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Nitrogen Supersaturation of AISI316 Base Stainless Steels at 673 K and 623 K for Hardening and Microstructure Control

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Abstract

The high-density plasma nitriding at 673 K and 623 K was employed to make 10% of nitrogen supersaturation on AISI316 base austenitic stainless steels. The processing parameters and nitrogen-hydrogen gas flow ratio were optimized to increase the yield of N_2^+ ion and NH -radical for efficient nitriding. The nitrided AISI316 specimens were prepared for multidimensional analysis to describe the fundamental features of low-temperature plasma nitriding. First, macroscopic evaluation revealed that nitrogen supersaturation induced the γ -lattice expansion and the higher nitrogen content than 4% of mass in depth. The mesoscopic analysis describes the holding temperature and initial grain-size effects on the microstructure changes. Plastic straining, grain-size refinement, and nitrogen zone-boundary diffusion processes advance with nitrogen supersaturation to drive the inner nitriding behavior. The microscopic analysis explains the microstructure refinement, the two-phase structuring, and the microstructure modification. Through this multidimensional analysis, the essential characteristics of the low-temperature plasma nitriding of 316 austenitic stainless steels were precisely understood to extend the engineering treatise on the bulk nitrogen stainless steels for surface modification and treatment of stainless steels by nitriding. This plasma nitriding was applied to strengthen and harden the AISI316 wire surfaces toward its application on surgery wires.

Keywords: high-density low-temperature plasma nitriding, AISI316 stainless steels, multidimensional analysis, nitrogen supersaturation, plastic straining, microstructure refinement, two-phase structuring, nitrogen zone-boundary diffusion, surgery wires

1. Introduction

Stainless steel was invented in 1915 as non-rusting steel with high chromium and nickel contents by the alloying design [1]. Since then, various kinds of stainless steels have been developed to improve their features in suitable to each application; e.g., austenitic, martensitic, ferritic, and two-phase stainless steels are widely

utilized in the present society [2]. As one of the high-strength austenitic stainless steels, AISI316 plates, bars, and wires have been widely utilized in industries [3]. In addition, it has a family of industrial grades such as AISI316L, low carbon AISI316, to improve the corrosion toughness [4] and AISI316LN, nitrogen-bearing AISI316, to improve the erosion and wear toughness [5]. In the history to develop these austenitic stainless steels, nitrogen was highlighted as its effective alloying element to reduce the amount of nickel consumption in fabrication. In this development of HNSS (High Nitrogen Stainless Steels), the role of nitrogen solute contents in the mechanical properties of stainless steels has been studied in [6]. In parallel to these studies on HNSS, various processes were developed to make nitrogen supersaturation to the γ -phase steels beyond their maximum nitrogen solubility. However, the nitrogen content in HNSS is still limited by 1 mass%. An increase of the nitrogen solute content in HNSS or nitrogen supersaturation is still a challenge to significantly improve the mechanical and functional properties of HNSS.

In parallel to R & D on HNSS, the nitriding process is another route to utilize this nitrogen in the surface treatment and modification of Fe-Cr base alloys and stainless steels [7]. The gas and liquid nitriding processes were first employed to form the thick nitrided layer with the use of the ammonia gas, the chloride ion, and cyanic liquids. The plasma nitriding process was gradually selected as an environmentally benign route of surface treatment instead of those processes [7, 8]. This plasma nitriding process is classified into two categories on the dependence of holding temperature and duration [8]; e.g., high-temperature plasma nitriding (HT-PN) with nitride precipitation into the nitrided layer for hardening, and low-temperature plasma nitriding (LT-PN) with the nitrogen supersaturation into the depth of matrix for hardening, strengthening and improvement of wear-/corrosion toughness.

Figure 1 depicts this categorizing on the plasma nitriding of AISI316 stainless steels. Above the master curve, the CrN (Chromium Nitride) or iron nitride precipitation governs the hardening process by HT-PN of AISI316 steels. Those nitrides precipitate in the AISI316 matrix to strengthen the stainless steel; their surface hardness increases but their nitrided layer thickness decreases with increasing the chromium content [7]. The nitriding process is governed by the nitrogen body-diffusion mechanism, so that the nitrogen solute content exponentially decreases from the surface to the depth [9], the nitrogen content at the surface is limited by the maximum solubility of 0.3 mass% [7], and the square of nitrided layer thickness is proportional to the holding duration [7, 10]. The metal chromium content decreases by synthesis of CrN in the nitrided layer and results in significant loss of corrosion toughness, intrinsic to AISI316. On the other hand, no nitrides are synthesized in the nitrided layer by LT-PN; nitrogen solute supersaturates the AISI316 matrix to form a thicker nitrided layer than 50 μm , to harden this layer up to 1400 HV, and to modify the microstructure of matrix at 673 K for 14.4 ks (or 4 h) [11–15]. Remember in HT-PN that 1) thinner nitrided layer is only formed in case of the high chromium contents, 2) surface hardness is limited by 1200 HV, 3) no significant change of microstructure is observed in the nitrided layer, and 4) microstructure below NFE remains the same as the original AISI316 before nitriding. In particular, the LT-PN at 673 K is characterized by the nitrogen supersaturation into the austenitic stainless steels with higher nitrogen content than 4 mass% and without iron and chromium nitride precipitates [13–17]. As studied in [12, 13], this nitrided layer improved the corrosion toughness of original AISI316 stainless steels. No chromium content was reduced even after the nitriding process due to the nitrogen supersaturation. Hence, LT-PN becomes a candidate processing to modify the AISI316 product surfaces to a HNSS layer with high nitrogen solute content and to improve its mechanical and functional properties.

Figure 1.
Two categories in the plasma nitriding process on the dependence on the holding temperature and duration.

In the present paper, the high-density plasma nitriding process is redesigned by using the plasma diagnosis to be working under the optimum conditions. In particular, OES (Optical Emissive-light Spectroscopy) is employed to search for the most suitable nitrogen – hydrogen gas flow rate to attain the higher yield of N_2^+ ions and NH radicals for efficient nitriding. AISI316 specimen is nitrided respectively at 673 K and 623 K under the optimized conditions to describe the nitrogen supersaturation process by using the multidimensional analysis. Macroscopic evaluation on the formation of the nitrided layer is performed by XRD and SEM–EDX. EBSD is employed to make a mesoscopic evaluation of the holding temperature and initial grain-size effects on the nitriding behavior in the nitrided layer and below the NFE. The plastic straining, the microstructure refining, and the two-phase structuring advance in synergy with nitrogen supersaturation and diffusion through the nitrided layer. This synergic relation among these processes is common to every nitriding behavior in LT-PN, irrespective of the holding temperature and initial granular structure. Microscopic analysis with the use of STEM is employed to describe the microstructure refining and two-phase structuring in the nitrided AISI316 at 673 K. STEM analysis directly prove that the microstructure refining process is driven by the shear localization in the plastic straining, two-phase structuring is induced by the microscopic disturbance of nitrogen content with its different chemical compatibility to iron, nickel, and chromium in AISI316, and that plastic straining still modifies the crystalline structure at the absence of nitrogen solutes even below NFE. The above multidimensional analysis demonstrates that low-temperature plasma nitriding is driven by the synergic relation of plastic straining, microstructure refining, and two-phase structuring with the nitrogen supersaturation and zone-boundary diffusion processes. The homogeneous inner nitriding of initially fine-grained AISI 316 is self-sustained by this synergic effect not to ignite the localization in nitrogen supersaturation even at 623 K. This self-sustainable nitriding is attractive to make surface treatment of stainless steel medical parts. Especially, the nitrided AISI316 wire is straightforwardly utilized as a surgery wire by its uniform high surface hardness and high loading capacity.

