Grain Size Effect on the Nitrogen Super-Saturation Process into AISI316 at 623 K

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Coarse and fine grained AISI316 substrates were prepared to describe the grain size effect on the inner nitriding behavior at 623 K by using the high density plasma nitriding without precipitation of nitrides. In case of coarse grained AISI316, the nitriding process advanced homogeneously in one part of nitrided layer with high nitrogen content, and, heterogeneously in its other part. In the former, γ–α’ two-phase, fine microstructure was uniformly formed by the phase transformation and plastic straining with the nitrogen supersaturation. In the latter, the nitrogen super-saturation localized to selectively modify the coarse grains to form the transformed α’-phase zones with the plastically strained γ-phase ones, even below the nitriding front end of 30 μm. In case of fine-grained AISI316, the nitriding took place homogeneously to form fine, two-phase microstructure down to the nitriding front end of 40 μm. This difference in the inner nitriding behavior came from the synergetic relationship between the nitrogen diffusion and super-saturation processes.

KEY WORDS: plasma nitriding; AISI316; initial grain size; nitrogen supersaturation; phase transformation; plastic straining; microstructure refinement; diffusion path.

1. Introduction

The austenitic stainless steels type AISI316 and AISI316L have been utilized in various engineering fields, especially as a die and mold material to be working even in warm and hot conditions. The heat treatments as well as surface treatments are indispensable to increase their surface hardness and wear resistance. The holding temperature in those treatments is needed to be lower as possible to be free from thermal distortion and loss of toughness and ductility. Low temperature surface modification is developed as an alternative to the case hardening, the gas and plasma processes.

Low temperature plasma nitriding has been high-lighted as a non-traditional surface treatment. This nitriding process is characterized by the nitrogen supersaturation into γ-lattices in the austenitic stainless steels without precipitation of chromium and iron nitrides. 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 strain energy density in each lattice, which drives the phase transformation from γ-phase to α’-phase. The misfit distortion between the nitrogen supersaturated γ-lattices is compensated by the plastic strain. This intense plastic straining often accompanies with the refinement of crystalline structure during the nitrogen supersaturation. In particular, after the analysis in, this nitrided stainless steel layer at 673 K has fine and two phase γ–α’ structure with the average grain size less than 100 nm. This unique microstructure with nano-grains in the nitrided layer, reflects on the mechanical properties of nitrided AISI316 substrates. As surveyed in, higher hardness than 1 400 HV is preserved from surface to the vicinity of the nitriding front end. The homogeneous nitriding at 673 K in the above follows the heterogeneous nitriding across the nitriding front end, where the transformed α’-phase zones distribute along the grain boundaries with the highly strained γ-phase zones in the original grains. This difference between two inner nitriding processes might be dependent on the nitrogen mobility in diffusion as well as the nitrogen supersaturation.

In the present study, the holding temperature is lowered to 623 K first to significantly decelerate the nitrogen diffusion rate and to enhance the transient from homogeneous to heterogeneous nitriding processes. In second, the average grain size in AISI316 substrate is controlled to be 15 μm and 1.7 μm, respectively, to investigate the effect of grain boundaries on the relationship between nitrogen diffusion

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and supersaturation. This grain-size effect on the inner nitriding at 623 K is precisely analyzed to understand the essential relationship among the nitrogen super-saturation, the phase transformation, the plastic straining and the microstructure refinement.

2. Experimental Procedure

2.1. Low Temperature Plasma Nitriding System

The present plasma nitriding system consisted of the vacuum chamber, the evacuation system, the RF (Radio Frequency) generator working in the frequency of 2 MHz in addition to the DC (Direct Current)-generator, the gas supply of N₂ and H₂, and, the heating unit located under the cathode plate as illustrated in Fig. 1. The hollow cathode device was utilized 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 \(3 \times 10^{17} \text{ ions/m}^3\), which was equivalent to that by the electron beam assisted plasma nitriding in low pressure. In the present experimental set-up, the specimen was placed and fixed in the electrically conductive hollow, which was connected to the DC-bias. Thermocouple was embedded into the cathode plate to make on-line monitoring of the holding temperature. Noises from RF-plasma was shut out from this measurement line by using the electric filtering device.

The nitrogen and hydrogen mixture 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 623 K. 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. After pre-sputtering, it was plasma nitrided for 14.4 ks or four hours at 623 K by 70 Pa with the RF-Voltage of 250 V and the DC-bias of −500 V, respectively. The mixture gas was controlled to have constant flow rates of 160 ml/min for nitrogen and 30 ml/min for hydrogen, respectively. After the nitriding process, the sample was cooled down in the vacuum chamber to prevent it from surface contamination.

