

Article

Application of Active-Screen Plasma Nitriding to an Austenitic Stainless Steel Small-Diameter Thin Pipe

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Abstract: Low-temperature active-screen plasma nitriding (ASPN) was applied in this study to improve the bending rigidity and corrosion resistance of a small-diameter thin pipe composed of austenitic stainless steel (SUS 304). The inner and outer diameters of the pipe were $\phi 0.3$ and $\phi 0.4$ mm, respectively, and the pipe length was 50 mm. The jig temperature was measured using a thermocouple and was adopted as the nitriding temperature because measuring the temperature of a small-diameter pipe is difficult. The nitriding temperature was varied from 578 to 638 K to investigate the effect of temperature on the nitriding layer and mechanical property. The nitriding layer thickness increased with an increase in nitriding temperature, reaching 15 μm at 638 K. The existence of expanded austenite (S phase) in this nitriding layer was revealed using the X-ray diffraction pattern. Moreover, the surface hardness increased with the nitriding temperature and took a maximum value of 1100 HV above 598 K. The bending load increased with an increase in the nitriding temperature in relation to the thicker nitriding layer and increased surface hardness. The nitrided samples did not corrode near the center, and corrosion was noted only near the tip at high nitriding temperatures of 618 and 638 K in a salt spray test. These results indicated that the bending rigidity of the small-diameter thin pipe composed of austenitic stainless steel was successfully improved using low-temperature ASPN while ensuring corrosion resistance.

Keywords: plasma nitriding; active screen plasma nitriding; austenitic stainless steel; expanded austenite; S phase; small diameter thin pipe; bending strength; corrosion resistance



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1. Introduction

Austenitic stainless steels are used in a wide range of items such as household products, construction materials and automobile parts as well as in applications related to power generation and chemical and food industries owing to its high functionality, excellent corrosion resistance, ductility and toughness. However, austenitic stainless steel is limited by a low-hardness poor bending rigidity and wear resistance [1–3]. Surface hardening treatments such as nitriding can improve the mechanical properties to extend the applicability of austenitic stainless steel to fine and precise machining [4–9]. An improvement of these characteristics without changing the design and material is highly advantageous, particularly for medical equipment and surgical instruments [10–12]. In particular, an improved bending rigidity of medical injection needles is desirable because a small needle diameter reduces invasiveness. However, a method for improving the bending strength of austenitic stainless steel without reducing the corrosion resistance has not yet been reported. Moreover, nitriding has not been applied to thin pipes with a small diameter such as medical injection needles.

It is widely accepted that nitriding treatment is useful for austenitic stainless steel because a nitriding layer with high hardness is formed by the diffusion of nitrogen from

the surface. However, this treatment can significantly reduce the corrosion resistance. Conventionally, a strong passivation film is formed on the surface of austenitic stainless steel whereby the stability of the film depends on the content of solute Cr in the steel. Inside the nitrided layer, N diffused from the surface and Cr contained in the steel combine to precipitate CrN, which reduces the amount of Cr in the solid solution. This prevents the passivation film from forming on the surface of the steel, which consequently reduces the corrosion resistance. Moreover, nitriding processes of nitrogen diffusion and chromium nitrogen formation are strongly influenced by temperature. By reducing the temperatures to under 698 K (425 °C), the deterioration of the corrosion resistance can be prevented [13–16]. The resultant nitrided layer with a good hardness and corrosion resistance is referred to as expanded austenite or the S phase. This layer does not contain CrN precipitates and has a face-centered cubic (FCC) structure with an expanded interstitial distance when compared with that in the normal austenite phase. However, this thick hardened layer is difficult to obtain due to the nitrogen diffusing at a low temperature.

Plasma nitriding is a thermochemical method in which a glow discharge is generated under a mixed gas of N₂ and H₂ to form nitride and solid-solution N by diffusion. Plasma nitriding does not require an external heating device because the processing material is heated by the collision energy of ions, and the processing time can be shortened using N atoms and ions in an active plasma state. It has been generally believed that gas nitriding has difficulty forming nitriding layer on stainless steels due to their surface's passive oxide films, which are a diffusion barrier for N atoms. Therefore, plasma nitriding is highly advantageous for treating stainless steel because a passivation film is removed by the collision of ions in the plasma without pretreatment. Active screen plasma nitriding (ASPN) is an excellent method for the further utilization of active species and the generation of uniform heating regions. The screen suppresses the edge effect by increasing the supply of active species such as N⁺, N₂⁺ and H⁺ and by heating the sample surface uniformly [17–32]. However, nitriding on small-diameter thin pipes has not been reported yet [30].