2. High-density plasma nitriding system

The high-density RF (Radio Frequency) - DC (Direct Current) plasma nitriding system is depicted in **Figure 2a**. It consists of the vacuum chamber, the evacuation system, the gas supply, the RF/DC-power generator, and the control panel. On the basis of the hollow cathode device [13, 18], the experimental setup was redesigned with the use of plasma diagnosis [19]. **Figure 2b** depicts a typical hollow-cathode setup for the present nitriding processes. High brightness only in the inside of the hollow proves how much the ion and radical populations are present in the ignited plasmas.

Figure 2. High-density plasma nitriding system. a) Overview of RF-DC plasma nitriding system, and b) hollow cathode set up for high-density nitriding process.

Figure 3. A typical optical emission spectrum from the nitrogen and hydrogen plasmas is measured by the plasma diagnosis.

Figure 4.
Variation of the intensity ratio (R_{NH}) of NH-radical peak to N_2^+ peak by OES with increasing the hydrogen gas content in $N_2 + H_2$ mixture gas.

Among various plasma diagnosis methods, OES (Optical Emissive-light Spectroscopy) was employed to describe the activated species in the nitrogen – hydrogen plasmas. **Figure 3** depicts a typical spectrum. Both N_2^+ and NH are main species with high intensity. After [20], N_2^+ is a mother species to generate a series of nitrogen ions by electron attachment and detachment reactions in plasmas. The N_2^+ peak with the highest intensity and the NH peak at $\lambda = 340$ nm was employed for diagnosis.

After optimizing the relationship among the RF-voltage, the DC-bias, and the pressure, the nitrogen–hydrogen gas ratio was varied to search for optimization of the intensity ratio (R_{NH}) of NH-radical peak to N_2^+ peak. **Figure 4** shows the variation of R_{NH} with increasing the hydrogen gas content $[H_2]$ to the nitrogen–hydrogen mixture gas. When $[H_2] < 5\%$, less NH-peaks were detected by OES; R_{NH} increases with increasing $[H_2]$. After R_{NH} becomes maximum at $[H_2] = 20\text{--}25\%$, this ratio significantly decreases with increasing $[H_2]$ due to the hydrogen quenching effect in the plasma synthesis of NH radicals. In the following nitriding experiments, the nitrogen and hydrogen gas flow rate were respectively fixed by 160 mL/min and 30 mL/min after this plasma diagnosis.

3. Macroscopic characterization on the plasma nitrided AISI316

XRD and SEM–EDX were utilized to describe the nitrogen supersaturation and nitrided layer formation in LT-PN of the AISI316 at 673 K and 623 K or 14.4 ks. **Figure 5** compares the three XRD diagrams of un-nitrided and nitrided AISI316 specimens.

The bare AISI316 is characterized by γ (111) peak at $2\theta = 44.3^\circ$ and γ (200) at $2\theta = 51.7^\circ$, respectively. These peaks shift to γ_N peaks in the shallow 2θ directions in both nitrided AISI316 specimens at 673 K and 623 K. This peak shift proves that

Figure 5.
XRD diagrams for plasma nitrided AISI316 specimens at 673 K and 623 K for 14.4 ks.

Nitrided AISI316	2θ-shift for γ (111) (degree)	Lattice strain (%)	2θ-shift for γ (200) (degree)	Lattice Strain (%)
673 K	44.3° → 41.4°	6.78%	51.7° → 48.05°	7.06%
623 K	44.3° → 40.5°	9.04%	51.7° → 46.6°	10.17%

Table 1.
Estimate the induced lattice strain by the nitrogen supersaturation into the nitrided AISI316 specimen at 673 K and 623 K.

nitrogen interstitial occupies the vacancy sites of austenitic lattice in AISI316 and the lattice expands by itself. That is, the nitrogen supersaturation to AISI316 is first defined by this lattice expansion in **Figure 5**. After theoretical study in [21], this lattice expansion is induced by the occupation of interstitial nitrogen atoms to the octahedral vacancy sites. Let us estimate the lattice strains by this nitrogen supersaturation. **Table 1** summarizes the peak shift and lattice strain induced by the

Figure 6.
SEM image and EDX mapping on the cross-section of nitrided AISI316 specimen at 673 K for 14.4 ks.

Figure 7.
Nitrogen solute content depth profiles for the nitrided AISI316 at 673 K and 623 K for 14.4 ks.

Nitrided AISI316	Nitrided layer thickness (μm)	Maximum surface nitrogen content (mass%)	Plateau nitrogen content (mass%)
673 K	60	6.5	4.0
623 K	30	5.3	4.2

Table 2.
Nitrogen content analysis on the nitrided layer of AISI316 at 623 K and 673 K for 14.4 ks.

nitriding at 673 K and 623 K, respectively. The nitrogen supersaturation induces the lattice strain of 7% at 673 K and 10% at 623 K in the nitrided layer, respectively.

SEM–EDX was utilized to describe the nitrogen solute distribution in the depth of nitrided AISI316 at 673 K and 623 K, respectively. SEM image and nitrogen mapping on its cross-section in **Figure 6** show that a thick nitrided layer with a thickness of 60 μm is formed to have uniform nitrogen solute content. To be noticed, the microstructure below NFE is slightly modified by the nitriding. The nitrogen content depth profiles are also depicted in **Figure 7**. Irrespective of the holding temperature, these profiles have a plateau with the constant nitrogen content of 4 mass% till NFE, as listed in **Table 2**.

This nitrogen content decreases at the vicinity of NFE, but a significant nitrogen content of 0.5 mass% is present even below NFE. The role of non-zero nitrogen content blow NFE is considered in the mesoscopic evaluation on the inner nitriding behavior.

4. Mesoscopic characterization on the plasma nitrided AISI316

EBSD was employed to describe the microstructure change before and after nitriding and to analyze the effects of holding temperature and initial grain size on nitriding behavior. In the EBSD analysis, three items are employed to disclose the mesoscopic view on the nitriding behavior; e.g., the phase mapping, the KAM (Kernel Angle Misorientation) distribution, and the IPF (Inverse Pole Figure) profile. As shown in **Figure 5**, the nitrided AISI316 is composed of the nitrogen super-saturated γ-phase (γ_N) and α-phase (α_N). The phase mapping on the cross-section of the nitrided layer depicts that nitrogen supersaturation induces the lattice

expansion and transforms γ - to α -zones and that plastic straining occurs in the nearest neighboring γ -zones to each lattice expanding zones. The dislocations are generated to compensate for the mismatched strains between the unsaturated γ -phase zones and the lattice strained α -/ γ -zones [22, 23].

KAM profile represents the equivalent plastic strain distribution which is induced by the lattice expansion during the nitrogen supersaturation after [24]. IPF provides information on the grain refinement and subgrain formation with crystallographic spin-rotation.