2.2. Preparation of AISI316 Specimens

The austenitic stainless steel type AISI316 plate with the size of 20 mm \(\times\) 40 mm \(\times\) 2 mm was employed as a substrate after heat treatment at 833 K for qualification of grains. Its chemical compositions are: \([\text{C}] = 0.08 \text{ mass}\%\), \([\text{Si}] = 1.00 \text{ mass}\%\), \([\text{Mn}] = 2.00 \text{ mass}\%\), \([\text{P}] < 0.045 \text{ mass}\%\), \([\text{S}] < 0.030 \text{ mass}\%\), \([\text{Ni}] = 12.0 \text{ mass}\%\), \([\text{Cr}] = 17.0 \text{ mass}\%\), and \([\text{Mo}] = 2.5 \text{ mass}\%\) for iron in balance. The sample surface was mirror-polished and cleaned by the ultrasonic cleaner before plasma nitriding. Two AISI316 specimens were prepared; the coarse and fine grained AISI316 substrates. The former specimen has the average grain size of 15 \(\mu\)m. The fine grained AISI316 with the same size as coarse grained AISI316, was fabricated by rolling the starting AISI316 billet with the thickness reduction of 90% as illustrated in Fig. 2(a). Its cross-sectional microstructure was shown in Fig. 2(b); its average grain size reached to 1.7 \(\mu\)m.

2.3. Analysis

The nitrided specimens were analyzed by XRD (X-ray diffraction; Rigaku SmartLab), SEM (Scanning Electron Microscopy; HITACHI SU-70 and JSDM-IT300LV; JOEL Co., Ltd.), and, EDX (Electron Dispersive X-ray spectroscopy; Pegasus, EDAX, Co., Ltd.) for material characterization from the surface down to the specified depth. Without notes on EDX analysis of interstitial elements with small atomic number, large statistical error contaminates the analytical results. In the present nitrogen mapping, SEM was adjusted to detect the peak intensity of nitrogen energy spectrum with sufficient resolution.

![Fig. 1. High density plasma nitriding system with use of the hollow cathode. (Online version in color.)](image1)

![Fig. 2. Preparation of fine grained AISI316 specimen. (a) Intense rolling of coarse grained AISI316 specimen by reduction of thickness, and, (b) Cross-sectional microstructure of fine-grained AISI316 specimen.](image2)
EBSD (Electron Back-Scattering Diffraction) was also used to analyze the microstructure refinement, the phase transformation and the plastic straining. IPF (Inverse Pole Figure) was utilized to describe the crystalline structure. Phase mapping was performed to understand the phase distributions from the surface to the depth. KAM (Kernel Average Misorientation) was also used to represent the intergranular misorientations among the neighboring grains. After 9), this KAM has correlation to the equivalent plastic strains; the KAM distribution represents the plastic straining state. In particular, the ion-milling was utilized to form the fine, smooth cross-section of nitrided AISI316 specimen for SEM-EDX and EBSD analyses without plastic distortion into microstructure.

3. Experimental Results

3.1. Plasma Nitriding of the Coarse Grained AISI316 at 623 K

XRD diagram of bare AISI316 stainless steels before nitriding is characterized by two \( \gamma \)-phase peaks as depicted in Fig. 3; e.g., \( \gamma (111) \) is detected at \( 2\theta = 43.5^\circ \), and, \( \gamma (200) \), at \( 2\theta = 50.7^\circ \), respectively. In the high temperature plasma nitriding, the diffusing nitrogen reacted mainly with chromium in AISI316 to synthesize the CrN precipitates.\(^{10,11}\) In those cases, the original \( \gamma \)-phase peaks were detected at the same \( 2\theta \) angles as before nitriding, together with the new peaks to CrN and \( \gamma' \)-Fe\(_4\)N. As shown in Fig. 3(a), these two \( \gamma \)-peaks before nitriding shift in the lower \( 2\theta \) directions after nitriding at 623 K for 14.4 ks. That is, \( \gamma (111) \)-peak shifts from the original position at 43.5\(^\circ \) to 40.5\(^\circ \), and, \( \gamma (200) \)-peak, from 50.7\(^\circ \) to 46.6\(^\circ \), 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 of AISI316. After the first principle calculation on this alloying process,\(^{12}\) the nitrogen solute atoms occupy the octahedral vacancy sites in the \( \gamma \)-lattices in AISI316. This in situ nitrogen solute occupation with vacancy sites in the \( \gamma \)-lattices accompanies with the \( \gamma \)-lattice expansion in elasticity and characterizes the nitrogen supersaturation process in the low temperature plasma nitriding.

