INNER NITRIDING BEHAVIOR AND MECHANISM IN STAINLESS STEELS AT 753 K AND 623 K

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ABSTRACT
Stainless steel specimens were plasma nitrided at 753 K and 623 K to describe the difference in inner nitriding behavior. The high temperature nitriding was characterized by precipitation of chromium nitrides in the surface layer. No microstructure change was seen below the nitriding front end. The low temperature nitriding was characterized by localization in the nitrogen supersaturation. This behavior was analyzed and described by observation and measurement of microstructure below the nitriding front end. This localized nitrogen supersaturation was driven by the grain boundary diffusion of nitrogen atoms. The effect of this localization on the microstructural change at the depth of 435 μm from the surface was further discussed to describe the essential mechanism of nitrogen supersaturation. This difference in these two inner nitriding processes was also theoretically discussed by the diffusion model.

Keywords: AISI316, High temperature plasma nitriding, CrN precipitation, Low temperature plasma nitriding, Homogeneous nitriding, Heterogeneous nitriding, Localized nitrogen supersaturation, Nitrogen grain-boundary diffusion

1. INTRODUCTION
The plasma nitriding under the higher holding temperature than 723 K, has been utilized as a commercial surface treatment; e.g., the ion nitriding by using the DC-plasma and the radical nitriding by the DC-pulse plasma as surveyed in [Aizawa & Sugita, 2012]. This high temperature plasma nitriding of tool and stainless steels was characterized by the chromium nitride precipitation [Granito, Kuwahara & Aizawa, 2002; Aizawa, & Sugita, 2013]. Hence, the hardening by these plasma nitriding was driven by the precipitation strengthening mechanism.

Low temperature plasma nitriding was discovered as a non-traditional surface treatment [Bell, 2002]. This nitriding process in the austenitic stainless steels is characterized by the nitrogen supersaturation into γ-lattices without precipitation of chromium and iron nitrides [Dong, 2011; Aizawa, 2018].

Since the nitrogen solute works as an alloying element in the γ-lattices by its occupation with the octahedral vacancy sites, the nitrogen supersaturated γ-lattices expand by themselves. This lattice expansion results in the increase of elastic energy density in each lattice, which drives the phase transformation from γ-phase to α’-phase [Aizawa, 2017; Farghali & Aizawa, 2019]. The misfit distortion between the nitrogen supersaturated and unsaturated γ-lattices is compensated by the plastic straining [Aizawa, 2018; Aizawa & Yoshihara, 2018]. This intense plastic straining accompanies with the refinement of crystalline structure during the nitrogen supersaturation. In particular, after the analysis in [Aizawa, Yoshihara, Morikawa, & Yoshihara, 2019], the nitried stainless steel layer at 673 K has fine, two phase γ – α’ structure with the average grain size less than 100 nm.

Almost all the previous studies [Dong, 2011; Brogioli, 2015] were performed by using the DC/DC-pulse plasmas at 673 K. In addition, the nitried layer thickness was reported to be less than 10 to 20 μm. Few microstructural analyses were reported on the nitrogen depth profile, the plastic strain distribution and the crystalline structures. Furthermore, few studies were reported on the effect of holding temperature below 673 K on the nitrogen supersaturation as well as the change of phase and microstructures. Difference in the inner nitriding mechanism of AISI316 stainless steels at 673 K and 623 K was first described by [Aizawa, 2018; Aizawa & Yoshihara, 2018]. The inner nitriding homogeneously advances into the depth of substrate at 673 K; the phase transformation, the plastic straining and the microstructure refinement take place concurrently with the nitrogen supersaturation. While, this nitrogen supersaturation localizes in the inner nitriding process at 623 K and results in heterogeneous microstructuring. More precise analysis is needed to describe the material scientific aspects on the heterogeneous nitriding as well as the localization of nitrogen supersaturation.
In the present paper, the stainless steel specimen with the normal grain size of 15 μm is prepared for plasma nitriding at 623 K and 753 K to describe the difference of inner nitriding behavior and mechanism between low and high temperature plasma nitriding. In the former, homogeneous nitriding process accompanies with nitride precipitation and its behavior is completely governed by the body diffusion of nitrogen atoms into the depth. No nitriding process takes place below the nitriding front end. This difference in inner nitriding between two processes is much discussed. In the latter, homogeneous nitriding process follows the heterogeneous nitriding where the original coarse grains are selectively modified and refined by localization of nitrogen supersaturation. Furthermore, the microstructural change even at the depth of 435 μm from the surface is further investigated to describe this heterogeneous nitrogen supersaturation.

