In all low temperature nitridation treatments (623 and 653 K), only plate-containing nitrided ferrite grains were observed, regardless of nitriding activities. The plates are paraequilibrium nitride, showing no segregation of any substitutional element, but they
are probably nitrogen-enriched. An OR was identified between the nitride and ferrite. Two orientational variants were observed in the ferrite grains and they intersect at ≈ 15°. DPs recorded from the plate-free region are similar to that of featureless grains, i.e., ferrite reflections in the DPs are severely elongated and arched.

Nitridation at lower temperatures and low activities generally gives a relatively low nitrogen concentration at the alloy free surface (2 ~ 3 at.% lower), which may mitigate the compressive residual stress. As mentioned earlier, the formation of featureless ferrite is a result of competition between dislocation formation and carbide/nitride formation. Since the lattice expansion of austenite is a linear function of nitrogen concentration [18], a 2 ~ 3 at.% lower nitrogen concentration on the free surface may roughly reduce the lattice expansion 10% (estimated based on a 20 at.% nitrogen surface concentration), which correspondingly may mitigate ≈ 1 GPa residual stress. Therefore, the mitigation of the residual stress (from 8 GPa to 7 GPa) seems to be insignificant and thus insufficient to explain the nitride formation.

In addition to residual stress that may contribute to the competition between the slip band formation and nitride formation, other factors, e.g., nitrogen concentration in the ferrite and kinetics of nitride formation, are taken into consideration.

First of all, because of the exothermic nature of nitrogen dissolution in ferrite, the equilibrium nitrogen concentration in the ferrite at low temperature is higher than that at high temperature, which would facilitate the nitride formation.
More importantly, the diffusion of nitrogen is much lower at low temperature. For example, for the same nitriding activity 144000, nitriding at 713 K yielded an 11 µm case, while only a 3 µm case was obtained at 653 K, i.e. a factor of 3 difference in nitrogen diffusivity. If a ferrite grain with a width of 2 µm (comparable to the distance between the tail and the plateau of a nitrogen concentration profile), during the nitridation at 713 K, the stress level of the ferrite changes from zero to several GPa in a matter of 4 h (roughly estimated based on a 20 h nitridation). However, during nitridation at 653 K, it would take up to 11 h to build up a similar but lower stress level around the same ferrite grain, due to a much slower nitrogen diffusivity. Therefore, kinetically, nitride would have a larger window to nucleation and grow before a critical stress level was achieved.

Therefore, even though generally nitride formation was favored at high temperature, but due to a much faster stress buildup, the nitride formation was inhibited, as a result of a competition between slip band formation and nitride formation. On the other hand, at low temperatures, a higher nitrogen content in the ferrite and a longer nitride formation window enable the nitride nucleation and growth, which also agrees with CALPHAD predictions (Fig. 4.57). However, these nitride plates tend to dissolve after featureless ferrite formation, due to a more favorable binding energy between nitrogen and dislocation cores.

The nitride observed in this study is not in a widely recognized OR [105, 106, 134]. It was only observed in the high Cr-containing steels, suggesting a possible composition-
related Cr$_2$N OR with ferrite. Two orientational variants observed in the ferrite grain are sharing the same habit plane. Because of the cubic symmetry of ferrite, the habit plane for nitride is limited to \{hhl\} or \{0kl\} planes [102]. Since the mirror plane of the nitrides is \{011\}, the habit plane is \{hhl\} and it may be \{112\} (the twinning plane of ferrite).

PBs usually serve as heterogeneous nucleation sites. As observed in this study, all plates were nucleated at austenite—ferrite PBs. Elongated precipitates with high aspect ratios generally form because of minimizing the strain energy or due to crystallographic anisotropy of the growth rate. Another possibility is that the observed aspect ratio may be ascribed to optimizing the precipitate volume under the given constraints of limited substitutional diffusion: while nitrides grow rapidly in the direction parallel to their long axis, their small extension in the direction orthogonal to the axis enables the required distance of substitutional element transport to be small enough to be realized under near paraequilibrium conditions [32].

In a plasma-nitrided Fe-18 mass% Cr alloy [134], Cr$_2$N was observed at the diffusion front together with CrN, however, only CrN was observed near the free surface, suggesting a Cr$_2$N to CrN transformation during nitridation. This is in agreement with the observation in this study that the matrix between the plates is featureless like, implying a possible M$_2$N$_{1-x}$ to MN$_{1-x}$ transformation following featureless appearance. When the nitrogen was introduced in the ferrite at relative low temperatures, the M$_2$N$_{1-x}$ plate formation is preferred. But as the stress continues increasing, featureless ferrite forms in companion with MN formation and the previously formed M$_2$N$_{1-x}$ transforms to MN$_{1-x}$. 
Even though the crystal structure of $\text{M}_2\text{N}_{1-x}$ used in the JEMS simulation of this study is an ordered structure, there are no corresponding superlattice reflections observed in DPs, indicating the nitrogen in the nitride is not ordered but rather in solid solution, which further suggests a nitrogen-deficient structure, in agreement with a lower $c$ value of the experimental lattice parameter.

6.2.4 Cellular precipitation at austenite—ferrite phase boundary

In the following, we propose a model to explain the experimental observations. The cellular precipitation reaction observed in this study can be written as,

$$\gamma_N \rightarrow \beta + \alpha \quad (6.2)$$

where $\gamma_N$ is nitrogen-supersaturated austenite, $\beta$ is $\text{MN}_{1-x}$, and $\alpha$ is ferrite with a minimum concentration of nitrogen. This cellular decomposition reaction of nitrogen-supersaturated austenite is due to the instability of this phase. Previous studies have shown that the nitrogen-supersaturated austenite in AISI 304 and 316 decomposes after annealing above a threshold temperature [8, 135, 136]. The incubation time for the decomposition depends on the concentration of both the interstitial and substitutional solute atoms. After annealing, a fine lamellar structure containing CrN was observed, nucleated at the surface, where the nitrogen concentration is highest [135]. This is different from the observation of this study, where the cellular precipitation nucleates at
the interphase interface but not at the surface, suggesting that the presence of the
austenite–ferrite interface is critical. The austenite–ferrite interface appears to be
preferred because it can serve as both a heterogeneous nucleation site and an enhanced
diffusion path that effectively facilitates nitrogen diffusion and reduces the incubation
time required for CrN formation.

Nitride formation, while energetically favored, appears to be retarded by insufficient
diffusion of the metal atoms. The presence of the austenite–ferrite interface facilitates
transport of metal atoms and therefore the nucleation and growth of the cellular product.
The nucleation energy is minimized, by having the ferrite in the same orientation, while
the nitride has a low energy OR with the original ferrite grain. DF images from the nitride
reflections in Fig. 5.6 (c) and 5.7 (b) not only show lamellar nitrides at the austenite–
ferrite interface, but also show the formation of the nitride precipitates in the ferrite.
These nitrides in the ferrite grain are extremely small due to the sluggish diffusion of
metal atoms, which confirms the important role of PBs in the lamellar formation. These
nitrides in the ferrite grain also give rise to the diffuse streaks along one of the ferrite
[001]_{BCC} direction in the DPs in Figs. 5.7 (a) and 5.8 (a).

This interface-controlled reaction can only take place with a mobile austenite–ferrite
interface. This has been verified by the TEM DF images taken using ferrite reflections, as
shown in Fig. 5.6 (b) and 5.7 (c). Both the original ferrite and the ferrite lamellae in the
austenite grain were bright in the DF image, implying that the lamellar ferrite is in the
same orientation of the original ferrite and that the austenite grain through which the migrating PB has passed decomposed into ferrite and nitride.

That Cr diffusion is enhanced can be estimated based on the atom-probe and TEM data. The diffusion coefficient of Cr in gamma-Fe at 713 K is \( \approx 5 \times 10^{-25} \text{ m}^2/\text{s} \) [3]. Accordingly, the diffusion distance \((Dt)^{1/2}\) under the nitriding condition should be of the order of 0.2 nm. Apparently, to obtain the observed structure, the diffusivity of Cr at the austenite–ferrite interface must be enhanced by almost two orders of magnitude. A three orders of magnitude increase of Ni diffusion was reported in the so-called expanded austenite after low-temperature carburization, which was postulated to arise from excess non-equilibrium structural defects and lattice expansion in the expanded austenite [12]. A similar explanation may hold for the enhanced Cr diffusion we observed during nitride formation.

Since the system is “closed” as far as Cr is concerned, a Cr depletion zone was left behind the nitride region in the austenite (between the 6 and 16 nm markers) shown in Fig. 5.3. However, a similar nitrogen depletion zone does not occur because the system is “open” to nitrogen during nitridation – this element is certainly present at high concentration in the nitride but a corresponding depletion zone is absent, due to the inward diffusion of nitrogen atoms.