Figure 8 depicts the phase mapping, the KAM distribution, and IPF profile on the cross-section of nitrided AISI316 at 623 K. As had been discussed in [22, 23, 25], most of the microstructure above NFE at the depth of 30 μm from the surface has two-phase structure, high plastic strains, and fine grain structure. Due to relatively homogeneous nitrogen supersaturation, the plastic straining and microstructure refinement processes co-work with the nitrogen supersaturation and zone-boundary diffusion processes. However, this synergic nitriding process commences to localize by itself near NFE and completely localizes below NFE. Since the α -phase is continuously formed along the a-path, the nitrogen atoms diffuse along this a-path to the depth of AISI316 matrix. This zone-boundary diffusion assists the further nitrogen diffusion into the neighboring grains such as A- and B-grains. As seen in **Figure 8**, the phase transformation, the plastic straining, and the grain size refinement advance even in A- and B-grains with this nitrogen supersaturation and diffusion processes.

Let us describe this local nitrogen supersaturation into A- and B-grains. **Figure 9** depicts the phase mapping, the strain distribution, and the grain refining in these grains. Compared between **Figure 9a** and **b**, the α -phase zones in A-grain are formed in the absence of plastic strains, and, the high KAM zones correspond to the γ -phase. Since these plastic strains are induced by the lattice expansion in the nitrogen supersaturated γ -phase, these lines and zones with high KAM

Figure 8. EBSD analysis on the cross-section of the nitrided AISI316 at 623 K for 14.4 ks. a) Phase mapping, b) KAM distribution, and c) inverse pole figure in the ND direction.

Figure 9. EBSD analysis on the cross-section below NFD for the nitrided AISI316 at 623 K for 14.4 ks. a) Phase mapping, b) KAM distribution, and c) inverse pole figure in the ND direction.

correspond to the nitrogen diffusing paths into A-grain. Most of these diffusing paths terminate intermediately so that nitrogen supersaturation and microstructure refinement processes also stop in the inside of A-grain. Comparing **Figure 9b** and **c**, high KAM zones in **Figure 9b** is just corresponding to fine-grained zones in **Figure 9c**. This demonstrates that the grain-size refinement is induced by the plastic straining.

Figure 9 reveals that the nitrogen supersaturation and zone-boundary diffusion processes localize below NFE. These processes co-work with the plastic straining, the two-phase structuring, and microstructure refinement in local to modify the crystallographic structure far below NFE. This heterogeneous nitrogen supersaturation process must be changed to be more homogeneous by controlling the external and internal nitriding conditions.

First, the holding temperature is increased from 623 K to 673 K to investigate its effect on this mode change. **Figure 10** depicts the phase mapping, the plastic strain distribution, and the IPF profile on the cross0section of nitrided AIS316 at 673 K for 14.4 ks.

Although the a-path for zone-boundary nitrogen diffusion is formed below NFE together with plastic strains and refined microstructures, the homogeneous nitrogen supersaturation process advances above NFE. The two-phase structuring in **Figure 10a**, the plastic straining in **Figure 10b**, and microstructure refining in **Figure 10c** co-work in synergy and co-terminates at $d = 60 \mu\text{m}$. The heterogeneous nitrogen supersaturation is suppressed to the local area below NFE. This proves that the mode-change from the heterogeneous nitriding to the homogeneous one is performed by simply increasing the holding temperature.

In addition to this external item, the initial grain size refinement is selected as an internal item to make the mode change. The intense rolling was employed to reduce the original AISI316 plate thickness by 90%. **Figure 11** shows the phase mapping, the plastic strain distribution, and the IPF profile on the surface of the fine-grained AISI316 (or GF-AISI316) plate. As well known in the rolling and stamping of AISI304 plates [26] and AISI316 bars [27], the transformation from γ -phase to α -phase is induced into AISI316 by this intense rolling as shown in **Figure 11a**. The agreement between the α -phase zones and the high strained zones proves this strain-induced transformation in comparison to **Figure 11a** and **b**. The initial grain size with its average of $15 \mu\text{m}$ is reduced to $1.5 \mu\text{m}$ in **Figure 11c** by rolling.

Figure 10. EBSD analysis on the cross-section of the nitrided AISI316 at 673 K for 14.4 ks. a) Phase mapping, b) KAM distribution, and c) inverse pole figure in the ND direction.

Figure 11. EBSD analysis on the surface of rolled AISI316 plate specimen before nitriding. a) Phase mapping, b) KAM distribution, and c) inverse pole figure in ND direction.

This GF-AISI316 specimen was nitrided at 623 K for 14.4 ks to investigate the effect of initial grain size on the mode change in nitrogen supersaturation. **Figure 12** shows the SEM image and nitrogen mapping on the cross-section of nitrided GF-AISI316 at 623 K for 14.4 ks. The uniform nitrided layer with a thickness of 40 μm was formed with a fine microstructure above NFE. The microstructure below NFE is also homogeneous and looks to be the same as the microstructure before nitriding in **Figure 12**. The hardness depth profile and the nitrogen solute content depth profile across NFE are respectively depicted in **Figure 13**.

The hardness with its average of 1400 HV above NFE drastically decreases down to the matrix hardness of 250 HV just across NFE in **Figure 13a**. The nitrogen solute

Figure 12.
SEM and nitrogen mapping on the cross-section of the rolled AISI316 specimen after nitriding at 623 K for 14.4 ks. a) SEM image on the cross-section, and b) nitrogen mapping to the depth.

Figure 13.
Hardness and nitrogen content depth profiles of the rolled AISI316 specimen after nitriding at 623 K for 14.4 ks. a) Hardness depth profile, and b) nitrogen content depth profile.

content depth profile with the average of 4 to 5 mass% also decreases down to zero across NFE in **Figure 13b**. These profiles reveal that the homogeneous nitrogen supersaturation advances to NFE and terminates at NFE. This is completely different from the heterogeneous nitrogen supersaturation process across NFE when using the AISI316 with the average grain size of 15 μm . Let us make EBSD analysis on the cross-section of nitrided FG-AISI316 with a comparison between **Figures 8** and **14**. As shown in **Figure 14a**, the two-phase structuring, the plastic straining, and the grain size refining take place only above NFE and no processes advance across NFE. The two-phase, highly strained, and grain-refined zone in **Figure 14a–c** is just equivalent to the nitrided layer. The phase map, the KAM distribution, and IPF profile below NFE in **Figure 14** are the same as those in **Figure 11**. That is, no nitrogen supersaturation takes place below NFE.

This comparison of EBSD results among **Figures 8**, **11**, and **14** reveals that the initial grain size refinement has a significant influence on the synergic relationship among the nitrogen supersaturation, the nitrogen zone-boundary diffusion, the plastic straining, the two-phase structuring, and the microstructure refining.

Let us reconsider the heterogeneous and homogeneous nitrogen supersaturation processes and their mode change. As depicted in **Figure 8**, the heterogeneous nitrogen supersaturation gradually turns to be homogeneous according to the

Figure 14. EBSD analysis on the surface of rolled AISI316 plate specimen after nitriding at 673 K for 14.4 ks. a) Phase mapping, b) KAM distribution, and c) inverse pole figure in ND direction.

nitrogen boundary diffusion mechanism change from the localized path to the network. Under the localized boundary diffusion mechanism, the nitrogen supersaturation, the plastic straining, the grain refining, and the phase transformation only advance at the vicinity of zone boundaries. Neglecting this localization, the synergic relationship to drive the inner nitriding process by heterogeneous nitrogen supersaturation is the same as that by homogeneous nitrogen supersaturation. Hence, if the localized nitrogen boundary diffusion is revised by the zone-boundary diffusion in a network, this heterogeneous nitrogen supersaturation process could be controlled to change itself to a homogeneous process. Both the holding temperature increase and the initial grain size refinement work as an external and internal trigger to enhance the nitrogen zone boundary diffusion mechanism.