The elastic strain (\( \varepsilon \)) is calculated by the difference of lattice constants before and after nitriding in Fig. 3(a) e.g., \( \varepsilon = 6.5\% \) from the peak shift for \( \gamma (111) \), and, \( \varepsilon = 7\% \) in case of \( \gamma (200) \), respectively. Besides for the original \( \gamma (111) \) peak at \( 2\theta = 43.5^\circ \), a new peak detected at \( 2\theta = 43.6^\circ \) in Fig. 3(b) is identified as \( \alpha' (110) \). This suggests that high elastic energy by \( \gamma \)-lattice expansion results in the phase transformation from \( \gamma \) to \( \alpha' \) in the nitrogen supersaturated \( \gamma \)-lattices. The transformed \( \alpha' \)-phase is considered to distribute in the original \( \gamma \)-phase matrix. In the following, the phase mapping by EBSD analysis is employed to describe this \( \alpha' \)-phase distribution with nitrogen supersaturation process.

Microstructure and nitrogen mapping on the cross-section of nitrided AISI316 specimen describe the average nitrogen diffusion layer from the surface. As shown in Fig. 4(a), the nitriding front end locates at the depth of 30 \( \mu \)m from the surface. Although the crystal grain size below this nitriding

Fig. 3. XRD diagram of normal grained AISI316 after plasma nitriding at 623 K for 14.4 ks. (a) XRD diagrams in the wide range for 35\(^\circ \) < \( 2\theta \) < 55\(^\circ \) with comparison to the original AISI316 before nitriding, and, (b) XRD diagram in the narrow range for 43\(^\circ \) < \( 2\theta \) < 44\(^\circ \) for the nitrided AISI316.

Fig. 4. SEM-EDX analysis of normal grained AISI316 after plasma nitriding at 623 K for 14.4 ks. (a) SEM image, and, (b) Nitrogen mapping. (Online version in color.)
front end remains the same as before nitriding, these grains are significantly refined in the nitrided layer. The nitrogen mapping in Fig. 4(b) proves that high nitrogen content uniformly distributes in the nitrided layer from the surface to the depth of 30 μm.

EBSD analysis is employed to describe the phase mapping, the plastic straining and the microstructure change from the surface across the nitriding front end toward the depth in Fig. 5. The phase mapping in Fig. 5(a) shows that most of the nitrided layer with the thickness of 30 μm has fine γ-α’ two-phase microstructure with higher plastic strains in partial, and, that other parts have heterogeneously nitrided microstructure; e.g., the grating zones in IPF mapping in Fig. 5(c). Figure 5(b) shows the equivalent plastic strain distribution across the nitriding front end. The plastic strains are also induced to compensate the strain misfit between the nitrogen super-saturated and un-saturated γ-lattices. Through comparison between Figs. 5(a) and 5(b), highly strained zone just corresponds to the two phase structured layer. Other coarse γ-phase grains than two-phase zones are partially distorted by lower plastic strains to have different crystallographic orientations from a mother grain.

This localization of nitrogen supersaturation and plastic straining changes the microstructure even below d = 30 μm.

Below the nitriding front end in Fig. 5, the original γ-phase grains at the vicinity along the grain boundary change themselves to have α’-phase zones in their inside. As denoted by the Grain-A and -B in Fig. 5(c), these originally γ-grains are composed of the transformed α’-phase zones as well as the refined γ-phase zones. This phase transformation proves that nitrogen atoms are transported to the inside of these grains and supersaturates the original γ-lattices. In parallel with this localization in nitrogen supersaturation, the plastic straining changes the crystallographic orientation of α’- and γ-zones in these grains and refines their grain size. Precise analysis on these grains provides a means to understand the relationship between nitrogen supersaturation and diffusion processes.

3.2. Plasma Nitriding of the Fine-grained AISI316 at 623 K

SEM image as well as nitrogen mapping on the cross-section of the fine-grained AISI316 after plasma nitriding at 623 K for 14.4 ks, are shown in Fig. 6. The nitriding front end is
located at $d = 40 \mu m$; the microstructure in this nitrided layer becomes more homogeneous and finer than that in Fig. 4. The volume fraction of $\alpha'$ phase in this fine two-phase structure is 70%, nearly the same as the two-phase structured zones in the coarse-grained AISI316. In the similar manner to Fig. 4(b), the nitrogen solutes distribute only in the nitrided layer with high concentration.