A model of the cellular precipitation is illustrated in Fig. 6.5 [82]. Cr, as a substitutional element, is practically immobile in the grain interiors, but can diffuse along the austenite–
ferrite interface. Nitrogen, on the other hand, is mobile everywhere and can diffuse to the interface from the interior of both grains to nucleate chromium nitride precipitates. Once the nitride nucleates, the growth is controlled by the long-range diffusion of substitutional elements. The growth of nitride nucleated at the PB is facilitated by the diffusion of Cr along the PB, but within the ferrite, nitride growth is inhibited by insufficient diffusion of Cr atoms. Ferrite with a minimum concentration of nitrogen is more stable with respect to nitrogen-supersaturated austenite, which drives the austenite–ferrite interface into the austenite. Further nitrogen diffusion from the austenite enables the nitride precipitates to grow into the austenite grain.
6.2.4 NiAl response to carburization and nitridation

The precipitation hardening phase of 17-7 PH stainless steel is NiAl of B2 structure. The as-received samples are all in condition A (mill annealed) that no aging process was applied and thus no NiAl present. However, NiAl particles (≈ 2 nm) were positively identified in the ferrite grains in the bulk material (after both carburization and nitridation cycles) by both APT and TEM. This is quite surprising, because the aging temperature of
17-7 is about 773 K. Especially for carburization, the processing temperature is well below the aging temperature. However, after long time exposure, e.g. 150 h for carburization, NiAl nucleates and is extremely small due to the sluggish diffusion of substitutional elements. The reaction in the ferrite is defined as follows,

\[
\text{Ni} + \text{Al} \rightarrow \text{NiAl}
\]  \hspace{1cm} (6.3)

The metallic Ni and Al combine to intermetallic NiAl, with a formation energy of 117.6 – 123.9 kJ/mol [137].

The NiAl clusters identified by APT show a 1:1 Ni-to-Al ratio, \( \approx 30 \text{ at.\%} \) of each and also contain an appreciable amount of Fe and Cr, which is in good agreement with previous study at the initial stage of NiAl aging [111, 112, 138]. Even though the NiAl particle is not well defined at this point, the reflections in DPs confirmed a B2 structure, obeying a cube-on-cube OR with respect to ferrite.

After carburization, the extra spots due to NiAl formation during the carburization were observed in both plate-containing and bulk core ferrite grains. A uniform precipitate distribution in the ferrite matrix, but not in the carbon-rich plates, was confirmed in the DF image, being consistent with the absence of the extra spots in the featureless grains, suggesting that NiAl particles were dissolved or did not form during plate formation. Even though the APT data still suggests the presence of the NiAl clusters in featureless ferrite, there is no indication of its presence in diffraction data, indicating the NiAl
particles lose their ordering during the formation of featureless grains. Because the composition of NiAl is still positively identified, the absence of the NiAl reflections has to be due to the disordereding of NiAl particles.

Given that, we suggest that in the presence of carbon, the activity coefficients of carbon and Al are mutually reduced in the solid solution (similar to the effect between carbon and Cr in austenite [12]), increasing the solubility of Al in ferrite and destabilizing NiAl clusters, leading to their disordereding. This can be defined as,

\[ \text{NiAl} \rightarrow \text{Ni} + \text{Al} \]  \hspace{1cm} (6.4)

According to eqn. 6.4, with the presence of carbon, the NiAl clusters were destabilized and dissolve back to metallic Ni and Al in solid solution. However, this is difficult to explain that NiAl clusters are still present in the ferrite matrix containing several atomic percent carbon between plates.

One further possibility is that the NiAl clusters were deformed by dislocations during the plate formation and do not provide diffraction evidence of their presence, i. e. the NiAl clusters lose their ordering. Due to the formation of massive dislocations in the ferrite grain, the NiAl clusters can be cut through by dislocations and got defragmented during the plate formation. Due to the presence of possible interfacial stress and strain, small clusters become unstable thermodynamically and tend to dissolve in the matrix [139].
Nevertheless, the dissolution of NiAl during low-temperature nitridation is totally different. The absence of NiAl reflections in the nitrided featureless ferrite grains is consistent with a random distribution of Ni and Al in solid solution revealed by APT. A DP acquired from a ferrite grain in transition shows diffused NiAl reflections as well as diffused streakings along a $[001]_{\text{BCC}}$ direction, suggesting a disordering of NiAl clusters during this transition.

The dissolution of NiAl during nitridation can be described as,

\[ \text{NiAl} + N \rightarrow \text{AlN} + \text{Ni} \]  \hspace{1cm} (6.5)

With the presence of interstitial nitrogen atoms, the NiAl clusters are destabilized. The Al in the intermetallic NiAl was “grabbed” by nitrogen and combined to form AlN nitride, due to a much higher formation energy of AlN ($> 200$ kJ/mol) compared with that of NiAl, i.e. AlN is much more stable than NiAl thermodynamically.

During the nitridation, the NiAl were nucleated as small clusters in the ferrite at nitriding temperature. But as nitrogen diffuses to the ferrite, due to the limited nitrogen solubility in ferrite, nitrogen tends to form nitride as the nitrogen chemical potential in the ferrite increases. Since the nitride is more stable than the NiAl formed earlier, the nitrogen can extract the Al from NiAl intermetallics and form AlN, at the expense of decomposition of the NiAl. Therefore, in a DP from a nitrided featureless ferrite grain, the reflections belong to NiAl disappear and are replaced by Mn$_{1-x}$ nitride reflections later.
6.3 Difference between carburization and nitridation on ferrite

The responses of ferrite to carburization and nitridation are significantly different, as summarized previously. The fundamental reasons are different species of carbon and nitrogen and the different properties of related carbides and nitrides.

First of all, carburization is an endothermic process, while nitridation is exothermic. This is very interesting because carbon and nitrogen is next to each other on a periodic table. The possible reason is the electron structure of carbon and nitrogen, which nitrogen has one more electron than carbon.

Moreover, the concentration profile of carbon and nitrogen is also significant different. The solubility of nitrogen is much higher than that of carbon in both austenite and ferrite. For example, at 713 K, assuming activities for nitridation, $a_N=7400$, and carburization $a_C=1$, the solubilities of nitrogen and carbon in austenite and ferrite are 34.9 at.% vs. 11.8 at.% and 0.15 at.% and 0.10 at.%, respectively [64]. The shape of nitrogen concentration profile gives a sharp transition (within 1 ~ 2 µm) from stress free to a compressive residual stress of 6 ~ 8 GPa. On the other hand, a smooth concave carbon profile yields a gradual increase of compressive residual stress from stress free in bulk material to up to 3 GPa at free surface [16].
Further, the carbide and nitride stability, i.e. formation energy, are substantially different as well. As summarized in Table 6.2 [133], the formation energy of cementite is positive and other Cr-carbides are slightly negative (≈ -50 kJ/mol). The formation energies for nitrides generally shifted to lower energy, e.g. the formation energies of Cr-nitrides are about -100 kJ/mol.

Table 6.2 Enthalpy of formation at 298 K $\Delta H_f$ kJ/mol

Under the paraequilibrium condition, the driving force for the paraequilibrium carbide and nitride formation was significantly decreased. If the original driving force of the reaction is small, like carbide formation, then it can be completely suppressed. On the other hand, if the original driving force is large, like nitride formation, there is still appreciable driving force for the phase transformation. Therefore, the nitride was observed but carbide was absent in the featureless ferrite.
All of these differences give rise to the different carburization and nitridation behaviors of ferrite grains in 17-7 PH stainless steel. The carbide was inhibited during carburization and the gradual stress gradient in carburized case can induce carbon-enriched plate formation in ferrite before transforming to a fully featureless appearance. The large stress and sharp stress gradient in nitrided case transforms an original ferrite to fully featureless directly, despite of nitride formation later.

Besides, NiAl was dissolved and disordered in nitrided ferrite, due to the formation energy of Cr-nitride and AlN are higher than that of NiAl. But NiAl in carburized ferrite was mechanically disordered or just dissolved back to solid solution, being ascribed to lower formation energy of carbide.
7. Conclusion

Both low-temperature carburization and nitridation were successfully applied on 17-7 PH stainless steel. An isothermal martensite-to-austenite phase transformation was observed after both carburization and nitridation. Carbon- and nitrogen-supersaturated expanded austenite was achieved on the alloy surface, significantly improving the surface hardness and pitting corrosion resistance. Generally, higher nitriding temperatures and activities give higher lattice expansion and case depth. Microtwins were identified in the expanded austenite and possible nitride pre-phase with superlattice was revealed under TEM.

Delta ferrite grains with astonishing amount of carbon/nitrogen were observed after carburization/nitridation. The interstitially-supersaturated ferrite shows featureless, i.e. uniform contrast, under TEM.

Featureless plates were observed in carburized ferrite grains near the interface between the interstitially-hardened layer and bulk material. These plates are enriched in carbon but do not form any carbide. A model based on the carbon-dislocation interaction is proposed to explain this phenomenon. During carburization, ferrite grains yielded under the strains arising from neighboring carbon-supersaturated austenite. Due to the high binding energy between carbon and dislocation cores, carbon segregates at dislocation cores and reduces the energy of the whole system. Therefore, new dislocations must be generated to accommodate more inward carbon diffusion, which leads to an extremely high dislocation density in the plate region. First-formed plates grow, and they will ultimately
fill up the whole ferrite grain. The carbon segregated at dislocation cores gives a very high carbon concentration but keeps the ferrite BCC structure.