In the case of the higher holding temperature, the nitrogen boundary diffusion rate is enhanced in similar manner to the increase of body diffusion rate in the traditional plasma nitriding processes such as ion- and radical-plasma nitriding. Although those HT-PN processes required a higher temperature than 773 K enough to sustain the diffusion path, the holding temperature of 673 K is enough to drive the homogeneous nitriding.

The HT-PN processes have no initial grain-size refinement effect on their nitriding behavior. On the other hand, the heterogeneous nitriding even at 623 K completely changes to be homogeneous when using the fine-grained AISI316 substrates. This mode change proves that grain-boundary diffusion works as a network to supply a sufficient amount of nitrogen solutes enough to sustain the synergic nitriding process at every spot above NFE. As demonstrated in **Figures 12–14**, NFE works just as a front end for homogeneous nitrogen supersaturation and diffusion.

5. Microscopic characterization on the plasma nitrided AISI316

Through the macroscopic and mesoscopic analysis, the plasma nitrided AISI316 is characterized by the refined and two-phase microstructure, by the plastically strained microstructure, and by the modified microstructure below NFE. STEM was employed to analyze the microstructure to microscopically describe the grain-size refining, the two-phase structuring, the plastic straining, and the microstructure modification below NFE during the plasma nitriding of AISI316 at 673 K for 14.4 ks.

The Cs-corrected STEM (Spherical Aberration Corrected Scanning Transmission Electron Microscope; JEM-ARM200F; JOEL, Tokyo, Japan) was employed for this microscopic characterization on the nitrided layer. This system has a cold FEG (Field Emission Gun) with a capacity of 200 kV and a resolution of 0.08 nm by using a Cs-corrector. Dual SDD (Solid State Detector)-EDS detector was utilized for local element mapping with Cs-STEM. Argon ion milling was used to make a thin slice of the plasma nitrided AISI316 specimen for Cs-STEM analysis.

Figure 15a depicts the STEM image in the vicinity of nitrided layer surface. This surface region is composed of two zones; e.g., a smooth zone and a rough zone. The electric diffraction at the former zone is shown in **Figure 15b**. Since a single spot is only detected, this former zone has a single-crystal like microstructure. On the other hand, the electric diffraction at the latter zone consists of two or three spots as shown in **Figure 15c**. That is, this zone has a polycrystalline microstructure.

Figure 15 proves that the nitrided layer with high nitrogen solute content is composed of single-crystal and poly-crystal grains. After [28], a single crystal grain with its size less than 10 nm has no dislocations or no defects in its lattice structure. Those defects in the fine single crystals have high free energy enough to be pushed out of the inside of crystals to fine-grain boundaries. Hence, this ultra-fine single-crystal zone also has no nitrogen solute to occupy the octahedral vacancy sites in the single crystal. That is, these fine single crystals are generated by the refining process

Figure 15.
TEM image on the surface of the nitrided AISI316 at 673 K for 14.4 ks. a) Cross-sectional TEM image with two zones, b) single-crystal like zone, and c) poly-crystal like zone.

through the cascading reduction of zone size, co-working with the intense plastic straining in the synergic relationship.

In later, the microstructure of this single crystal zone is precisely analyzed by HAADF (High-Angle Annular Dark-Field)-imaging, ABF (annular bright-field)-imaging, and LAADF (Low-angle annular dark-field)-imaging, respectively. Most of the microstructure in **Figure 15a** consists of the poly-crystal zones. Remember that the nitrated layer consists of the fine two-phase structures in the mesoscopic characterization. This poly-crystal zone is expected to be formed by two neighboring crystals with different lattice structures. In later, HAADF, ABF, and LAADF imaging methods are also utilized to describe this correlation.

In the STEM analysis, HAADF-imaging produces an annular dark-field image formed by very high angle, incoherently scattered electrons (Rutherford scattered from the nucleus of the atoms). ABF provides a robust technique for simultaneous imaging of light and heavy elements since its contrast has a low scaling rate with the atomic number. LAADF receives the diffracted or inelastically scattered electrons at low to medium angles (25 to 60 mrad) using an ADF (annular dark-field) detector.

Figure 16 shows the HAADF, ABF, and LADDF-images at the single-crystal zone in **Figure 14b**. ABF-imaging explains that every constituent atom is aligned in (111) direction. From LAADF imaging, this single crystal with (111) and (200) crystallographic orientations. The above nano-structural analysis reveals that this single-crystal has γ -phase, the crystallographic orientation of which coincides with the easiest slipping plane orientation of (111). Remember that the mesoscopic analysis on the nitrated layer. The γ -phase zones coexist with α -phase zones to form the fine two-phase nanostructures and the nitrogen unsaturated zones are plastically strained to compensate for the strain incompatibility between the nitrogen saturated and unsaturated zones. ABF-imaging in the above proves that a refined

Figure 16.
HAADF, ABF, and LAADF analysis on the single-crystal-like zone at the surface of nitrated AISI316 at 673 K for 14.4 ks.

γ -phase zone with its average size of 5 nm is formed by plastically straining the nitrogen unsaturated γ -phase region.

In the mesoscopic characterization, the network of zone boundaries plays an essential role to transport the nitrogen solute from the surface to the NFE of the nitrated layer and to drive the homogeneous nitrogen supersaturation. **Figure 16** also proves that zone boundaries in this single-crystal should work as a fine network of nitrogen diffusion paths and propel the nitrogen supersaturation to the un-nitrated regions. The grain size refinement co-works with the homogeneous nitrogen supersaturation and terminates itself at this formation of ultrafine γ -phase single crystals without nitrogen solutes.

In **Figure 15**, this refined γ -phase single-crystal is neighboring to the poly-crystal zones; the other phase in the refined two-phase microstructure corresponds to this poly-crystal. Let us make STEM analysis on this point.

Figure 17 shows the HAADF, ABF, and LAADF-images on the poly-crystal zone at the vicinity of nitrated AISI316 specimen surface at 673 K for 14.4 ks. These imaging methods in low magnification prove that two zones with different crystallographic structures are aligned in series and in parallel in the inside of the poly-crystal. After STEM analysis in high resolution and dual SDD-EDX detection, either of these two zones mainly consists of nitrogen-enriched chromium or Cr (N) rich lattices. On the other hand, another zone consists of nitrogen-poor iron and nickel or Fe/Ni (N). HAADF and KAADF images also prove that two neighboring zones have different nitrogen content. In correspondence to the mesoscopic analysis on the two-phase structure, this nitrogen-rich Cr (N) has a γ_N -phase structure while the nitrogen-poor Fe/Ni(N) has α_N -phase structure.