2. EXPERIMENT PROCEDURE
2.1 RF-DC plasma nitriding system

The present RF (Radio Frequency) – DC (Direct Current) plasma nitriding system consists of the vacuum chamber, the evacuation system, the DC-RF generators working in the frequency of 2 MHz, the gas supply of N₂ and H₂, and, the heating unit located under the cathode plate as illustrated in Figure 1. In the nitriding at 753 K, the specimens were placed on the DC-biased table and subjected to RF-DC plasmas under the nitrogen and hydrogen mixture gas flow.

In particular, the hollow cathode device is utilized in the nitriding at 623 K to confine the RF-ignited nitrogen- and hydrogen plasmas and to have higher ion and electron densities than those in the standard nitriding process. The maximum nitrogen ion density reached to 3 x 10¹⁷ ions/m³, which was equivalent to that by the electron beam assisted plasma nitriding in low pressure.

![Figure 1. RF-DC plasma nitriding system.](image)

In this experimental set-up, the specimen was placed and fixed in the electrically conductive hollow, which was connected to the DC-bias. The nitrogen and hydrogen mixed gas was supplied from the either inlet of hollow. After placing the sample in the hollow cathode setup, the chamber was evacuated down to 0.1 Pa in pressure, and, then filled with the nitrogen gas with the flow rate of 160 ml/min until the pressure was constant by 300 Pa before heating up to the specified holding temperature. Next, the sample was pre-sputtered for 1.8 ks to remove any oxide passive layer from its surfaces. This pre-sputtering process was operated by using the DC discharge with the bias of -600 V in pure nitrogen gas by 60 Pa.

2.2 Plasma nitriding process conditions

After the same presputtering in nitrogen gas flow, the RF-DC plasma nitriding system was commonly utilized to make nitriding at 753 K and 623 K respectively for 14.4 ks (or 4 hours) at the pressure of 70 Pa. The plasma nitriding conditions were slightly different between high and low temperature plasma nitriding processes. In the former, the RF-voltage was 250 V, and, the DC-bias, -400 V; the RF-voltage was also 250 V but the DC-bias, -500 V in the latter.

The mixture of nitrogen and hydrogen gasses was provided to have the ratio of 160 ml/min for nitrogen to 30 ml/min for hydrogen. After the nitriding process, the sample was cooled down in the vacuum chamber to prevent from surface contamination.

2.3 Measurement and observation

The nitrided specimens were analyzed by the X-ray diffraction (XRD; Rigaku SmartLab), SEM (Scanning Electron Microscopy; HITACHI SU-70), and, EDX (Electron Dispersive X-ray spectroscopy) for material characterization from the surface down to the specified depth. EBSD (Electron Back-Scattering Diffraction) was also used to analyze the microstructure refinement, the phase transformation and the plastic straining. The inverse pole figure was utilized to describe the crystalline structure. The phase mapping was performed to understand the phase distributions from the surface to the depth. The KAM (Kernel Average Misorientation) was also used to represent the intergranular misorientations among the neighboring grains. In particular, the ion-milling was utilized to form the fine, smooth cross-section of nitrided AISI316 specimen for SEM-EDX and EBSD analyses.