There are no discrete dislocation lines that can be resolved from experimental APT data, but rather a uniform carbon distribution. This could be due to the entangled dislocation network and severely overlapped Cottrell atmospheres. Carbon distribution within the massive dislocation network can be expected to be nearly random, which also holds for the carbon-enriched plates.

Similarly, the dislocation mechanism holds for high nitrogen ferrite as well. But high nitriding temperature promotes rocksalt-structured nitride $\text{MN}_{1-x}$ formation in a Bain orientation relationship with respect to ferrite matrix. The uniformly distributed dislocations present in the ferrite serve as heterogeneous nucleation sites, but the nitride particle size is limited by the sluggish bulk diffusion under nitridation temperature. Low nitridation temperature prefers $\text{M}_2\text{N}_{1-x}$ formation in a shape of plate with another orientation variant in an orientation relationship with respect to ferrite. Continuing nitriding tends to dissolve $\text{M}_2\text{N}_{1-x}$ and forms featureless grain with $\text{MN}_{1-x}$.

NiAl aging product forms during both carburization and nitridation in ferrite. However, it loses ordering in both carbon and nitrogen supersaturated ferrite grains. The massive dislocations in the carburized ferrite mechanically deform the NiAl and make it disordered, even though the composition of NiAl is still present. On the other hand, due
to the formation of more stable nitride, NiAl in nitrided ferrite is dissolved and lost ordering and replaced by nitride.

In spite of processing condition designed to eliminate long-range diffusion of substitutional solute atoms, decomposition of austenite into ferrite and nitride was observed to occur during low-temperature nitridation. These observations demonstrate that phase transformations involving long-range transport of metal atoms are possible even under the processing conditions of low-temperature nitridation. Internal interfaces, and particularly those that facilitate long-range diffusion of metal atoms, can effectively facilitate the precipitation of nitrides.

Controlling the microstructure, including the chemistry, defects (dislocation) and interfaces, of the alloy is of great importance for successful surface hardening by low-temperature carburization and nitridation.
AI. Preliminary results on 17-7 PH stainless steel condition T and TH

The same nitriding treatments were applied on 17-7 PH stainless steels of condition T and TH (as shown in Fig. 1.1). Compared with condition A, a quenching process was applied on the alloy to trigger an austenite-to-martensite phase transformation. Therefore, martensite phase dominates the microstructure of T and TH conditions. Following quenching, an aging process was applied and a precipitate-hardening phase (NiAl) was formed inducing the hardening effect of the alloy. Some preliminary results were acquired nitriding treatments (as summarized in Table 2.1).

The microhardness was acquired by 50 gf from plan view of as-cleaned surface after nitridation. The non-treated condition T sample gives a similar value as that of condition A. However, the hardness of nitrided T condition can be up to 1600, which is much higher than that of condition A (1200). But the variation of hardness values is also significant for condition T. The trend of the surface hardness is not clear. The highest hardness was achieved in the highest nitriding temperature but not the highest nitriding potential, which is surprising. Hardness of nitrided sample in condition TH is similar to that of condition T, which is due to a similar martensitic microstructure.
In order to compare the different responses to nitridation, hardness of samples of different conditions was acquired and summarized in Fig. AI.2. The surface hardness of condition T and TH is generally higher than that of condition A, which is probably due to a thicker case as carbon diffusion is faster in martensite. Higher nitriding temperature yields higher hardness, which is due to a higher surface nitrogen concentration.
Fig. A I.2 Microhardness on 17-7 PH stainless steel in condition A and T nitrided at 653 K and 713 K with the same nitriding activity of 7400.

Nanohardness was acquired from cross sections of different samples. A series of hardness were acquired from a finely polished cross-section after nitriding at 713 K with 7400 nitriding activity. The maximum hardness obtained at the surface is about 16 GPa, which doubles its bulk hardness.

Fig. A I.3 Nanohardness obtained from cross section of sample in condition T after nitriding at 713 K with 7400 nitriding activity.

Metallographic images of nitrided sample of condition T were shown in Fig. A I. 4. Compared with the case formed in the austenite, the cases formed in martensite are still corrosion resistant. But the case seems to be not as intact as expanded austenite after etching. Cracking occurs more severe in nitrided condition T surfaces.
Fig. A 1.4 Metallographic images of nitrided samples of condition T 713 K with 7400 (a) and 144000 (b) activity, (c) and (d) condition T and TH nitriding at 653 K with 3000 activity.

XRD patterns were acquired from nitrided sample of condition T and TH, in order to identify the phases in the nitrided case. Patterns from as-received samples were obtained as well, as shown in Fig. A1. 5. Compared with condition A, the microstructure of condition T and TH are dominated by martensite. There is no significant difference between condition T and TH. This is probably due to similar lattice parameters of NiAl and ferrite, whose peaks would severely overlap.
Fig. A I.5 XRD patterns of as-received 17-7 PH stainless steel in condition A, T and TH.

XRD patterns from condition T and TH were acquired from samples nitrided at 713 K with 144000 activity. Peaks belong to austenite shift to the lower diffraction angle. The shift is comparable to the observation in condition A, suggesting a similar lattice expansion in the austenite after the same nitriding process. However, the volume percent of expanded austenite is significantly higher in condition T than that of condition TH, even though the austenite volume percent is comparable in as-received materials, as shown in Fig. AI. 5. This suggests a possible martensite-to-austenite phase transformation induced by nitridation. However, unlike condition A, this possible transformation is “incomplete”, i.e. there is still a significant amount of martensite in the as-nitrided sample.

On the other hand, martensite peaks do not shift after nitridation, indicating a minimal lattice expansion, if there is any. Instead, the peak intensity is significantly reduced and
the FWHM got substantially increased, which is well documented in literatures. Due to significant peak broadening and overlap, it is difficult to identify any possible nitride formation on the sample surface.

Fig. A I.6 XRD patterns of as-nitrided 17-7 PH stainless steel in condition T and TH.

In order to investigate possible nitrides, XRD patterns were obtained at slow-scanning rate showing in Fig. A I. 7. Besides the austenite peak (41.5 °) and martensite peak (44.76 °), there is one more peak observed at 44.8 °, which is probably belongs to austenite (200). Therefore, the nitrided case of 17-7 PH stainless steel in condition T and TH is comprised of expanded austenite and martensite with minimal expansion.
In addition, there are two peaks observed at low angle range (33.7° and 35.7°), which is probably due to the formation of oxide on the surface during the processing, as discussed previously (section 4.1). It is a close match with Fe₂O₃ (PDF #871166) for the two strongest peaks. These peaks were not observed on as-received samples.

Nitrogen concentration of nitrided 17-7 PH stainless steel in condition T was acquired by using AES line scan on a cross-sectional finely polished surface, as shown in Fig. AI.8. The nitrogen concentration profile obtained is similar to that of condition A, i.e., the maximum nitrogen concentration in the case is ≈ 20 at.% and delta ferrite grain also contains a significant amount of nitrogen. Therefore, it is interesting to investigate the microstructure of the nitrided case, since the nitrogen content in the case is well above any equilibrium prediction of nitrogen solubility in martensite and ferrite.
Magnetic phase map of nitrided 17-7 PH stainless steel in T condition is shown in Fig. A1.9 (b). There is no distinct boundary separating nitrided case region and bulk material. No strong magnetic domains were observed in delta ferrite as observed in condition A. There are still many paramagnetic regions in the case, suggesting the presence of austenite in agreement with XRD results.
Fig. A I.9 AFM (a) and corresponding MFM (b) images of nitrided cross-sectional 17-7 PH stainless steel in condition T.

A plan view TEM foil was prepared by FIB technique from a nitrided 17-7 PH stainless steel of condition T after nitriding at 653 K with 3000 activity. A STEM image was acquired as shown in Fig. A1. 10. Needles were observed nucleated at the free surface. However, the needles only appear in certain range of tilting angles, suggesting the appearance of these needles may be due to diffraction. In the elemental mapping, delta ferrite grains were identified running parallel to the surface by showing Cr enrichment and corresponding Ni depletion. At the austenite-ferrite PB, Cr-enriched particles were observed, which is probably due to nitride formation as discussed previously.
Fig. A I.10 (a) STEM image and (b) elemental mapping of the corresponding area of 17-7 PH stainless steel of condition T after nitriding at 653 K with 3000 activity.

Chemical information was investigated by XEDS and summarized in Table AI.1. It confirms that delta ferrite grain possess higher nitrogen content than its neighboring grains qualitatively, in agreement with previous AES line scan results.
Fig. A I.11 STEM image showing where the composition information was acquired.