In the present study, low-temperature ASPN is applied to improve the bending rigidity and corrosion resistance of an austenitic stainless-steel pipe with a small diameter. The nitrided sample properties of layer thickness, layer structure, surface hardness, bending load and corrosion resistance are evaluated by varying the changing nitriding temperature.

2. Materials and Methods

2.1. Materials

A small-diameter thin pipe composed of SUS 304 stainless steel was used as the sample material. The nominal composition of the material is shown in Table 1. This pipe was produced using a drawing process. The inner and outer diameters of the pipe were $\phi 0.3$ and $\phi 0.4$ mm, respectively, and the pipe length was 50 mm.

Table 1. Nominal composition of SUS 304 stainless steel used in the present study (JIS G4304-2012).

C	Si	Mn	P	S	Ni	Cr
≤0.08	≤1.00	≤2.00	≤0.045	≤0.030	8.00–10.50	18.00–20.00

2.2. Plasma Nitriding

Figure 1 shows a schematic of the plasma nitriding process. The samples of the small-diameter thin pipe were mounted at the circumference of a ring-shaped jig. The jig was suspended from a screen that was placed on the cathodic sample stage. Consequently, plasma was formed on both the sample pipe and screen. The screen material was an expanded mesh composed of SUS 304 stainless steel with a 22.7% open area, diameter of 90 mm and height of 400 mm. The distance between the pipe and screen was 12.5 mm. The jig temperature was measured using a thermocouple and adopted as the nitriding temperature because measuring the temperature of a small-diameter pipe is difficult. Moreover, a pulsed power supply was used for plasma generation. Table 2 shows the experimental

conditions. The plasma nitriding was conducted for 4 h at 578–638 K (305–365 °C) under a 50% N₂–50% H₂ atmosphere with a pressure of 200 Pa.

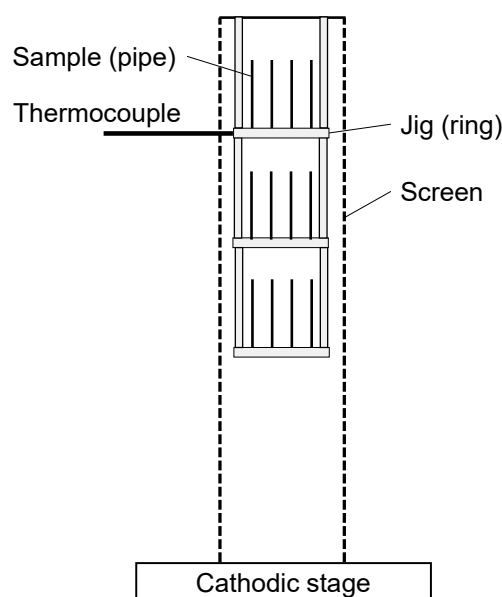


Figure 1. Schematic of the plasma nitriding setup.

Table 2. Experimental conditions.

Nitriding Time/h	Nitriding Temperature/K	Gas Pressure/Pa	Gas Flow Ratio (N ₂ :H ₂)	Discharge Voltage/V	Pulse Width/μs
4	578, 598, 618, 638	200	1:1	−500	100