3. EXPERIMENTAL RESULTS

High and low temperature plasma nitriding treatments were performed to describe the difference in the inner nitriding process. In particular, precise microstructure analyses were conducted to state the superiority to lower temperature plasma nitriding as a surface treatment of tool and die steels.

3.1 Inner nitriding at 753 K

Figure 2 depicts a typical cross-sectional optical-microscopic image of nitrided tool steels at 753 K after nittar solution etching. Although no white layers were seen in Figure 2, the nittar-corroded layer corresponds
to the CrN (Chromium nitride) precipitated zone from the surface. This layer corresponds to the nitrided layer; its thickness is estimated to be 50 \( \mu m \).

3.2 Inner nitriding at 623 K

The holding temperature was lowered from 753 K down to 623 K; high density plasma nitriding with use of the hollow cathode device was employed to describe the low temperature inner nitriding of AISI316. As estimated by Figure 4, this inner nitriding at “B” far below the master curve, must be different from “A” above the master curve. Let us first analyze the structure of nitrided AISI316.

The XRD diagram of bare AISI316 stainless steels before nitriding is characterized by two \( \gamma \)-phase peaks as depicted in Figure 5; e.g., \( \gamma \) (111) is detected at 20 = 44.3\(^o\), and, \( \gamma \) (200), at 20 = 51.7\(^o\), respectively. In the high temperature plasma nitriding, the diffusing nitrogen reacted mainly with chromium in AISI316 to synthesize the CrN precipitates. In those cases, the original \( \gamma \)-phase peaks remain to be detected at the same 20 angles as before nitriding, together with the new peaks to CrN. As shown in Figure 5, these two \( \gamma \)-peaks before nitriding shifted in the lower 20 angles after nitriding at 623 K for 14.4 ks. That is, \( \gamma \) (111) shifted from the original position at 44.3\(^o\) to 40.5\(^o\), and, \( \gamma \) (200), from 51.7\(^o\) to 46.6\(^o\), respectively. This implies that nitrogen solute atoms do not react with the constituent atoms such as iron and chromium in AISI316 but work as a constituent alloying element in the \( \gamma \)-lattice. Due to the first principle calculation on this alloying process [Domain, et al., 2004], the nitrogen solute atoms occupy the octahedral vacancy sites in the \( \gamma \)-lattices in AISI316.

This in situ occupation of the diffusing nitrogen solutes with the vacancy site in the \( \gamma \)-lattices during the low temperature plasma nitriding, characterizes the nitrogen supersaturation process. Hence, this process is governed by the reaction between the diffusing nitrogen atoms and the \( \gamma \)-lattice as well as the diffusion mechanism of nitrogen atoms into the depth of substrate.

Let us reconsider the inner nitriding mechanism on Figure 4. High temperature plasma nitriding including “A” is driven by the nitrogen diffusion with the chromium nitride precipitation into the original matrix. The holding temperature decreases with increasing the
nitriding duration time since the nitrogen diffusion rate reduces with decreasing the holding temperature. As far as using the normal plasma nitriding, the temperature of 673 K must be the lowest limit in the inner nitriding. On the other hand, low temperature plasma nitriding, including “B” is driven by the nitrogen diffusion with the nitrogen supersaturation and alloying into the original γ-phase crystalline cells. In particular, when the holding temperature is far below 673 K like “B”, every inner nitriding process must advance by this nitrogen diffusion and supersaturation process, irrespective of the nitriding time.

3.3 Homogeneous inner nitriding at 623 K

SEM-EDX analyses were performed to describe the nitrided layer from the surface. As shown in Figure 6, The nitrided layer is formed uniformly even at 623 K; the nitriding front end (NFE) locates at the depth of 30 μm. This layer thickness is a little thinner than 50 μm by the nitriding at 753 K in Figure 2.

The nitrogen mapping in Figure 7 by EDX analysis proves that high nitrogen concentration is measured above this NFE. This reveals that thick nitrided layer with high nitrogen solute concentration is formed by nitrogen supersaturation into AISI316 matrix.