Table A I.1 Composition of regions of interest shown in Fig. A I. 11

<table>
<thead>
<tr>
<th>At.%</th>
<th>N</th>
<th>Al</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>19.4</td>
<td>2.5</td>
<td>1.3</td>
<td>17.1</td>
<td>-</td>
<td>57.2</td>
<td>2.5</td>
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<tr>
<td>Point 2</td>
<td>16.6</td>
<td>2.0</td>
<td>1.0</td>
<td>14.6</td>
<td>0.8</td>
<td>59.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Point 3</td>
<td>12.2</td>
<td>2.2</td>
<td>0.9</td>
<td>15.7</td>
<td>0.6</td>
<td>62.8</td>
<td>5.5</td>
</tr>
<tr>
<td>Point 4</td>
<td>13.8</td>
<td>2.1</td>
<td>1.0</td>
<td>15.2</td>
<td>0.7</td>
<td>61.8</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Needle-shaped features were observed in conventional BF image (Fig. A I. 12), which is probably the needles observed in previous STEM image. In the needle features, there are fine structures in each needle. DP was acquired from the encircled region in Fig. A I. 12. Fig. A I. 13 matches DP of a twinned FCC along a zone axis $<011>$, which is a common twinning mechanism for FCC structure. DF images were acquired from two twinning reflections. The two DF images are complimentary, agreeing with twin characteristics. In addition, the DF images clearly show a heavily faulted twin structure, which is probably due to the low kinetics of austenite formation. The defects in the needle could promote
the austenite formation with limited thermodynamic driving force. This is totally different from the observation of previous carburization-induced martensite-to-austenite phase transformation, where large equiaxed grains were observed. In order to confirm the FCC structure, microdiffraction was carried out. The electron beam was focused in order to include one side of the twin only. The microdiffraction pattern agrees with FCC DP along a $<011>_{\text{FCC}}$ zone axis, confirming the FCC structure induced by nitridation even in condition T, although its heavily faulted twin morphology is significantly different from condition A.

Fig. A.1.2 BF image of nitrided T condition sample with free surface on the right.
Fig. A I.13 (a) DP recorded from needles in the case and DF images using the twinning reflections in circle (b) and rectangle (b) in (a).
Fig. A I.14 Microdiffraction pattern recorded from one side of the twin.
AII. Electron-beam-induced oxidation on nitrided 17-7 PH stainless steel

TEM foils were prepared in order to investigate the nitrided alloy microstructure. However, on thin nitrided TEM foils (HRTEM images could be acquired), significant differences were observed on the foil before and after electron beam exposure under high magnification.

Figure AII.1 shows a featureless ferrite grain in the nitrided case region. Apparently, some areas of the featureless grains were damaged. The ferrite grain was previously exposed under electron beam in TEM under high magnifications (> 500 k). The beam current under such magnifications is extremely high, on the order of $10^6$ e/nm$^2$.s ($\approx 10^6$ A/m$^2$). In addition to severely damaged ferrite grain, there are fringes in the neighboring austenite grain as well, indicating a possible electron beam dispersion around a highly-focused beam. Damaged areas were observed under higher magnifications, as shown in Fig. AII.2. In Fig. AII.2 (a), the damaged areas generally show circular shapes, being consistent with expected beam shape. However, under higher magnification (Fig. AII.2 (b)), detailed microstructure in the damaged area suggests the presence of a new phase in a different spot morphology. Some of these spots with low contrast were trailed by tails, implying a possible growth mechanism.
Fig. AII. 1 STEM image of nitrided 17-7 PH stainless steel with 7400 nitriding activity at 713 K. Free surface on the right.
Fig. AII. 2 STEM images of electron-beam-exposed ferrite.
The new phase was confirmed by TEM DPs, as shown in Fig. AII.3. From a pristine nitrided ferrite (Fig. AII.3 (a)), a DP consisting ferrite and nitride reflections were obtained. After beam exposure in TEM for 1 ~ 2 h, apparently, extra reflections appear in the DP and relative intensity between the ferrite and nitride changes as well, indicating the new phase formation. After beam exposure, the nitride reflection intensity is much stronger compared to that of ferrite, implying a possible electron-exposure-promoted nitride formation. Extra reflections appeared at the half reciprocal spacing of nitride (220) reflections, which may be ascribed to an electron-beam-induced nitrogen reordering in the highly nitrogen-deficient rocksalt-structured nitride. However, this is not consistent with nitrogen-ordered rocksalt-structured nitride, due to the absence of reflections at the half reciprocal spacing of nitride (200) reflections.

Fig. AII. 3 DPs acquired from electron-beam-damaged area. (a) Before and (b) after beam exposure.
A possible candidate of such phase is spinel-structured Fe$_3$O$_4$, whose DP was simulated along a [001] viewing direction, as shown in Fig. AII. 4. This matches with experimental DP shown earlier, suggesting an \textit{in situ} electron-beam-induced oxidation. The Fe$_3$O$_4$ formed on the ferrite is epitaxial and therefore the extra reflections are well-aligned with nitride reflections.

However, the source of oxygen atoms in TEM is a mystery, since the residual oxygen in the TEM column would be extremely low. One possible oxygen source of is from the foil surface, which inherited from plasma cleaning.
XEDS was used trying to confirm the presence of oxygen in the beam-damaged area. In the XEDS spectrum, oxygen peak is in a well-defined shape in the beam-damaged area (Fig. AII. 5 (c)), confirming the \textit{in situ} oxidation under the electron beam.

Fig. AII. 5 XEDS analysis on beam-damaged area. (a) area of interest showing where XEDS spectrum were acquired. (b) and (c) were acquired from point 1 and 2 respectively.

The oxide was much easier to identify in conventional BF and DF images. In order to facilitate the oxide growth, the foil was exposed to the electron beam in TEM for an
extended period of time. DF images acquired from extra reflections clearly show the oxide formation within the ferrite, where beam damage is most severe. In addition, oxide formation was also observed along the austenite–ferrite PB. This is very interesting, if it is related with cellular nitride formation investigated previously, implying it is the highly nitrogen-deficient nitride formed in the ferrite and on the phase boundary that is preferentially oxidized under the electron beam. The cellular morphology stemming from the phase boundary generally resembles the nitride revealed earlier. Moreover, the oxide particles in the ferrite grain also agree with nitride particle formed in the ferrite grain as discussed before.

Fig. AII. 6 DF images of a nitrided foil after 5 hour electron beam exposure.
One HRTEM image was acquired from the damaged ferrite area. The FFT of such image basically shows a spinel [001] zone axis, indicating the whole area transforms into oxide due to ferrite disappearance.

Fig. AII. 7 (a) A HRTEM image of electron-beam-damaged ferrite area and (b) the FFT of (a).
AIII. Various coating on aluminum alloys 5083 and 7075

We have been studying two Al alloys, 5083 H116 and 7075 T651, before and after deposition of DVD coating designed to enhance the corrosion resistance of these structural Al alloys. Alloy 5083 is a strain-hardenable Al-Mg alloy, whereas alloy 7075 is an Al-Zn-Mg age-hardenable alloy.

AIII.1 Characterization of base alloys

AIII.1.1 Microstructure

The microstructures of these two alloys were characterized by metallography, electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). For metallography purpose, samples from both alloys were cut along both a transverse direction (TD) and a rolling direction (RD). RD is the direction, in the plane of the sheet, perpendicular to the axes of the rolls during rolling. Materials along the RD usually exhibit elongated microstructures. TD is the direction perpendicular to the rolling direction.

7075 T651

For the 7075 alloy, Keller’s etchant is used, which is composed of 95 ml H₂O, 2.5 ml HNO₃, 1.5 ml HCl and 1.0 ml HF. The sample was polished to 1 μm diamond paste before etching. Etching was done by immersion until the microstructure could be resolved. The microstructure obtained in the TD is shown in Figs. AIII. 1 (a) and (b). The
~100 μm grains appear equiaxed. On the other hand, the grain structure along the RD is highly elongated. The length along the RD is similar to the grain size observed on the TD plane. The grain width ranges from 10 to 30 μm, hence the respect ratio is around 10:1. This suggests a pancake grain shape which is consistent with previous test results [A1].

Fig. AIII. 1 7075 etched by Keller’s etchant (a) TD 100x, (b) TD 400x, (c) RD 100x and (d) RD 400x

5083 H116

We had difficulty finding a good etchant for the 5083 alloy. The etchants tried were Keller’s and Weck’s (100 ml H₂O, 4 g KMnO₄, 1 g NaOH) and 10% H₃PO₄ at 50 °C.
Therefore, EBSD was used as an alternative. Two methods were tried to prepare EBSD samples. The first was mechanical polishing, finishing with colloidal silica on a VibroMet 2 vibratory polisher for 2 h. The other method is electropolishing in a solution of 100 ml methanol and 20 ml perchloric acid at 10 V voltage and room temperature for several minutes.

The EBSD results from a mechanically polished sample are shown in Fig. AIII. 2. The aluminum alloy matrix cannot be indexed after polishing, however, the inclusions can be readily identified. The indexed inclusions match with orthorhombic Al₆Mn, which is a common inclusion in 5083 alloy [A2, A3].
Fig. AIII. 2 EBSD result of 5083 H116. (a) overlay of index inclusion and image, (b) indexed orthorhombic Al₆Mn EBSD pattern and (c) indexed Al₆Mn inclusions from another region.