2.3. Characterization

The layer thickness and phase structure of the nitrided sample surfaces were characterized by analyzing the cross sections of micrographs (GX71, Olympus Corporation, Tokyo, Japan) and X-ray diffraction (XRD, RINT-2500, Rigaku Corporation, Tokyo, Japan), respectively. To examine the microstructures, the samples were etched in a solution of Marble's reagent (composed of 4 g CuSO₄, 20 cc HCl and 20 cc H₂O). In the XRD measurement, 10 pipes were placed in a side-by-side arrangement with no gaps among them. The surface hardness was measured under a load of 0.5 N using a Vickers microhardness tester (HM-211+AT-400, Mitsutoyo Corporation, Kanagawa, Japan). The pipe was fixed with resin embedding for hardness test. The bending load of the pipe was measured by applying the three-point bending test (EMX-1000N-FA-KX-0023-1, Imada Co. Ltd., Aichi, Japan), as shown in Figure 2. The distance between the fulcrums at a radius of R2.5 was 30 mm. The bending load is defined as the load at a 1-mm displacement when pushing the pipe at a speed of 0.5 mm/min. The bending load improvement was calculated by a comparison with an untreated sample. The bending load measurements were conducted using 18 samples for each condition. The corrosion resistance was evaluated by a 96-h salt spray test based on the JIS Z 2371 standard. The pipes were set in a Styrofoam block at an angle of approximately 60°.

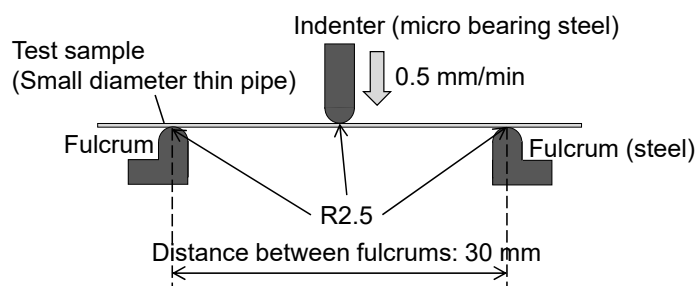


Figure 2. Schematic of the bending load measurement.

3. Results and Discussion

3.1. Nitrided Layer Thickness and Phase Structure

Figure 3 shows the micrograph of the cross sections obtained at the center position in the length direction of the plasma-nitrided samples. A white layer that was not corroded by the Marble's reagent was generated under all treatment temperature conditions. As the nitriding temperature increased, the white nitriding layer thickened. The etched areas of black corrosion were scattered on the surface at nitriding temperatures of 618 and 638 K. Figure 4 shows the effect of the nitriding temperature on the layer thickness. The nitriding thickness increased monotonically with the nitriding temperature.

The XRD patterns of the untreated and plasma-nitrided samples are shown in Figure 5. The pattern of the untreated sample showed three distinct peaks. Two peaks at 43.7° and 50.8° represent γ -Fe, which is the main element of the austenitic stainless-steel sample. The other, third peak at 44.7° represents α' -Fe formation of strain-induced martensite during the drawing process of the small diameter pipe. The pattern of the plasma-nitrided samples showed two wide peaks from the austenite phase of the untreated samples that shifted to a low angle, indicating that the S phase with N supersaturation was formed. This represents the formation of the white layer observed in the microstructure cross sections shown in Figure 3. At low temperatures of 578 K, a small peak of γ -Fe at 50.8° was also observed. This peak was detected from the substrate because the nitrided layer was thin. Moreover, under high nitriding temperature conditions of 618 and 638 K, a small peak was observed at approximately 44° . This indicates the formation of CrN and corresponds to the corroded areas scattered on the surface, as shown in Figure 3.

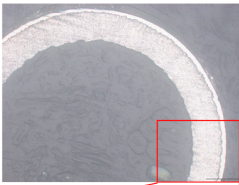
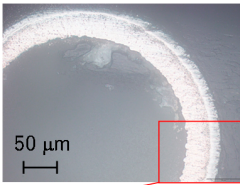
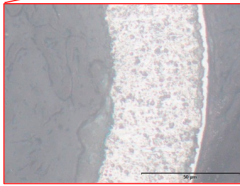
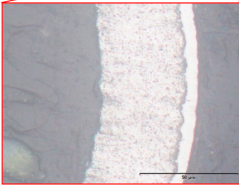
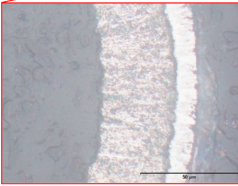
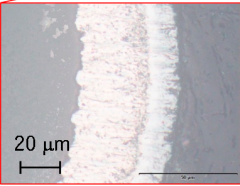
Nitriding temperature			
578 K	598 K	618 K	638 K
			
			
Nitrided layer thickness: 3.5 μm	7 μm	11 μm	15 μm

Figure 3. Micrographs showing the cross sections of plasma-nitrided samples.