Let us reconsider the elastic straining into this homogeneously nitrided layer from XRD analysis. The original γ-lattice expands by itself by housing a nitrogen solute as an alloying element in its inside. The elastic strain (ε) is calculated by the difference of lattice constants before and after nitriding in Figure 5; e.g., ε = 9% from the peak shift of γ (111), and, ε = 10% in case of γ (200), respectively. This high elastic energy by lattice expansion results in the phase transformation from γ to α’ in the nitrogen supersaturated γ-lattices. That is, the homogeneously nitrided layer might consist of γ- and α’-phases.

In each austenitic grain in AISI316, a part is nitrogen supersaturated to elastically expand by itself; the other part of grain is not nitrogen supersaturated and remains as before. As discussed in [Aizawa & Yoshino, 2018], this misfit of elastic distortion must be compensated by the plastic straining in the unsaturated lattices. This plastic straining accompanies with spin rotation for each subgrain and with grain size refinement. That is, the homogeneously nitrided layer might have fine crystalline structure. Let us experimentally demonstrate the above estimate by EBSD.

Figure 6. SEM image on the cross-section of the nitrided AISI316 at 623 K.

Figure 7. Nitrogen mapping on the cross-section of nitrided AISI316 at 623 K.

Figure 8. KAM and phase mapping on the cross-section of nitrided AISI316 specimen at 623 K.
transformation and plastic straining processes reflects on the microstructural change.

Figure 9 depicts the IPF (Inverse Pole Figure) distributions in three axes on the cross-section of nitrided AISI 316 specimen at 623 K. The grain size refines only in the homogeneously nitrided region; as had been reported in [Aizawa, 2018], the average grain size is refined to be less than 0.1 μm.

![IPF distribution on the cross-section of nitrided AISI316 specimen at 623 K.](image)

Although the grains are never homogeneously nitrided even above NFE, they are modified to change their crystallographic orientation. In particular, this local modification behavior is described closely below NFE. In the following, two grains are selected for analysis of heterogeneous nitriding behavior; e.g., the Grain-A and Grain-B in Figure 9.

### 3.4 Heterogeneous inner nitriding at 623 K

As shown in Figure 9, the phase transformation from γ- to α’-phase and high plastic straining partially take place on both grains. The original Grain-A with the orientation (211) in the ND-axis is modified to have subgrains with (111) in the ND-axis; in those subgrains, the γ-phase transforms to the α’-phase together with relatively high plastic straining.

![Spin rotation of subgrains by the heterogeneous nitrogen supersaturation in the Grain-A and –B.](image)

That is, the inner nitriding advances in this Grain-A with phase transformation and plastic straining but only accompanies with spin rotation of each original grain into subgrains without grain size refinement. This localization in plastic straining characterizes the heterogeneous nitrogen supersaturation.

Let us describe this spin rotation with phase transformation for these adjacent grains in Figure 9. Figure 10 depicts the spin rotation in the Grain-A and –B by localized nitrogen supersaturation. The original γ-phase parts in both grains rotate their original crystallographic orientation in ND axis with γ to α’-phase transformation. To be noted, the direction in spin rotation in both grains becomes inverse to each other. Besides for the localization in the above, the grain boundary is also heterogeneously nitrogen supersaturated to have high plastic straining together with phase transformation. The original grain boundary turns to be an assembly of finer subgrains, which work as a nitrogen diffusion path into the depth.

### 3.5 Precise analysis on the microstructure at 623 K

The heterogeneously nitrided Grain-A in Figures 8 and 9 is more precisely analyzed with finer spatial resolution. Figures 11 (a), (b) and (c) depict the inverse pole figure in the normal direction, the phase mapping and the equivalent plastic strain distribution, respectively, around the Grain-A.
Most of the original γ-phase transformed massively to α'-phase in this Grain-A. The γ-phase parts between these large α'-phase regions were highly strained in plastic and refined into smaller subgrains. This implies that massive α'-phase regions in the Grain-A are almost free from plastic straining and microstructural refinement; while the residual γ-phase regions are severely plastic strained and refined into finer subgrains. In particular, the localized heterogeneous nitrogen supersaturation (L-HNS) plays an important role to increase new subgrain boundaries and to promote the nitrogen diffusion into the depth of Grain-A.