Electropolishing (EP) was employed in order to improve the EBSD indexing rate on the matrix. After EP, the sample surface is shiny but under the microscope there are many uniformly distributed pits (Fig. AIII. 3). Most pits correspond to the bright regions in the backscattered image, indicating the pits are formed by the removal of inclusions containing heavy elements. This is supported by the EDX mapping result shown in Fig. AIII. 4 that the pits are enriched in Fe, Mn and Si which is the same composition as the inclusion revealed before the EP as demonstrated later. This suggests a possible corrosion mechanism that inclusions act as local cathode with respect to the matrix. In fact, the Mn/Fe containing inclusions have noble potential compared to the aluminum matrix [A4].
Fig. AIII. 3 SEM and backscattered images of 5083 alloy after EP. (a) SEM and (b) backscattered image of uniformly distributed pits, (c) and (d) are enlarged area from (a).
The grain structure of the EP samples is revealed by EBSD. The grain size along the RD is again 100–200 μm in length, some 10 to 20 μm in width. In the TD, the grain size is still large and can be 100 μm or so. Therefore, the grain structure of 5083 is also pancake-shaped. The grain orientation along the RD displays similar color as shown in Fig. AIII. 5 (a) indicating a possible in <111> texture in the alloy.
Fig. AIII. 5 EBSD from 5083 (a) RD and (b) TD and (c) orientation legend of aluminum matrix
Moreover, though the grain size of 5083 is very large as revealed by EBSD, the orientation within a certain grain varies. Combined with TEM observations where a much smaller apparent grain size is observed, we conclude that subgrains are present, whose misorientation is less than $5^\circ$.

STEM images on these two alloys from an RD foil are shown in Fig. AIII. 6, and indicate the dimension of 5083 subgrains is around $1.5 \, \mu m$ by $0.5 \, \mu m$. For 7075, the subgrain appear to be about $2 \, \mu m$ by $1 \, \mu m$. These subgrains show a smaller aspect ratio compared to that revealed by metallography.
In sum, the grains for two alloys are both pancake-shaped $\approx 100 \, \mu m$ wide by $\approx 20 \, \mu m$ thick. Subgrain size shown in STEM image differs in two alloys. 7075 has larger subgrains $\approx 2 \, \mu m$ by $\approx 1 \, \mu m$, while the subgrain size in 5083 is around $\approx 1.5 \, \mu m$ by $\approx 0.5 \, \mu m$.

AIII.1.2 Inclusions

There are various kinds of inclusions present in aluminum alloys. The composition of inclusions in both alloys was characterized by XEDS (X-ray energy dispersive spectroscopy). For 7075, two kinds of inclusions are present those are that Fe/Cu-rich and
those that are Mg/Si-rich. Possible inclusions in 7075 are $\text{Al}_{25}\text{Mn}_5\text{Zn}$ [A5, A6], $\text{Al}_6(\text{Mn,Fe})$ [A7], $\text{Al}_7\text{Cu}_2\text{Fe}$ [A7], $(\text{Al,Cu})_6(\text{Fe,Cu})$ [A7, A8], $\text{Mg}_2\text{Si}$ [A8]. Compared with our XEDS results on 7075, $\text{Al}_7\text{Cu}_2\text{Fe}$ and $(\text{Al,Cu})_6(\text{Fe,Cu})$ are possible inclusions. XRD patterns also match with $\text{Mg}_2\text{Si}$. Quantitative EDX result on one inclusion is summarized in Table AIII. 1. The atomic ratio between Al, Fe and Cu suggests the possible inclusion is $(\text{Al,Cu})_6(\text{Fe,Cu})$. However, this could not be identified in a XRD pattern taken from 7075.

![XEDS result on 7075 alloy](image)

**Fig. AIII. 7 XEDS result on 7075 alloy**

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt.%</th>
<th>Error</th>
<th>At.%</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg K</td>
<td>0.00</td>
<td>+/-0.00</td>
<td>0.00</td>
<td>---</td>
</tr>
<tr>
<td>Al K</td>
<td>58.17</td>
<td>+/-2.29</td>
<td>75.28</td>
<td>+/- 2.97</td>
</tr>
</tbody>
</table>

Table AIII. 1 XEDS quantitative analysis on 7075 Fe/Cu-rich inclusion (circled area in Fig. 7)
<table>
<thead>
<tr>
<th>Element</th>
<th>K</th>
<th>Value</th>
<th>Error</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.00</td>
<td>+/-0.00</td>
<td>0.00</td>
<td>---</td>
</tr>
<tr>
<td>Ti</td>
<td>K</td>
<td>0.50</td>
<td>+/-0.50</td>
<td>0.37</td>
<td>+/- 0.81</td>
</tr>
<tr>
<td>Cr</td>
<td>K</td>
<td>0.45</td>
<td>+/-0.45</td>
<td>0.30</td>
<td>+/- 0.98</td>
</tr>
<tr>
<td>Mn</td>
<td>K</td>
<td>0.91</td>
<td>+/-0.91</td>
<td>0.58</td>
<td>+/- 1.44</td>
</tr>
<tr>
<td>Fe</td>
<td>K</td>
<td>21.83</td>
<td>+/-3.48</td>
<td>13.65</td>
<td>+/- 2.15</td>
</tr>
<tr>
<td>Cu</td>
<td>K</td>
<td>9.19</td>
<td>+/-5.32</td>
<td>5.05</td>
<td>+/- 2.89</td>
</tr>
<tr>
<td>Zn</td>
<td>K</td>
<td>8.95</td>
<td>+/-6.17</td>
<td>4.78</td>
<td>+/- 3.24</td>
</tr>
</tbody>
</table>

Fig. AIII. 8 shows basically three kinds of inclusions present in 5083, i.e. Fe/Mn-rich, Fe/Mn/Si-rich and Mg/Si-rich. From various papers, inclusions identified in 5083 alloy include Al₆Mn, whose structure is also identified by EBSD. Therefore, combined with XEDS result, these could be Al₆(Mn, Fe) [A5]. For Mg/Si-rich particles, it should be Mg₂Si [A3, A4] whose presence can also be identified in XRD pattern. Various other inclusions identified in 5083 include like MgO, Al(MnFe)Si, AlCrMg and SiO₂ [A3]. In XEDS mapping, the distribution of oxygen does not match with respect to silicon and magnesium, so their oxides are not possible. The Cr exhibits a uniform distribution in the matrix without any sign of segregation. A possible Al(MnFe)Si inclusion is present in the matrix, but this cannot be confirmed by XRD. The XRD pattern from the 5083 alloy is very complicated. Other than the FCC aluminum matrix and the Mg₂Si peaks identified from the pattern, there are extra peaks belongs to inclusions that cannot be related to any inclusion just mentioned.
Besides XEDS analysis from TD sample of both alloys, electron backscatter images from the RD of both alloys are shown in Fig. AIII. 9. The inclusion distribution of 5083 along
the RD is similar to that along the TD. However the inclusions in 7075 align themselves with the RD. The inclusions compositions are identified as the same to the inclusions along the TD.

Fig. AIII. 9 Electron backscatter images from RD of 7075 (a) and 5083 (b)

In both alloys, Mg₂Si can be identified. Other inclusions, though their compositions are clarified by EDX mapping, cannot be identified in XRD patterns. Element substitution occurs frequently in these intermetallic inclusions.

AIII. 1.3 Dispersoids and Fine Precipitates

**7075**

The STEM image shown in Fig. AIII. 6 (b) reveals a microstructure contains fine precipitates distributed uniformly in the matrix; their size is around 10 nm. The precipitates are identified as MgZn₂ (eta or eta prime phase) in the literature [A7, A9,
A10, A11]. These precipitates are soluble at elevated temperature but exhibit decreasing solubility with decreasing temperature. The dispersoids, on the other hand, are larger second phase particles. They normally have limited solubility even at high temperature. There are mainly three kinds of dispersoids in 7075: Al$_2$Zr [A6, A7, A12], Al$_{24}$Mn$_6$Zn [A5, A6] and Al$_{18}$Cr$_2$Mg$_3$ [A1, A6, A13, A14]. The size of dispersoids observed along the grain boundary (GB) is not larger than those within the grain, as illustrated in Fig. AIII. 10. This may be the reason for the absence of precipitate-free zone. Their composition as examined by XEDS is shown in Fig. AIII. 11. They are rich in Cr compared to the matrix. Therefore it is tentative to conclude these dispersoids observed in 7075 are Al$_{18}$Cr$_2$Mg$_3$.

Fig. AIII. 10 STEM images of 7075 (a) grain boundary included and (b) in the grain
TEM bright field images (Fig. AIII. 12) show the dispersoids can be heterogeneous nucleation sites for the fine precipitates. The dark field images (Fig. AIII. 13) of the dispersoids exhibit feature indicating there may be some planar faults in the structure. Al$_{18}$Cr$_2$Mg$_3$ has extensive planar faults along (111) [A7], suggesting that the dispersoids are Al$_{18}$Cr$_2$Mg$_3$. 