To be described later, the microstructure of AISI316 below NFE has no separation among iron, nickel, and chromium contents. This local segregation of chromium from iron and nickel is induced by the difference in chemical compatibility to

Figure 17.
HAADF, ABF, and LAADF analysis on the poly-crystal like zone at the surface of nitrated AISI316 at 673 K for 14.4 ks.

nitrogen among the three elements. In the austenitic stainless steels, chromium is a substitutional element to occupy the iron site without significant change of the original lattice constant for iron [7]. Nickel works to stabilize the fcc-structure [8]. In the absence of nitrogen solute in AISI316 substrate, its crystalline system has γ -phase while this local system has a fine mixture of γ_N - and α_N -substructures by their chemical compatibility to nitrogen solutes. This local separation of a constituent element in AISI316 among chromium, nickel, and iron, drives the nitrogen supersaturation and zone-boundary diffusion to advance into the original matrix. The zone boundaries between Cr (N) and Fe/Ni (N) work as a local network of nitrogen diffusion paths to modify the original, homogeneous AISI316 matrix to a fine two-phase crystalline structure of Cr (N) and Fe/Ni (N). This formation of nitrogen supersaturated γ - and α -phase zones reveals that nitrogen solute diffuses through the zone boundary network to the inside of each nano-crystalline zone.

Figure 17 also proves that the chemical compatibility of AISI316 constituent elements to nitrogen solute separates the homogeneous γ -phase crystalline structure into two-phase zone structure. Hence, the interface between two nano-crystalline structure distorts by itself to form an irregular zone boundary.

Let us summarize the microscopic view on the nitrided layer at the vicinity of the surface. Its microstructure consists of the γ -phase single-crystal structure and the γ_N/α_N , two-phase polycrystalline structure. The former structure is sparsely formed in the nitrided layer by plastic straining with nitrogen supersaturation. The fine grain boundaries with co-orientation of (111) are also formed along (111) slipping planes so that no nitrogen solute is present in its inside and it diffuses to the depth through these fine and larger grain boundaries. The latter structure is common to the nitrogen supersaturated zones. Each zone is composed of nitrogen-rich, γ -phase crystal and nitrogen-poor, α -phase one. This formation of the two-phase nanostructure is induced by different chemical compatibility of nitrogen solute to Cr and {Fe, Ni} in local. The local disturbance of nitrogen solute content triggers the local phase separation; this continuously propagates into the depth of the nitrided layer to form the fine two-phase structure.

Remember that the nitrogen supersaturated zones are advancing into the A- and B-grains in **Figure 9**. The highly strained zones are present in neighboring to the fine, two-phase zones. This local area in **Figure 9** is just resembling the microstructure at the surface of nitrided AISI316 in **Figure 15**. The γ -phase single-crystals are yielded by highly plastic straining in the similar manner to the fine distribution of high KAM zones in **Figure 9b**. Each refined γ -phase single crystal in **Figures 9** and **15** is formed by enclosure of slipping lines with the orientation (111). The fine two-structured poly-crystals are also formed just near these high KAM zones in **Figure 9c**. Under high nitrogen enrichment through the single crystal zones, a two-phase nanostructure is formed by nitrogen supersaturation with its different chemical compatibility.

STEM analysis was utilized to describe the microstructure below NFE. In the mesoscopic analysis by EBSD, the α -phase zones, the modified grains, and the plastic strains are observed even below NFE in **Figure 10**. STEM analysis provides proof of microstructure modification by plastic straining. **Figure 18** shows the HAADF, ABF, and LAADF images below NFE. In the low-resolution imaging, the original AISI316 grain is divided into several subgrains in correspondence to the IPF profiles in **Figure 10c**. To be noticed in the HAADF image, this subgrain boundary has almost (111) plane; these subgrains are formed by the plastic straining in the easiest slipping lines. In addition, the inside of the subgrain also has slip-lines in (111) direction as seen in both ABF and LAADF images. This cross-slipping in (111) direction is just corresponding to the formation of γ -phase single-crystals in **Figure 16**. When the plastic straining co-works with the nitrogen supersaturation

Figure 18.
HAADF, ABF, and LAADF analysis on the microstructure of the nitrided AISI316 just below NFE.

and boundary-diffusion processes, the microstructure in **Figure 18** is further modified and refined by the cross-slipping in plastic straining to be a single-crystal with the zone boundaries in (111) directions. Since the nitrogen content is nearly zero below NFE, the synergic relationship among the nitrogen supersaturation, the boundary diffusion, the plastic training, and the microstructure refinement stops intermediately to leave the plastically strained granular structure below NFE.

6. Application of nitrided AISI316 to surgery wire

A surgery wire requires high strength enough to apply the higher force for linkage of bones and tissues and for handling the miniature knife and tweezers. In addition, a surgery wire is demanded to have the high surface hardening enough to be free from damages and defects in mechanical troubles. Since the alloying elements for metallic medical parts and tools are strictly regulated, very few methods are useful to improve their mechanical properties and performance in practice. LT-PN is one of the most suitable methods to make surface treatment of AISI316 surgery wires without change of their constituent elements and element concentrations. In addition, the nitrogen supersaturated layer or NHSS layer has chemical inertness and sufficient corrosion toughness. No deterioration is expected to occur even by chemical polishing and pasteurization.

Figure 19 depicts the experimental procedure from the preparation of fine-grained AISI316 (FG-AISI317) wire to its uniaxial tensile testing. The FG-AISI316 wires with the average grain size of 1.5 μm , the diameter of 2.6 mm, and the length of 200 mm were prepared for LT-PN at 623 K for 14.4 ks. Other plasma processing conditions were the same as stated in Section 2. After nitriding, the side surface of wires is homogeneously nitrogen supersaturated to have a thick nitrided layer.

Figure 19.

An experimental procedure from the preparation of bare FG-AISI316 wire to the uniaxial tensile testing.

Mesoscopic analysis with the use of SEM–EDX is performed to verify the homogeneous nitriding behavior. The uniaxial tensile testing system (AUTOGRAPH AGS-X 10 kN; Shimadzu Co., Ltd., Tokyo, Japan) is employed to measure the applied stress to stroke relationship both for bare and nitrided FG-AISI316 wires. This uniaxial loading was terminated when the maximum applied load reached 6 kN before fatal ductile fracture for microstructure analysis.

The FG-AISI316 wire was uniformly nitrided to have the nitrogen supersaturated layer with the thickness of 40 μm ; the un-nitrided FGSS316 matrix is continuously capped by this nitrided surface layer. Since this nitrided layer thickness is nearly equal to 40 μm in the nitrided FGSS316 plates at 623 K in **Figure 14**, the nitrogen supersaturation process advances from the circumferential surface of wire to the depth in a similar manner to low-temperature nitriding in the FG-AISI316 plates.

Figure 20 depicts the nitrogen solute mapping and IFP mapping in the circumferential and longitudinal cross-sections of nitrided FG-AISI316 wire, after uniaxial tensile loading. With respect to the nitriding mapping in both cross-sections, the nitrogen solute distribution is nearly the same as as-nitrided FG-AISI316 as compared between **Figures 12, 20a** and **c**. **Figure 20b** and **d** prove that the super-fine grained crystalline state with the two-phase structure in the nitrided FG-AISI316 is sustained during the uniaxial loading. To be noticed, the original equiaxed AISI316-matrix grains are elongated to be fibrous in the longitudinal direction as shown in **Figure 20d**. In addition, the FG-AISI316 matrix in the circumferential cross-section has bundle structure where each bundle of fibrous grains has specific crystallographic orientation as depicted in **Figure 20b**.