After this precise analysis, the heterogeneous nitrogen supersaturation is characterized by two mechanisms. First, the L-HNS with high plastic straining drives the nitrogen diffusion through the newly built subgrain boundaries. Second, the main γ-phase part transforms massively to α'-phase via elastic distortion. These two processes take place exclusively in the inside of the Grain-A. The original γ-phase Grain-A divides into the massive α'-phase regions and the distorted γ-phase parts.

![Figure 12. EBSD analysis on the heterogeneously nitrogen supersaturated AISI316 at the depth of 435 μm.](image)

**3.6 Exotic inner nitriding into the depth at 623 K**

After the precise analysis on the heterogeneously nitrided microstructure in the above, this heterogeneous nitrogen supersaturation in local must be mainly driven by the grain boundary diffusion of nitrogen solutes. As analyzed by EBSD in Figures 8 and 9, the nitrogen supersaturated grain boundary regions are present even in the depth of AISI316 matrix. Hence, the microstructure of matrix at further depth is thought to be affected in the similar mechanism. That is, the original γ-phase grains transform to α'-phase and L-HNS grains. Let us experimentally demonstrate this inner nitriding fur below NFE.

Figure 12 depicts the inverse pole figure as well as the phase mapping by EBSD analysis at the depth of 435 μm, much deeper from the surface. The Grain-C consists of the massive α'-phase region as well as the L-NHS regions with the highly plastic straining and the refinement into finer subgrains. This proves that the depth of AISI316 matrix is also heterogeneously nitrogen supersaturated to make massive phase transformation from γ to α'-phase and to make microstructure refinement into finer subgrains via the plastic straining.

**4. DISCUSSION**

The common knowledge on the plasma nitriding in industries stood on the experimental results at the high holding temperature. The nitrided tool and stainless steels were hardened by the fine precipitation of nitried in their matrix with its higher volume fraction [Kuwahara 1992, Granito, Kuwahara & Aizawa, 2002]. Higher temperature and longer nitriding time were needed to have thick nitrided layer for improvement of wear resistance. The classical theory was also held on to predict the nitrided layer thickness (E) in the function of the nitriding time (t). After [Aizawa & Sugita, 2013], E² grows in proportional to t as depicted in Figure 13.

![Figure 13. Relationship of E² to t in the plasma nitrided tool steels at 753 K. Regression line for SKD61 has R² = 75 %](image)

This prediction of inner nitriding behavior by the classical theory implies that the nitrogen solute makes body diffusion with the precipitation reaction of chromium to diffusing nitrogen at the nitriding front end. Due to this principle on the nitriding at higher temperature, the original corrosion toughness to stainless steels decreases with decreasing the chromium content by precipitation reaction. Since the nitrogen body diffusion coefficient is strongly dependent on the holding temperature, there was no...
possibility to lower the holding temperature down to 673 K in practice.

Since the first finding on the nitrogen supersaturation in stainless steels even under lower temperature in [Bell, 2002], there have been reported many studies on the lower temperature inner nitriding in the austenitic stainless steels, as surveyed in [Aizawa, 2019-1]. Their understanding was still limited to the overall description on the inner nitriding behavior in Figure 4. Although their studies concentrated on the effect of nitrogen supersaturation on the modification of hardness and corrosion resistance, few results were reported on the nitrided microstructure below 700 K.