Fig. AIII. 11 XEDS on the 7075 alloy dispersoids
Fig. AIII. 12 Bright field image of dispersoids
Fig. AIII. 13 TEM bright field (a), (c) and dark field (b), (d) images from two regions

5083

A similar TEM study has been done on 5083. STEM imaging (Fig. AIII. 6 (a)) shows clear grains with only several dispersoids dispersed in the matrix. XEDS results (Fig. AIII. 14) indicate a Mn, Ni and Cr-rich particle. Diffraction pattern (Fig. AIII. 15) taken for the dispersoids matches a Al₆Mn [032] pattern simulated by JEMS. It is suggested that Mn is partly substituted by Ni and Cr. In order to confirm this, diffraction patterns from other zone axis are needed.
Fig. AIII. 14 XEDS on 5083 dispersoids
AIII.2 Zr coated 5083 alloy

Zirconium coated 5083 has been fabricated at UVa and studied. In the EB-DVD processing chamber, there are two target materials, 5083 alloy and pure Zr. The content of Zr was controlled by the rate of evaporation with respect to that of 5083 target. Before the coating process, plasma etching was applied on the substrate 5083 alloy. The coating covers the substrate relatively uniformly as shown in Fig. AIII. 16 (a), despite of some defects present on the surface that exposes the matrix (b). Small clusters appear in plane view. The film thickness revealed from the sample cross-section (Fig. AIII. 17) is less than 0.5 μm. The EDX results from the cross section (Fig. AIII. 18) suggest the concentration of Zr be around 12 at.%, as summarized in table 2. The image implies the adhesion between the coating and the substrate is poor; the film peeled off from the matrix. The coating along the cross-section edge is not continuous, as illustrated in Fig. AIII. 19, which indicates the coating peeled off during the cross-section sample cutting-
off preparation. There are visible cracks in the remaining coating as well, implying the coating may be inherently brittle.

Fig. AIII. 16 Coating surface on 5083 alloy plane view (a) uniform coating and (b) coating defect
Fig. AIII. 17 Cross-section image of Zr coated sample

Fig. AIII. 18 The EDX analyzed cross-section region

Table AIII. 2 Quantitative results of point 1 and 2 on the coating cross-section from Fig. AIII. 18

<table>
<thead>
<tr>
<th>At.%</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ca</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Cu</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1</td>
<td>0.29</td>
<td>84.34</td>
<td>1.22</td>
<td>0.22</td>
<td>-</td>
<td>1.17</td>
<td>0.44</td>
<td>0.46</td>
<td>11.86</td>
</tr>
<tr>
<td>Pt2</td>
<td>0.43</td>
<td>82.51</td>
<td>2.43</td>
<td>0.18</td>
<td>0.12</td>
<td>1.17</td>
<td>0.68</td>
<td>0.46</td>
<td>12.03</td>
</tr>
</tbody>
</table>
Zr-coated sample 504 went through electrochemical corrosion testing and showed promising corrosion improvement. The intact coating area looked the same as before the test. However, the localized pitting spots can be easily identified on the coated sample surface. Under the optical microscope, as shown in Fig. AIII. 20, it can be clearly seen that the coating was broken and the matrix alloy was exposed. Under the spalled coating surface, the base alloy was severely corroded and some crystallographic features were revealed. A TEM sample was prepared by the focus ion beam (FIB) lift-out technique. The sample was ion milled from a dense coating area, as illustrated in Fig. AIII. 21.
Fig. AIII. 20 (a) Localized pitting spot and (b) spalling coating interface and (c) localized coating failure region under SEM
During the lift-out thinning process, holes at the coating-matrix interface start to appear. Combined with the observation of voids beneath the coating on a cross-section, as shown in Fig. AIII. 17, these voids are present after the coating process. This could be a possible reason for poor coating adhesion. From the overview of the lift-out sample (Fig. AIII. 22), the interface region on the left is intact while two obvious voids are on the other side. The STEM image of the top of sample shows the protective Pt and Pd coating deposited before the lift-out. The Zr-coating can be easily identified just beneath protective coating; its thickness is less than 400 nm. However, between the Zr coating and the matrix, there is an unexpected white thin layer. Within the void region, there is an additional layer
detached from the coating. Contrast in the matrix is attributed to the heavy element-containing intermetallic inclusions, as demonstrated previously.

![Image of a lift-out Zr 504 sample](image)

Fig. AIII. 22 Overview of lift-out Zr 504 sample

The intact interface region is shown in Fig. AIII. 23. On top of the Zr coating layer, there is a weak contrast between the Pt and Pd coating, due to their similar atomic number. The Zr-coating appears to be porous. The presence of porosity may be due to the low processing temperature, which is typical zone I feature, as illustrated schematically in Fig. AIII. 24 [A15]. Though the coating matrix interface seems to be continuous under low magnification, there are still pores present at the interface. Detailed XEDS results were summarized in Table AIII. 3. It is clear that the Zr content in the coating area is around 20 at.%, which is slightly higher than that obtained from the coating cross-section.
The bright band between the Zr-coating and the matrix is higher in Zr content, around 40 at.%. Between the Zr-enriched band and the matrix, there is a thin oxygen-rich layer detected, which appears to have 25 at.% oxygen. It implies the matrix is oxidized for some reason before the coating was deposited. This can be another source of the poor adhesion between the coating and the matrix.

Fig. AIII. 23 Zr-coated sample intact interface region.
Fig. AIII. 24 Typical as-deposited microstructure as a function of substrate temperature and argon pressure during PVD process

Fig. AIII. 25 5083 coating area (504) analyzed by XEDS

Table AIII. 3 Quantitative analysis of XEDS point shoot on Zr-coated sample 5083 (504)
The bright field (BF) images in Fig. AIII. 26 from the Zr coating show nano-crystallinity, the grain size being around 50 nm. The Zr-enriched layer at the interface distinguishes itself from the coating by exhibiting a layered non-crystalline structure.

<table>
<thead>
<tr>
<th>At.%</th>
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<th>Al-K</th>
<th>Si-K</th>
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<th>Fe-K</th>
<th>Ni-K</th>
<th>Zr-K</th>
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<tbody>
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<td>0.49</td>
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<td>1.54</td>
<td>0.36</td>
<td>6.58</td>
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<tr>
<td><em>Pt2</em></td>
<td>3.03</td>
<td>1.78</td>
<td>70.01</td>
<td>--</td>
<td>0.19</td>
<td>2.40</td>
<td>--</td>
<td>--</td>
<td>22.60</td>
</tr>
<tr>
<td><em>Pt3</em></td>
<td>12.94</td>
<td>1.11</td>
<td>64.99</td>
<td>0.83</td>
<td>0.17</td>
<td>2.53</td>
<td>0.65</td>
<td>--</td>
<td>16.77</td>
</tr>
<tr>
<td><em>Pt4</em></td>
<td>9.71</td>
<td>0.35</td>
<td>69.86</td>
<td>--</td>
<td>0.24</td>
<td>3.88</td>
<td>--</td>
<td>0.20</td>
<td>15.76</td>
</tr>
<tr>
<td><em>Pt5</em></td>
<td>25.35</td>
<td>2.54</td>
<td>26.78</td>
<td>--</td>
<td>0.57</td>
<td>2.45</td>
<td>2.10</td>
<td>0.23</td>
<td>39.31</td>
</tr>
<tr>
<td><em>Pt6</em></td>
<td>27.85</td>
<td>2.85</td>
<td>26.50</td>
<td>--</td>
<td>0.47</td>
<td>2.39</td>
<td>2.04</td>
<td>--</td>
<td>37.90</td>
</tr>
<tr>
<td><em>Pt7</em></td>
<td>24.90</td>
<td>36.23</td>
<td>38.42</td>
<td>0.33</td>
<td>0.11</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td><em>Pt8</em></td>
<td>0.73</td>
<td>4.16</td>
<td>95.11</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>--</td>
</tr>
</tbody>
</table>

Fig. AIII. 26 BF images from two areas of Zr-coated sample 504
The diffraction pattern (DP) from the coating is a polycrystalline ring pattern. The square ratios of the ring radius to the innermost ring are 1, 2, 3, 4, 5, 6, 8 and 11. This matches a primitive lattice DP in principle. Another DP from the interface region is taken, which includes diffraction information from the Al matrix. The matrix Al grain was tilted to a $\langle \bar{1}12 \rangle$ zone axis. The $(1\bar{1}1)$ diffracted beam is on the third diffraction ring which can be used to calibrate the coating lattice spacing ($d_{\text{spacing}}$). By adopting the lattice parameter of pure aluminum ($a = 0.405$ nm), the $d_{\text{spacing}}$ of the coating can be calculated as summarized in Table AIII. 4. The calculation indicates the coating is a new phase with a primitive cubic structure. The dark field (DF) images (Fig. AIII. 28) of the coating confirm the innermost rings $(001)/(011)$ originates from the coating and the grain size approaches 50 nm in DF from the $(111)/(200)$ rings.