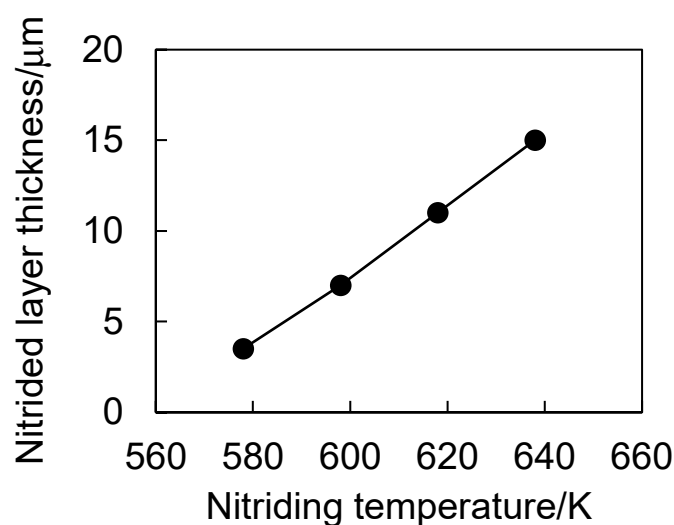


Figure 4. Effect of the nitriding temperature on the nitrided layer thickness.

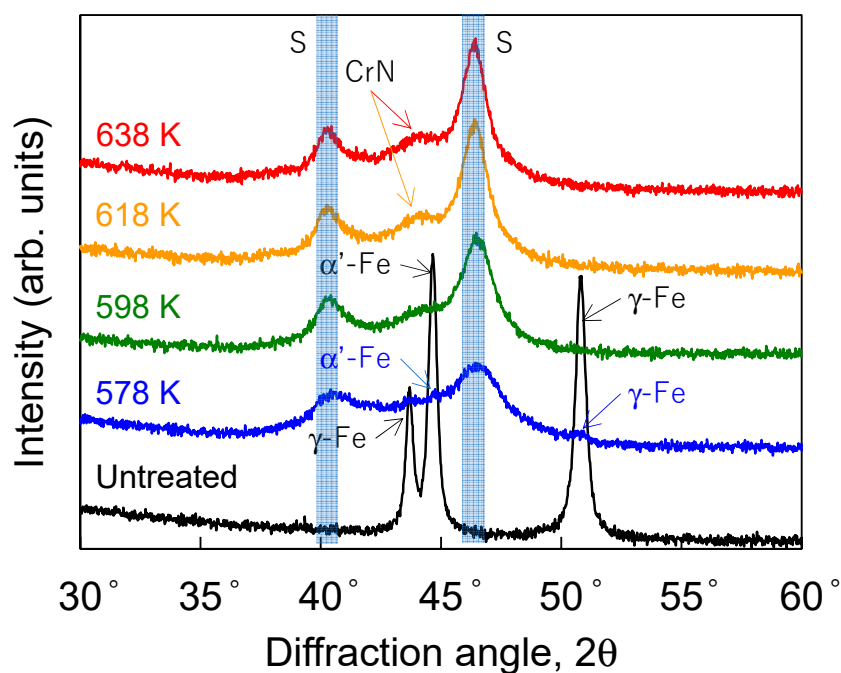


Figure 5. X-ray diffraction patterns of the plasma-nitrided samples.

3.2. Mechanical Properties

Figure 6 shows the effect of the nitriding temperature on the surface hardness. The surface hardness was higher in the nitrided samples than in the untreated sample. The hardness increased with the nitriding temperature and was saturated at 1100 HV owing to the N-supersaturated solid solution under nitriding temperatures above 598 K. At a nitriding temperature of 578 K, the surface hardness was influenced by the base metal because the nitrided layer was thin.

Figure 7 shows the effect of the nitriding temperature on the bending load. The bending load increased with the nitriding temperature because the nitriding layer became thicker and the surface hardness increased, as shown in Figures 4 and 6. These results reveal that low temperature ASPN is effective in improving the bending strength of small-diameter thin pipes composed of austenitic stainless steel.