**Figure 7** compares the nitrogen content depth profiles between coarse and fine grained AISI316 substrates. As expected from Figs. 4(b) and 6(b), the nitrogen content in the nitrided layer becomes nearly constant from the surface to the nitriding front end by 4.5 mass% or 16 at% in average, irrespective of the initial grain size. In particular, more uniform nitrogen solute distribution with higher content than 4 mass% is attained in the fine grained AISI316. This reveals that inner nitriding takes place more homogeneously by decreasing the initial grain size.

**Figure 8** shows the phase mapping, the equivalent plastic strain distribution and the inverse pole figure, respectively. The nitrided layer above $d = 40 \mu m$ has homogeneous two-phase $\gamma$-$\alpha'$ microstructure with high plastic strains and finer grain size than 0.1 $\mu m$, besides for the vicinity of surfaces. To be noticed, less microstructure modification is

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**Fig. 7.** Comparison in the nitrogen content depth profile between the coarse- and fine-grained AISI316 substrates after plasma nitriding at 623 K for 14.4 ks.

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**Fig. 8.** EBSD analysis of fine grained AISI316 substrate after plasma nitriding at 623 K for 14.4 ks. (a) Phase mapping, (b) KAM distribution, and (c) Inverse pole figure in the normal direction.

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**Fig. 9.** Fine EBSD analysis on the cross-sectional microstructure around the Grain-A in Fig. 5 for normal grained AISI316 specimen after nitriding at 623 K. (a) Phase mapping, (b) KAM distribution and (c) Inverse pole figure.
seen below the nitriding front end. The grain size distribution remains the same as the state with the average grain size of 1.7 μm before nitriding. This proves that no nitrogen supersaturation takes place beyond the nitriding front end of 40 μm; homogeneous nitriding terminates at d = 40 μm after duration of 14.4 ks.

3.3. Grain Size Effect on the Inner Nitriding at 623 K

In case of the coarse grained AISI316 specimen, the homogeneous nitried layer with fine two-phase microstructure narrows toward the nitriding front end at d = 30 μm in Figs. 4 and 5. This localization in nitrogen supersaturation advances across the nitriding front end. Since the average nitrogen content by EDX is still 0.7 mass% beyond d = 30 μm, the nitrogen atoms diffuse across the nitriding front end and drive this heterogeneous nitriding. Let us precisely analyze this nitriding behavior below d = 30 μm.

Figure 9 depicts the phase mapping, the plastic straining and the inverse pole figure, respectively, around the Grain-A in Fig. 6 at the depth around 45 μm. Through comparison between Figs. 9(a) and 9(b), the transformed α'-phase domains are formed in complementary to the plastically strained γ-phase domains. That is, the Grain-A, which was fully in γ-phase before nitriding, consists of the four transformed α'-phase zones and the plastically strained γ-phase ones. Four α'-phase zones in Fig. 9(a) with less plastic strains, are aligned in lateral to each other in the inside of Grain-A. On the other hand, the γ'-phase zones, sandwiched by these four α'-phase ones, are plastically strained to surround these four α'-zones as depicted in Fig. 9(b). In particular, the highly strained γ-zones in Fig. 9(b) have fine microstructure as shown in Fig. 9(c). This heterogeneous nitriding in Grain-A describes the relationship between the nitrogen diffusion and super-saturation processes. The slip-lines with high plastic strains in Fig. 9(b) become the fine zone boundaries with significant misfit orientation angles in Fig. 9(c). These zone boundaries work as a diffusion path to transport more nitrogen atoms into the inside of Grain-A and to drive further nitrogen supersaturation. The fine-grained, two-phase structure is formed at these highly strained zones in similar to that seen in Fig. 8. Grain-B located near the original grain boundary, GB-1, has also heterogeneously nitried microstructure.

In case of the fine-grained AISI316 substrate, the nitrogen supersaturation advances more homogeneously and accompanies with the phase transformation, the plastic straining and the microstructure refinement at the same time. No heterogeneous nitriding is induced as a preceding process of this homogeneous nitriding. Difference in the nitrogen diffusion and supersaturation processes reflects on the grain size effect on the inner nitriding at 623 K between Figs. 8 and 9.