Fig. AIII. 27 DP of the Zr coating (a) and the DP from the coating/matrix interface (b)
Table AIII. 4 Calculated Zr coating plane spacing

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>d spacing nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.405</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0.286</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.234   Al (111)</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.203</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0.181</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0.165</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0.143   Al (220)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>0.135</td>
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</tbody>
</table>

In order to confirm the observation in sample 504, another lift-out sample was prepared on sample 503 which is also Zr-coated but with a different Zr content. The BF image

Fig. AIII. 28 DF images of the Zr coating, (a) from inner ring (001)/(011) and (b) from ring (111)/(200)
(Fig. AIII. 29 a) shows similar coating microstructure as sample 504, as does the DP. The XEDS analysis (summarized in Table AIII. 5) on the coating shows a higher Zr content, approaching 25% and distributed more uniformly. There is still an appreciable amount of oxygen at the interface region compared to the oxygen content through the coating thickness.

Fig. AIII. 29 (a) BF of Zr-coated 5083 (503) and (b) DP from the coating
According to the Al-Zr phase diagram, the first equilibrium phase is ZrAl₃, which is body centered tetragonal (BCT) (space group 139, I4/mmm). However, this phase
(a=b=0.39993 nm and c=1.7283 nm) cannot match the coating ring DP observed due to the large lattice spacing along the c direction. However, there is one metastable phase Al$_3$Zr (space group 221, Pm3m), known as the L1$_2$ structure which fits the profile [A16].

The lattice parameter of this cubic ordered phase is 0.401 nm, which is nearly the same as the Al matrix. This is the reason for the observation of the Al matrix diffracted beam coinciding with the coating ring pattern. Due to its ordered nature, “forbidden” diffraction rings of the FCC structure are present but weak, as observed in the DP. Therefore, instead of the equilibrium BCT ZrAl$_3$ phase, the coating possesses a metastable L1$_2$ structure.

**Fig. AIII. 31** Equilibrium phase diagram of Al-Zr binary alloy system

Al$_3$Zr is reported to possess a higher open-circuit potential compared to Al alloys, which was also confirmed in the corrosion tests. The passive film on Al$_3$Zr coating surface is different compared to the Al matrix, due to the presence of Zr in the film. Moreover,
zirconium oxide is noble compared to aluminum oxide. Therefore, the noble Zr available in the coating increases the coating pitting potential.

AIII. 3 Ta-coated 5083 alloy
Tantalum was also applied on the 5083 substrate following the same procedure as Zr-coated samples. The Ta-coated sample after electrochemical test shows some cracks on the coating surface and the pitting region can be easily identified as well, as shown in Fig. AIII. 32. The XEDS results on Ta-coated surface (Table AIII. 6) indicate the coating is pure Ta.

![Ta-coated sample after electrochemical test (a) and exposed base alloy in pitting region (b)](image)

Fig. AIII. 32 Ta-coated sample after electrochemical test (a) and exposed base alloy in pitting region (b)
Fig. AIII. 33 Localized pitting region boundary where XEDS analysis was carried out

Table AIII. 6 XEDS analysis on Ta coated 5083 sample

<table>
<thead>
<tr>
<th>At.%</th>
<th>Mg-K</th>
<th>Al-K</th>
<th>Ta-L</th>
</tr>
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<td>Pt3</td>
<td>--</td>
<td>--</td>
<td>100.0</td>
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<tr>
<td>Pt4</td>
<td>2.6</td>
<td>97.4</td>
<td>--</td>
</tr>
<tr>
<td>Pt5</td>
<td>--</td>
<td>--</td>
<td>100.0</td>
</tr>
</tbody>
</table>

On the sample cross-section (Fig. AIII. 34 (a)), the coating is not continuous, indicating poor adhesion between the coating and matrix. The coating thickness is around 1 µm. The plan view of the coating indicates that some coating was removed along the cut edge and there is also some cracking visible on the coating. The wavy Ta coating morphology (Fig. AIII. 35) is different from that seen on the Zr-coated sample.
Fig. AIII. 34 (a) Cross-section of Ta-coated 5083 and (b) coating from plan view

Fig. AIII. 35 The surface morphology of pure Ta-coated 5083 sample

One lift-out sample was prepared from the coating surface. The coating was continuous as observed in Fig. AIII. 36. The absence of porosity at the coating interface indicates improved adhesion between the coating and the matrix. A closer look between the
coating and substrate shows there is an interlayer that appears bright in the STEM image. The XEDS results indicate the coating as pure Ta while the Ta content of the interlayer is less than 50%, as shown in Table AIII. 7. Another point worth noting is that the oxygen content is much lower compared with the oxygen content detected in the Zr coating. The low oxygen contamination at the coating interface possibly ensures better adhesion of the Ta coating.

Fig. AIII. 36 Overview of pure Ta-coated 5083 sample
The BF image shown in Fig. AIII. 38 indicates that the grains in the pure Ta coating are elongated. The DP acquired from the area exhibits ring patterns. The ring radius square
ratios are 1, 2, 3, 4, 5, 6, 7, implying the coating is BCC which is the equilibrium structure of Mo at room temperature. The DF images taken from the innermost ring confirm the grains in the coating are elongated to more than 100 nm which is totally different from the nanocrystalline equiaxed Zr coating.

Fig. AIII. 38 BF image of pure Ta coating (a), (b) DP from the coating area, (c) and (d) DF images from innermost ring.
At the coating interface, larger grains are observed. As indicated by XEDS, the Ta content in these grains is low compared to the coating. The Al matrix is tilted to a <011> zone axis. In the BF image (Fig. AIII. 39 a), the matrix is dark compared to the coating interlayer. In the coating interface DP, there is a poorly defined speckled ring. DF image from this ring shows grains in the interlayer. Due to the low Ta content, these grains can be FCC, as observed in the 10% Ta coated sample shown later.
Fig. AIII. 39 (a) BF image of pure Ta coating interface, (b) DP from the interface region, (c) DF from Al matrix diffracted beam and (d) DF from diffracted ring pattern

AIII. 4. Ta-coated 5083 (513 10 at\%)

In addition to pure Ta-coated 5083, partial Ta-coated 5083 samples were also fabricated. Unfortunately, the spallation of the coating on the as-received sample is marked. Under the SEM (Fig. AIII. 40 a), the contrast in the backscatter image indicates two layers in the coating, with lower Ta on the top part of the coating than on the bottom. The coating surface exhibits flake-like morphology. The XEDS analysis confirms this two-layer structure. The average Ta content through the coating thickness is only around 5 at.\%, while the content doubles in the lower part of the coating, as summarized in the Table AIII. 8.

![Fig. AIII. 40 (a) backscatter and (b) SEM images of 10% Ta-coated 5083 sample](image-url)
Fig. AIII. 41 Area analyzed by XEDS point shoot of 10 at.% Ta-coated sample 5083.

Table AIII. 8 XEDS analysis on 10% Ta-coated 5083 sample

<table>
<thead>
<tr>
<th>At.%%</th>
<th>Al</th>
<th>Mg</th>
<th>Mn</th>
<th>Ta</th>
<th>Fe</th>
<th>Cr</th>
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<tr>
<td>Point 1</td>
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<td>1.03</td>
<td>5.05</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Point 3</td>
<td>80.3</td>
<td>6.0</td>
<td>1.88</td>
<td>11.8</td>
<td>1.18</td>
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</tr>
<tr>
<td>Point 5</td>
<td>92.8</td>
<td>6.67</td>
<td>0.51</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

The STEM image, Fig. AIII. 42, shows a multilayered coating structure. The top coating surface consists of two distinct regions, showing dark and cluster-like regions. There is a layered structure beneath the top coating surface. Under the layered structure is the uniform coated region, where the Ta content is much higher than expected. The interface region between the coating and the matrix is thick and porous.
Fig. AIII. 42 Overview STEM of 10% Ta-coated 5083 sample

Fig. AIII. 43 Area analyzed by XEDS point shoot of 10% Ta-coated sample 5083

Table AIII. 9 XEDS analysis on 10% Ta-coated 5083 sample

<table>
<thead>
<tr>
<th>At.%</th>
<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Ti</th>
<th>Mn</th>
<th>Ta</th>
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<tr>
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<td>16.5</td>
<td>--</td>
<td>69.9</td>
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<td>0.67</td>
<td>12.9</td>
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<tr>
<td>Pt3</td>
<td>15.6</td>
<td>3.18</td>
<td>62.4</td>
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<td>0.94</td>
<td>17.9</td>
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<tr>
<td>Pt4</td>
<td>17.0</td>
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<td>60.2</td>
<td>0.16</td>
<td>0.80</td>
<td>18.9</td>
</tr>
<tr>
<td>Pt5</td>
<td>3.38</td>
<td>--</td>
<td>96.1</td>
<td>--</td>
<td>--</td>
<td>0.54</td>
</tr>
<tr>
<td>Pt15</td>
<td>5.84</td>
<td>--</td>
<td>93.0</td>
<td>--</td>
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<tr>
<td>Pt4</td>
<td>20.7</td>
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<td>--</td>
<td>0.71</td>
<td>28.2</td>
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<tr>
<td>Pt5</td>
<td>12.8</td>
<td>3.49</td>
<td>60.8</td>
<td>--</td>
<td>1.12</td>
<td>21.8</td>
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</table>
In the magnified top coating, as shown Fig. AIII. 44, the dark region shows planar facets, while the other regions show clusters of small particles. Based on XEDS result, the dark regions are dominated by Al, while the cluster-like regions are Ta-enriched. The clusters appear to be nanoparticles from the coating process, similar to what is observed in Zr-coated sample. The presence of the Al-dominant grains suggests the coating fabrication condition is close to the equilibrium condition, because the solid solubility of Ta in Al is negligible. The growth of Al grains excludes the Ta from the grain.