The essential mechanism to sustain this inner nitriding process lies in the synergetic loop among the nitrogen diffusion, the phase transformation, the plastic straining and the grain size refinement [Aizawa & Yoshihara, 2018; Aizawa, 2019]. As seen in the homogenous and heterogeneous nitriding process, the high density of nitrogen atom penetration from the surface drives the body and grain-boundary diffusion processes for main stream of nitrogen solutes. In particular, they also diffuse along the boundaries between γ-phase and the α'–phase zones as well as the newly built subgrain boundaries for their fine diffusion paths into the depth. Phase transformation takes place in the nitrogen supersaturated γ-phase grains or subgrains, while plastic straining advances in the unsaturated γ–phase zones. These two processes work concurrently to form two-phase fine-grained microstructure as seen in Figures 8 to 10. This micro-structuring yields lots of new zone and grain boundaries as a nitrogen diffusion path.

To be noticed, this nitrogen solute content is not zero mass % in the nitrided layer as shown in Figure 14. This extraordinary high nitrogen solute is responsible for the heterogeneous localized nitrogen supersaturation in Figures 9 and 11 as well as the microstructure change even at the depth from the surface by this low temperature plasma nitriding.

Finally, let us discuss this constant nitrogen solute concentration in the nitrided layer at 623 K. As had been discussed in [Farghali & Aizawa, 2018] and [Aizawa, T., Yoshino, T., Morikawa, T., and Yoshihara, S-I., 2018], the original AISI316 crystalline super-cell houses nitrogen solutes as an alloying element and turns to the expanded γ-phase and the α’-phase subgrains. The average nitrogen content among the expanded γ-phase and transformed α”-phase zones corresponds to this measured nitrogen concentration by EDX in Figure 14. Further precise analysis undergoes to describe the nitrogen alloyed crystalline nano-structure.

5. CONCLUSIONS

The stainless steel type AISI316 with the normal grain size was employed to describe the difference of plasma nitriding process by the holding temperature. Inner nitriding at 753 K is driven by the nitrogen body-diffusion process as well as the precipitation into CrN at the nitriding front end. This is common to the high temperature plasma nitriding.

The inner nitriding process at 623 K is driven by two mechanisms; homogeneous and heterogeneous nitrogen supersaturation processes. The former process is characterized by the synergetic relations among the phase transformation by the elastic expansion, the plastic straining, and, the microstructural refinement. In the latter process, the massive phase transformation takes place exclusively with the plastic straining and refinement into subgrains. This unique performance in the heterogeneous nitrogen supersaturation comes from the grain boundary diffusion of nitrogen solutes. The nitrogen solute atoms transport themselves mainly through the original grain boundaries and newly built subgrain boundaries by the localized heterogeneous nitrogen supersaturation. Then, the nitrogen saturated regions are forced to make massive phase transformation. This mechanism still works even at deeper zone from the nitrided surface or the nitriding front end. Further studies on this heterogeneous nitrogen supersaturation process provides us to understand the role of nitrogen grain boundary diffusion in the nitriding process and to develop a new type of plasma nitriding method.

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Figure 14. Nitrogen solute content depth profile in the nitrided AISI316 at 623 K.

This synergetic effect on the inner nitriding at 623 K reflects on the nitrogen solute distribution. In the high temperature plasma nitriding without synergetic effect, the nitrogen solute content decays exponentially into the depth toward the nitriding front end by the nitrogen body-diffusion process. In the low temperature plasma nitriding, the nitrogen solute diffuses uniformly in the inside of the nitried layer along the main and fine streaming paths. As a result, the nitrogen solute content becomes nearly constant by 5 mass % in the nitrided layer as shown in Figure 14. To be noticed, this nitrogen solute content is not zero beyond the nitrogen front end but nearly 1 mass%, which is still higher than the maximum nitrogen solubility limit of 0.1 mass% at 623 K. This extraordinary high nitrogen solute is responsible for the heterogeneous localized nitrogen supersaturation in Figures 9 and 11 as well as the microstructure change even at the depth from the surface by this low temperature plasma nitriding.
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PHOTOS AND INFORMATION

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