Figure 20. Microstructure of the nitrided FG-AISI316 after uniaxial tensile testing. a) Nitrogen mapping in the lateral cross-section, b) its IPF profile, c) nitrogen mapping in the longitudinal cross-section, and d) its IPF profile.

This change of crystallographic structure in the FG-AISI316 matrix after uniaxial tensile loading, reveals that each original FG-AISI316 grain is elongated to fibrous grain by tensile loading and its crystallographic orientation is gradually rotated and aligned to the loading directions under the mechanical constraint by the nitrided layer. In particular, these fibrous grains are gradually sheared under this constraint to form a bundle structure with nearly the same crystallographic orientation. Let us investigate the effect of this crystallographic change in matrix on the mechanical properties of nitrided wire before and after uniaxial tensile loading.

Figure 21 compares the hardness profile on the lateral cross-section of nitrided wire before and after loading. The nitrided layer before uniaxial loading has a hardness of 1400 HV in agreement with the average hardness of the lateral cross-section of the nitrided FGSS316 plate in **Figure 13a**. This hardness abruptly decreases from 1400 HV to 400 HV at the nitriding front end of 40 μm ; this hardness of 400 HV becomes constant toward the center of the inner matrix. After uniaxial loading, the matrix hardness remains the same as 400 V; the work hardening is not enhanced by this uniaxial tensile loading to accumulate the inner strains. On the other hand, the high hardness in the nitrided layer is further enhanced to be 1600 HV. This increase of hardness in the nitrided layer by uniaxial loading only corresponds to the further microstructure evolution and phase transformation from γ_{N} -phase to α_{N} -phase in the nitrided layer. That is, the microstructure change is locally induced in the nitrided layer by the applied plastic straining during the uniaxial loading.

The uniaxially applied stress (σ_{app}) to stroke (δ) relationship is compared between the bare and nitrided FG-AISI316 wires in **Figure 22**. The stiffness (K) is defined as the average change of the applied stress to the measured stroke up to $\delta = 1 \text{ mm}$; e.g., $K = \sigma_{\text{app}}/\delta$. In the original FG-AISI316 wire, its stiffness becomes $K_0 = 500 \text{ MPa/mm}$ before nitriding; while the nitrided FG-AISI316 wire has a slightly greater stiffness (K_{N}) than K_0 ; e.g., $K_{\text{N}} = 580 \text{ MPa/mm}$. The present nitrided wire is presumed as a composite of the nitrided layer with stiffness K_1 and

Figure 21.
Comparison of the hardness profile on the lateral cross-section of nitrided FG-AISI316 wires before and after the uniaxial tensile testing.

Figure 22.
Comparison of the applied stress to stroke relationship between the bare and nitrided FG-AISI316 wires in the uniaxial tensile testing.

the FG-AISI316 matrix with K_0 . After the rule of thumb for the stiffness of composite materials [29], K_N is simply estimated by $K_N = (1 - f) \times K_0 + f \times K_1$, where f is the area fraction of the nitrided layer on the cross-section of the wire. In the present case, this f is only 6% because of the nitrided layer thickness of 40 μm of the wire lateral cross-section with a diameter of 2.6 mm. Assuming that $K_1 = (1600 \text{ HV}/400 \text{ HV}) \times K_0$, $K_N = 1.19 \times K_0 \sim 590 \text{ MPa}$. This implies that the FG-AISI316 matrix in the nitrided wire is elastically constrained by the nitrided surface layer with higher hardness and stiffness similar to the lateral composite material.

7. Discussion

In HT-PN, the nitride layer of AISI316 was characterized by fine precipitation of ion and chromium nitride into the AISI316 matrix without its microstructure

modification [7–10]. In bulk HNSS, the AISI316 matrix was supersaturated by nitrogen solute with is low content to stabilize the g-phase structure [6]. LT-PN of AISI316 substrate is characterized by its multi-dimensional structure. In the macroscopic view, the homogeneously nitrided AISI316 plates and wires at 673 K and 623 K have a nitrogen supersaturated layer or HNSS layer with an average nitrogen content of 4 mass% and an average hardness of 1400 HV. The initial γ -phase structure changes to be γ_N/α_N , two-phase structure. Through the mesoscopic view, the nitrogen supersaturation process with two-phase structuring in the macroscopic view is further understood to investigate the synergic role among the nitrogen superstation, the plastic straining, the two-phase formation, the microstructure refinement, and the nitrogen boundary-diffusion. EBSD analysis on the heterogeneously nitrided matrix below NFE reveals that this synergic process advances to the localized grains near the nitrogen diffusing boundaries. This heterogeneous process is changed to be homogeneous by increasing the holding temperature and refining the initial grain size. In particular, the nitrided layer with the plateau of high nitrogen content by 4 mass%, the high hardness of 1400 HV, the fine two-phase microstructure, and the high plastic strains advances into the depth by the assistance of nitrogen boundary diffusion network in LT-PN of AISI316 with refined grain size. Microscopic analysis reveals that the nitrided layer consists of the g-phase single crystals with the grain size of 5 nm and the g-phase Cr (N) – a-phase Fe/Ni (N) poly-crystals. This single crystal is yielded by plastic straining to have fine (111)-oriented grain boundaries in parallel to the easiest slipping directions. High KAM zones or highly plastic-strained zones in EBSD analysis correspond to these single crystals. Nitrogen solute and dislocations induced by plastic straining are not housed in these single crystals but they transport through these crystals to the depth of the matrix. Fine two-phase structure in IPF profile by EBSD analysis also corresponds to this fine poly-crystal of Cr (N) and Fe/Ni (N) zones. This fine phase separation by the chemical compatibility of nitrogen solute among Cr, Fe, and Ni proves that nitrogen supersaturation into AISI316 induces the phase separation from g-phase AISI316 to two distinct phases with a locally neighboring system of nitrogen-rich and nitrogen-poor zones. A very fee study [30] in the literature reports that phase-separation selectivity is enhanced by nitrogen doping. In the present nitrogen-induced phase separation, high nitrogen solute content with its average of 4 mass% disturbs locally with separation to nitrogen-rich and –poor phases. Remembering the IPF profile in **Figures 8, 10, 14, and 20**, where this two-phase structure forms a thick layer from the surface to the depth of nitrided AISI316. This local phase separation and nitrogen disturbance occur in a large volume with the advancement of nitrogen supersaturation and diffusion into the depth. The fine network of nitrogen zone- and grain-boundary diffusion paths in **Figures 16 and 17** sustains this large-scaled phase separation and nitrogen solute disturbance.

Localization of the nitrogen supersaturation and diffusion below NFE in **Figures 8 and 9**, and plastic straining effect on the formation of subgrains below NFE in **Figure 18**, also teaches the important role of synergic relation of plastic straining to nitrogen supersaturation and diffusion.

The mode-change from heterogeneous to homogeneous nitriding processes is controlled by refining the initial grain size of AISI316 substrates. In HT-NT, the nitriding behavior is sensitive to the holding temperature and chromium content; it has nothing to do with the microstructure. No studies were reported in the literature on LT-PN; This initial grain size effect on the inner nitriding is essential to understand the nitriding mechanism at low temperature. In the previous studies on HT-PN and LT-PN, the inner nitriding process is mainly dependent on the nitrogen body-diffusion process [7, 9]; hence, both HT-PN and LT-PN were thought to have

nothing to do with the grain size in the microstructure. The mode-change by refining the initial grain size implies that the nitrogen solute at the lower holding temperature does not diffuse through the lattices in microstructure but diffuse through the zone and subgrain boundary network.