Fig. AIII. 44 Magnified top coating part of 10% Ta-coated 5083 sample
The BF image (Fig. AIII. 45 (a)) of the same region implies that Ta nano-grains are only a few nanometers in size. The Al grains are much larger and have defects in them. The DP taken from the Ta cluster region shown in Fig. AIII. 45 (b), displays a polycrystalline ring pattern. On the basis of ring radius square ratios (3, 4, 8, 11), the Ta coating particles have an FCC structure, suggesting the Al dominates the structure since Al content approaches 90 at.%. Another DP taken from the Al grain confirms the single FCC grain in a <001> zone axis orientation. The oxygen distribution provided by XEDS is similar to the Ta distribution. The oxygen is depleted in the Al grain, but abundant in Ta-rich nanoparticles. In short, the top part of the coating consists of two FCC phases, one the Al matrix and the other Ta-containing nanoparticles.
There is more Ta in the layer structure beneath the top part of the coating and appears brighter. The BF images still shows cluster-like particles but without any trace of Al grains. The DP shown in Fig. AIII. 44 indicates the coating is crystalline but the structure is different and the pattern is more complicated compared to the Ta-rich particles on the top. The ring radius square ratio measured is close to 2, 3, 5, 7, 8, 10, 12, which implies it is BCT structure. The equilibrium phase shown in the phase diagram is BCT Al$_3$Ta. There is no L1$_2$ structure reported for Al$_3$Ta, as there was for Al$_3$Zr. Al$_3$Ta can form an ordered BCT phase known as D0$_{22}$ structure. In the DP, there is no sign of ordered structures.

Fig. AIII. 45 (a) the BF image of top part of the coating, (b) the DP of Ta-containing clusters and (c) the DP of Al grain.
The coating is uniform at the bottom as shown in the STEM image (Fig. AIII. 47 a), while the interface region is porous and as thick as 100 nm. From the XEDS results, the Ta content in the uniform coating is as high as 50 at.% and the interface region is basically a porous oxide. BF images at the interface (Figs. 47 (b) and (c)) from two different areas show the oxide is porous and thus poor adhesion between the coating and...
substrate can be expected. There is no sign of a complex oxide in the DP taken from the interface region. The Al matrix grain is tilted to a $\langle \overline{1}14 \rangle$ zone axis and as can be seen, two diffracted beams (220) and (3$\overline{1}1$) are almost on the ring patterns. Once again, the d-spacing of the coating can be calibrated by these two beams as summarized in the table below. The ring radius square ratios on the DP are 1, 2, 3, 4, 5, implying a possible simple cubic or BCC structure. The lattice parameter of BCC Ta at room temperature is 0.330 nm. The corresponding planar spacing is also calculated and is close to the measured one, as summarized in table 10. Over 50 at.% Ta can dominate the coating structure by its inherent BCC structure. But because it is not pure Ta, a smaller lattice constant can be expected by the presence of Al atoms.
Fig. AIII. 47 (a) Magnified STEM image of coating interface, (b) and (c) two areas of porous oxide interface and (d) DP of the coating interface

<table>
<thead>
<tr>
<th>Ring Radius square ratio</th>
<th>Al matrix point 0.405 nm</th>
<th>$d_{\text{spacing}}^{\text{measured}}$ (nm)</th>
<th>$d_{\text{spacing}}^{Ta}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.212</td>
<td>0.233</td>
</tr>
<tr>
<td>2</td>
<td>(220)</td>
<td>0.146</td>
<td>0.165</td>
</tr>
<tr>
<td>3</td>
<td>(3-11)</td>
<td>0.122</td>
<td>0.135</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.106</td>
<td>0.117</td>
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</table>
The Ta coating on 5083 sample was also studied. The coating adhesion is poor due to porous oxide at the interface. Two phases are identified on the coating top part, FCC Al grain and FCC Ta-containing nanoparticles. The layered structure observed in the coating is BCT Al$_3$Ta, following the equilibrium phase diagram. The uniform coating at the bottom is probably a BCC structure dominated by the high Ta content. The multiphase coating system can be beneficial for corrosion performance. Because different phases normally possess different open-circuit corrosion potentials, different phases present in the coating can redirect and redistribute the corrosion current instead of causers of pitting. In addition, the presence of Ta in the oxide film can improve the pitting potential as well.

Fig. AIII. 48 Equilibrium phase diagram of binary Al-Ta system
AIII. 5. 40 at.% Mo-coated 5083

Mo was incorporated in the Al-dominated coating as well. Unfortunately, coating spallation was observed in the as-received coated 5083 sample. There are two layers in the Mo coating as shown in Fig. AIII. 49 (a). The surface of the coating shows some scattered clusters. From the tilted image, defects in the coating can be seen and this can be attributed to the observation of a two-layered coating. The XEDS results obtained from the coating indicate the Mo content is high through the coating thickness but is lower at the bottom of the coating. It is rich in oxygen.
Fig. AIII. 49 (a) SEM image of Mo coating spalling region, (b) Mo coating surface morphology and (c) spalled coating observe with 40 deg tilting.

Fig. AIII. 50 Area analyzed by XEDS point shoot of 40% Mo-coated sample 5083

Table AIII. 11 XEDS analysis on 40% Mo-coated 5083 sample
A TEM sample was prepared by FIB lift-out to reveal the coating from the cross-section and the interface region. The overview of the coating is shown in Fig. 51 (a). The coating appears uniform although some pores are present near the bottom of the coating. The presence of these pores can be the reason for the observation of coating delamination. At the interface region, it can be clearly seen in Fig. 51 (b) that the coating is already detached from the matrix. XEDS results suggest variation of Mo content near the coating interface region but generally lower than the content detected from a plan view sample. A higher oxygen content is observed at interface region which is the same as was found on previous coatings. Surprisingly, there is an appreciable amount of La detected at the interface region, which may deteriorate the coating adhesion by its large atomic size compared to Mo. In order to verify the presence of La, another mapping was done on the same area, as illustrated in Fig. 53. The mapping demonstrates the La is present and accompanied by oxygen at the interface and is distributed within a width of 100 nm. This can be the reason for the readily delaminated coating interface -- the extremely large atomic size of La strains the interface more than Mo.
Fig. AIII. 51 STEM image of (a) Mo coating on 5083 sample and (b) the coating interface.
Fig. AIII. 52 Area analyzed by XEDS point shoot of 40% Mo-coated sample 5083.

<p>| | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
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<td>4.09</td>
<td>1.75</td>
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<td>16.73</td>
<td>25.17</td>
<td>4.35</td>
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<td>24.65</td>
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<td>2.95</td>
<td>1.06</td>
<td>1.32</td>
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<td>0.02</td>
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<td>--</td>
<td>6.63</td>
<td>6.03</td>
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</table>

Table AIII. 12 XEDS analysis on 40% Mo-coated 5083 sample
The gap between the Mo coating and the matrix is clearly shown in the Fig. 54. The DP taken at the interface suggests the coating may be amorphous, since only one diffuse ring is observed. In order to confirm this observation, another DP was taken from the top of the coating which shows likewise. Therefore it is tentatively concluded that the Mo coating is amorphous distinguishing itself from other coatings studied. The exact reason for the amorphous nature of this coating is not clear.
Fig. AIII. 54 BF image of Mo coating interface (a), DP from the coating interface (b) and DP from the coating top part (c)
The delaminated coating area was part of the lift-out TEM sample and was studied by XEDS. Though no La is detected, the amount of Mo is minimized as well. In addition, enrichment of oxygen and magnesium in the coating remnant is shown clearly.

Fig. AIII. 55 STEM image of delaminated Mo coating region

Fig. AIII. 56 Area of delaminated Mo coating analyzed by XEDS point shoot

Table AIII. 13 XEDS analysis on delaminated Mo coating
<table>
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<tr>
<th>At.%</th>
<th>O-K</th>
<th>Mg-K</th>
<th>Al-K</th>
<th>Si-K</th>
<th>Cr-K</th>
<th>Mn-K</th>
<th>Fe-K</th>
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