4. Discussion

A few paper reported on the plasma nitriding of austenitic stainless steels at 623 K and on the nitrogen diffusion process in low temperature. The nitried layer thickness was 2.0 μm and the nitrogen diffusion coefficient was estimated to be 2.7 × 10^{-16} m^2/s in 13). The effect of internal stress on the diffusion process was considered to validate the experimental data; the estimated layer thickness at 623 K was 6 μm and the estimated diffusion coefficient at 653 K was 1.68 × 10^{-16} m^2/s by curve-fitting in 14). The nitried layer thickness at 623 K in this study is 30 μm for coarse grained AISI316 and 40 μm for fine grains one; 15 to 20 times thicker than those reported in the above. After the classical theory, the square of nitried layer thickness is proportional to the diffusion coefficient times the nitriding time. Then, the diffusion coefficient in the present nitriding is estimated to be in the order of 5 × 10^{-14} to 10^{-13} m^2/s at 623 K. This enhancement of diffusion coefficient cannot be explained by the previous models but must be discussed by considering the in situ formation of nitrogen diffusion paths during inner nitriding with the intense plastic straining.

The nitrogen solute atoms, supplied from high density plasma sheath, penetrate to γ-lattices in AISI316 and stay as an interstitial element to occupy the vacancy sites in lattices together with diffusing into the depth. This alloying by nitrogen super-saturation induces large elastic strain to drive the phase formation. Intense plastic strains are also induced at the same time to compensate the misfit between nitrogen saturated and un-saturated lattices even in the original grain. As shown in Figs. 5 and 9, the transformed α'-phase zones are formed to be exclusively neighboring to the highly strained γ-phase ones in the same original γ-phase Grain-A. To form this micro-structure, the nitrogen solutes penetrate into the depth of Grain-A along the plastic slip-lines with high geometric misorientation. This in situ formation of nitrogen diffusion paths by nitrogen supersaturation, improves the nitrogen diffusivity and enhances the nitried layer thickness up to 30 to 40 μm even at 623 K for 14.4 ks.

This in situ diffusion path formation is ready to work when reducing the initial grain size. Comparing the microstructure in the depth between Figs. 5(c) and 8(c), the average grain size is much reduced by 1/10 to 1/20; the grain boundary area increases by 10^1 times. In case of fine grained AISI316, the nitrogen atom first diffuses into the dense network of grain boundaries and next penetrates into the inside of grains along the slip-lines formed by nitrogen supersaturation. Homogeneous nitriding behavior seen in Fig. 8, reveals that these two diffusion processes concurrently advance into the depth without localization of nitrogen supersaturation. This homogeneous nitriding terminates at the nitriding time limit of 14.4 ks in process; the layer thickness of 40 μm corresponds to the actual nitrogen diffusion length into AISI316 alloy with high concentration by 4.5 mass% in Fig. 7 at the temperature of 623 K.

On the other hand, in case of the coarse grained AISI316, homogeneous nitriding changes itself to heterogeneous one by localization in nitrogen supersaturation as depicted in Fig. 5. This localization might be caused by less diffusion path density at 623 K; the nitrogen diffusion selectively advances through the highly strained paths such as GB-1 in Fig. 5. In other words, the reduction of initial grain size works to stabilize the homogeneity in the inner nitriding into AISI316 at 623 K without localization in nitrogen supersaturation process.

5. Conclusion

Fine-grained AISI316 substrate is homogeneously
nitrided to have two phase $\gamma$-$\alpha'$ microstructure with the average grains size less than 0.1 $\mu$m down to the nitriding front end of 40 $\mu$m by plasma nitriding at 623 K for 14.4 ks. No nitrogen diffuses below this end; its microstructure remains the same as before nitriding. This homogeneous nitriding is supported by insitu formation of nitrogen diffusion paths along the high density slip lines with high plastic strains during nitrogen supersaturation. On the other hand, in the coarse grained AISI316, the nitrogen supersaturation process gradually localizes even below the nitriding front end, and, forms the heterogeneously nitrided zones in the grains which are located along the initial grain boundaries. In those grains, the transformed $\alpha'$-phase zones are formed by the nitrogen supersaturation along the insitu formed slip-lines with high plastic strains in the $\gamma$-phase domains.

Low temperature nitriding is characterized by the synergetic relationship between the nitrogen supersaturation and diffusion along the insitu-formed nitrogen transportation paths. Nitrogen supersaturation forms the fine slip-line networks in the inside of grains while the nitrogen diffusion through these paths transports a sufficient nitrogen content to drive the further nitrogen supersaturation. When nitriding the coarse grained AISI316, this nitrogen supersaturation process gradually localizes along the limited network of diffusion paths. The fine grained AISI316 is homogeneously nitrogen supersaturated to have fine two-phase microstructure with the thickness of 40 $\mu$m after nitriding at 623 K for 14.4 ks. High density network of nitrogen diffusion paths are insitu formed by this homogeneous nitrogen supersaturation.

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