Assuming that each grain geometry with its size of D is modeled by a sphere with the diameter of D , its surface area is represented by πD^2 . Let us calculate the number (N) of grains in a unit cubic cell with the edge length of L ; e. g., $N = (L/D)^3$. Then, the grain boundary area (A) in the cubic cell is estimated by $A = \pi D^2 N = \pi L^3/D$. When the initial grain size is refined from D_0 to D_1 , the grain boundary extension rate (E_r) is calculated by (D_1/D_0) . In the present experiment, $D_0 = 15 \mu\text{m}$ and $D_1 = 1.5 \mu\text{m}$; E_r becomes 10, or the initial grain boundary extends to be 10 times larger than the original AISI316. This enlargement of the grain boundary diffusion network area is responsible for the initial grain effect on the mode change.

Once the homogeneous nitriding is triggered by this initial grain refining, this nitriding process is sustained by the synergic relation among the nitrogen supersaturation, the plastic straining, the two-phase structuring, the microstructure refining, and the nitrogen boundary diffusion. To be remembered in [15, 16, 22, 23], the textures in the intensely rolled stainless steels completely disappeared through LT-PN. The pre-existing refinement in the granular structure of substrates is a key point to make sustainable and homogeneous nitriding of stainless steels. Other factors, mechanically induced by pre-straining, have nothing to do with nitriding behavior. This suggests that pre-forging provides yield the refined surface specimen for this homogeneous and sustainable LT-PN.

The metallic parts and tools in the medical application require various engineering items to improve their performance in practical use. The nitrided austenitic stainless steels have superior chemical inertness and corrosion toughness to the bare AISI316 products in addition to their high hardness. As reported in [31, 32], the nitrided nickel-free and martensitic stainless steels have sufficient corrosion toughness even in NaCl and etching solutions. Furthermore, the nitrided layer of AISI316 has enough machinability to be finished by using the PCD (Poly-Crystalline Diamond) - chipped and CBN (cubic boron nitride) - chipped milling tools [33–35]. The NHSS layer of nitrided AISI316 products can be precisely finished to have functional surfaces and interfaces owing to this feature of nitriding.

AISI316 has many derivatives such as AISI316L and AISI316LN. The former is selected and used as a high-strength sheet for piercing and metal-forming to fuel injection orifices [36]. The latter is also utilized as a structural component in the design of experimental fusion reactors [37]. Instead of those traditional alloying designs on AISI316L, the nitrogen can be utilized to reduce the effect of carbon interstitials to the mechanical performance by the nitrided AISI316 layer. AISI316LN can be exchanged by the nitrided AISI316 to prevent the structural component surface from the severe damages by spontaneous emission of particles. NHSS-layered AISI316 works as a structural member to be working instead of AISI316L and AISI316LN. Further studies are necessary to describe the interstitial solute as an alloying element in the redesign of AISI316 derivatives in its family.

8. Conclusion

The high-density plasma nitriding process is redesigned by using the plasma diagnosis to be working under the optimum conditions. In particular, OES (Optical Emissive-light Spectroscopy) is employed to search for the most suitable nitrogen–hydrogen gas flow rate to attain the higher yield of N_2^+ ions and NH radicals for low-temperature nitriding. AISI316 specimen is nitrided at 673 K and 623 K under

the optimized conditions to describe the nitrogen supersaturation process by using multidimensional analysis.

Macroscopic evaluation on the formation of the nitrided layer is performed by XRD and SEM-EDX. The nitrogen supersaturation process with its higher content than 4 mass% induces the γ -lattice expansion and forms a plateau in the nitrogen content depth profile. This lattice expansion only occurs at the nitrogen diffusing zones so that the strains become incompatible between the nitrogen supersaturated and unsaturated zones. The unsaturated zones are plastically strained to distort their constituent grains.

EBSA is employed to make a mesoscopic evaluation on holding temperature and initial grain-size effects on the nitriding behavior in the nitrided layer and below the NFE. The plastic straining, the microstructure refining, and the two-phase structuring advance in synergy with nitrogen supersaturation and diffusion processes through the nitrided layer. This synergetic relation among these processes is observed in the heterogeneous nitriding process at 623 K. The microstructure refinement and two-phase structuring co-work, at the vicinity of localized nitrogen diffusion paths, with the nitrogen supersaturation and diffusion processes. This synergic working among four processes is the same as that in homogeneous nitriding. Through this localized nitrogen diffusion and supersaturation processes, the matrix microstructure far below NFE is also modified heterogeneously.

This heterogeneous nitriding turns to be homogeneous with increasing the holding temperature from 623 K to 673 K since the nitrogen diffusion rate is enhanced to reduce the localization behavior. To be noticed, the synergic process in the above is common to those heterogeneous and homogeneous nitriding processes. By refining the initial grain size of AISI316 before nitriding, this heterogeneous nitriding at 623 K also turns to be homogeneous even at 623 K. In addition, no localization in nitrogen supersaturation and diffusion occurs below NFE. The microstructure below NFE becomes the same as the original matrix of the original grain refined AISI316. This implies that the localization in nitrogen supersaturation and diffusion processes is suppressed by the enlargement of nitrogen diffusion paths.

Microscopic analysis with the use of STEM is employed to describe the microstructure refining and two-phase structuring in the nitrided AISI316 at 673 K. A single-crystal and poly-crystal like zones are formed at the vicinity of its surface. STEM analysis on the former reveals that the γ -phase grain is much refined to have the size of 5 nm and the orientation of (111) by the synergic process in nitriding. The original coarse grain is nitrogen-supersaturated with its high nitrogen content and completely simple-sheared in (111)-direction by plastic straining to form very fine single-grain with no dislocations and nitrogen solutes left in its inside. STEM analysis discloses the two-phase structuring mechanism. After the phase mapping in EBSD analysis, this two-phase structure is only defined as a fine mixture of α - and γ -grains. The nitrogen-rich zone with more compatibility to chromium forms one phase while the nitrogen-poor zone with less compatibility to iron and nickel becomes another phase. In addition, these two-phase poly-crystals formed in nearest neighboring to the γ -phase single crystals. Furthermore, the STEM analysis on the microstructure below NFE proves that the sheared polycrystalline grains by the plastic straining are formed even in the absence of nitrogen solute.

The above multidimensional analysis demonstrates that low-temperature plasma nitriding is driven by the synergic relation of plastic straining, microstructure refining, and two-phase structuring with the nitrogen supersaturation and zone-boundary diffusion processes. The homogeneous inner nitriding of initially fine-grained AISI 316 is self-sustained by this synergic effect not to ignite the localization in nitrogen supersaturation even at 623 K. This self-sustainable nitriding is

attractive to make surface treatment of stainless steel medical parts. Especially, the nitrided AISI316 wire is straightforwardly utilized as a surgery wire by its uniform surface hardness and high loading capacity.

Instead of the conventional alloying design such as AISI316L and AISI316LN, this self-sustainable nitriding provides a new way of high nitrogen structured AISI316 to industrial and medical applications.

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Conflict of interest

The authors declare no conflict of interest.

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References

- [1] Cobb HM. The History of Stainless Steel. Materials Park, OH: ASM International; 2010
- [2] Peckner D, Bernstein IM. Handbook of Stainless Steels. New York: McGraw Hill; 1977
- [3] Stainless Steels for Design Engineers. ASM International. 2008
- [4] Available from: <https://www.oshwin.com/blog/difference-between-316-and-316l.html> [Retrieved at 2021/12/1]
- [5] Wu C, Li S, Zheng C, Wang X. Microstructural evolution in 316LN austenitic stainless steel during solidification process under different cooling rates. Journal of Materials Science. 2016;51:2529-2539
- [6] Imai Y, Murata T, Sakamoto M. High Nitrogen Steels. Agne-Publisher; 2005
- [7] Kuwahara H. Surface modification of iron alloys by plasma nitriding and carburizing [PhD Thesis]. Kyoto University; 1992
- [8] Anzai M, editor. Heat and Surface Treatment of Die Materials. Tokyo, Japan: Nikkan-Kogyo-Shinbunsha; 2011
- [9] Hiraoka Y, Inoue K. Prediction of nitrogen distribution in steels after plasma nitriding. Denki-Seiko. 2010;86: 15-24
- [10] Aizawa T, Sugita T. High density RF-DC plasma nitriding of steels for die and mold technologies. Research Reports SIT. 2013;57(1):1-10
- [11] Bell T. Surface engineering of austenitic stainless steels. Surface Engineering. 2002;18:415-422
- [12] Borgioli F, Galvanetto E, Bacco T. Low temperature nitriding of AISI300 and 200 series austenitic stainless steels. Vacuum. 2016;12:51-60
- [13] Aizawa T. Low temperature plasma nitriding of austenitic stainless steels. Chap. 3. In: Stainless Steels. London, UK: InTechOpen; 2019. pp. 31-50
- [14] Aizawa T, Yoshihara S-I. Homogeneous and heterogeneous micro-structuring of austenitic stainless steels by low temperature plasma nitriding. IOP Conference Series: Materials Science and Engineering. 2018;372:012059
- [15] Aizawa T, Yoshino T, Shiratori T, Yoshihara S-I. Grain size effect on the nitrogen supersaturation process into AISI316 at 623 K. ISIJ International. 2019;59:1886-1892
- [16] Aizawa T. Advanced technologies for die materials and manufacturing. Bulletin, JSTP. 2021;4(41):291-296
- [17] Farghali A, Aizawa T, Yoshino T. Microstructure/mechanical characterization of plasma nitrided fine-grain austenitic stainless steels in low temperature. Nitrogen. 2021;2:244-258
- [18] Benda M, Musil J. Plasma nitriding enhanced by hollow cathode discharge – A new method for formation of superhard nanocomposite coatings on steel surfaces. Vacuum. 1999;55(2): 171-175
- [19] Yunata EE. Characterization and application of hollow cathode oxygen plasma [PhD Thesis]. SIT; 2016
- [20] Aizawa T, Rsadi I, Yunata EE. High density RF-DC plasma nitriding under optimized conditions by plasma diagnosis. Journal of Applied Sciences. 2021 (in press)
- [21] Domain C, Becquart CS, Foct J. Ab initio study of foreign interstitial atom

- (C, N) interactions with intrinsic point defects in α -Fe. *Physical Review B*. 2004;**69**:144122
- [22] Aizawa T, Yoshihara S-I. Inner nitriding behavior and mechanism in stainless steels at 753 K and 623 K. *The SEATUC Journal of Science and Engineering (SJSE)*. 2019;**1**:13-20
- [23] Aizawa T, Yoshihara S-I. Inner nitriding behavior and mechanism in stainless steels type AISI316 at 623 K. In: *Proc. 13rd SEATUC Conference* (March 13th, 2019; Hanoi, Vietnam). pp. 121-127
- [24] Kamaya M, Wilkinson AJ, Titchmarsh JM. Quantification of plastic strains of stainless steel and nickel alloy by electron backscatter diffraction. *Acta Materialia*. 2006;**54**:539-548
- [25] Aizawa T, Shiratori T, Komatsu T. Micro-/nano-structuring in stainless steels by metal forming and materials processing. Ch. 1. In: *Electron Crystallography*. London, UK: IntechOpen; 2019. pp. 1-23
- [26] Tomimura K, Takaki S, Tokunaga Y. Reversion mechanism from deformation induced martensite to austenite in metastable austenitic stainless steels. *ISIJ International*. 1991; **31**(12):1431-1437
- [27] Aizawa T, Shiratori T, Komatsu T. Integrated manufacturing of fine-grained stainless steels for industries and medicals. Ch. 1. In: *Engineering Steels and High-Entropy Alloys*. London UK: IntechOpen; 2019. pp. 3-26
- [28] Korchuganova AV, Tyumentseva AN, Zolnikova KP, Litovchenko IY, Kryzhevich DS, Gutmanas E, et al. Nucleation of dislocations and twins in fcc nanocrystals: Dynamic of structural transformations. *Journal of Materials Science and Technology*. 2019;**35**(1): 201-206
- [29] Nemat-Nasser S, Hori M. *Micromechanics: Overall Properties of Heterogeneous Materials*. Amsterdam, Netherlands: North-Holland; 1992. p. 113
- [30] Yuan N, Chen J, Zhou H, Ali MC, Guan M, Qiu H. Nitrogen-doping to enhance the separation selectivity of glucose-based carbon dots –modified silica stationary phase for hydrophilic interaction chromatography. *Talanta*. 2020;**218**:121140
- [31] Borgioli F, Galvanetto E, Bacci T. Corrosion behavior of low temperature nitrided nickel-free, AISI200 and AISI300 series austenitic stainless steels in NaCl. *Corrosion Science*. 2018;**136**: 352-365
- [32] Aizawa T, Yoshihara S-I. Microtexturing into AISI420 dies for fine piercing of micropatterns into metallic sheets. *Journal of Service Theory and Practice*. 2019;**60**(698): 53-57
- [33] Aizawa T, Fukuda T. Microstructure and micro-machinability of plasma nitrided AISI420 martensitic stainless steels at 673 K. In: *Top 5 Contributions in Materials Science*. London: Avid Science. 2019;**2**(6):1-24
- [34] Aizawa T, Morita H, Fukuda T. High machinability of plasma-nitrided HPM80 dies at 673 K by PCD-tools for hot mold-stamping. *Procedia Manufacturing*. 2020;**47**:725-731
- [35] Aizawa T, Morita H, Fukuda T. Nitrogen supersaturation into AISI420 mold for precise machining. In: *Proc. 23 ESAFORM Conf. 2022* (In press)
- [36] Aizawa T, Sato T, Shiratori T. Micro-joining of shaped stainless steel sheets for fuel injection orifice with high misting capability. In: *Proc. 22nd Int. ESAFORM Conf. AIP Conf. Proc.* 2019. 2113 pp. 050007-1 – 050007-6

[37] Ferrara L, Palmieria A, Papatob A, Prevedellb A, Dimab R, Udupb E. Production quality controls and geometric characterization of the IFMIF-RFQ modules via the usage of a coordinate measuring machine. *Fusion Engineering and Design*. 2017;**115**:23-32

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