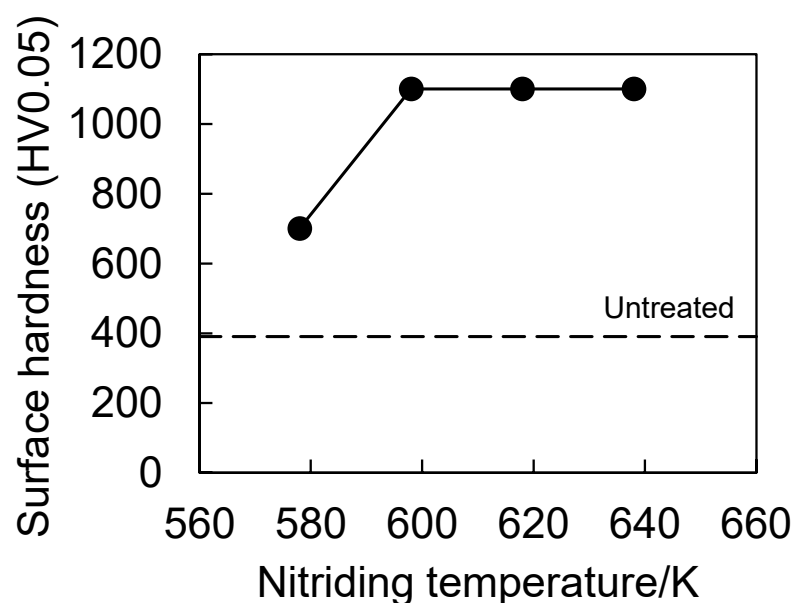


Figure 6. Effect of the nitriding temperature on the surface hardness.

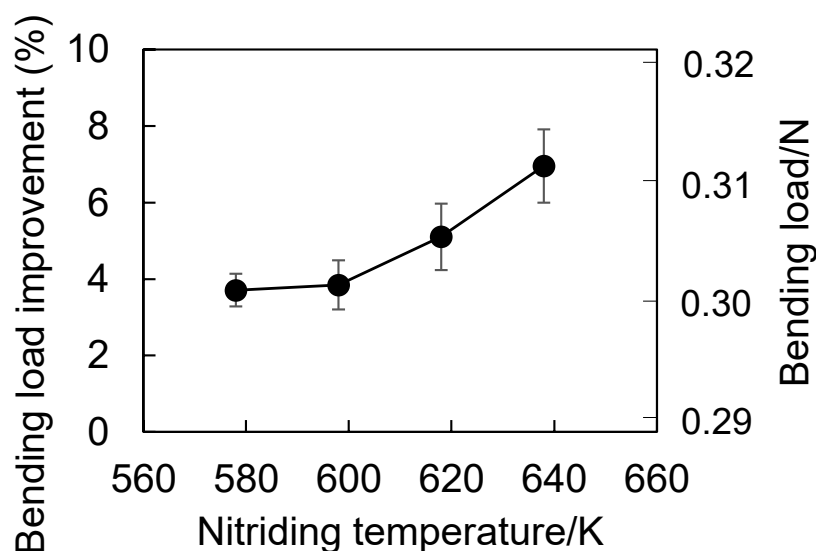


Figure 7. Effect of the nitriding temperature on the bending load.

3.3. Corrosion Resistance

Figure 8 shows the results of the corrosion resistance evaluation according to the salt spray test. No corrosion was observed under low nitriding temperature conditions of 578 and 598 K. At high nitriding temperatures of 618 and 638 K, corrosion was observed near the tip of the pipe; no corrosion was observed near the center of the pipe.

To investigate the cause of the corrosion at the tip of the pipe, a vertical cross-section micrograph was obtained near the tip of the pipe, as shown in Figure 9. A nitriding layer was also formed on the inner surface of the pipe at approximately 1 mm from the tip. At high nitriding temperatures of 618 and 638 K, a thin black corrosive layer of CrN was observed on the surface of the tip. This CrN layer is the cause of the corrosion near the tip shown in Figure 8. CrN was also formed near the center of the pipe, as shown in Figure 3, but the pattern was scattered rather than layered. Therefore, the corrosion resistance was strong near the center of the pipe.

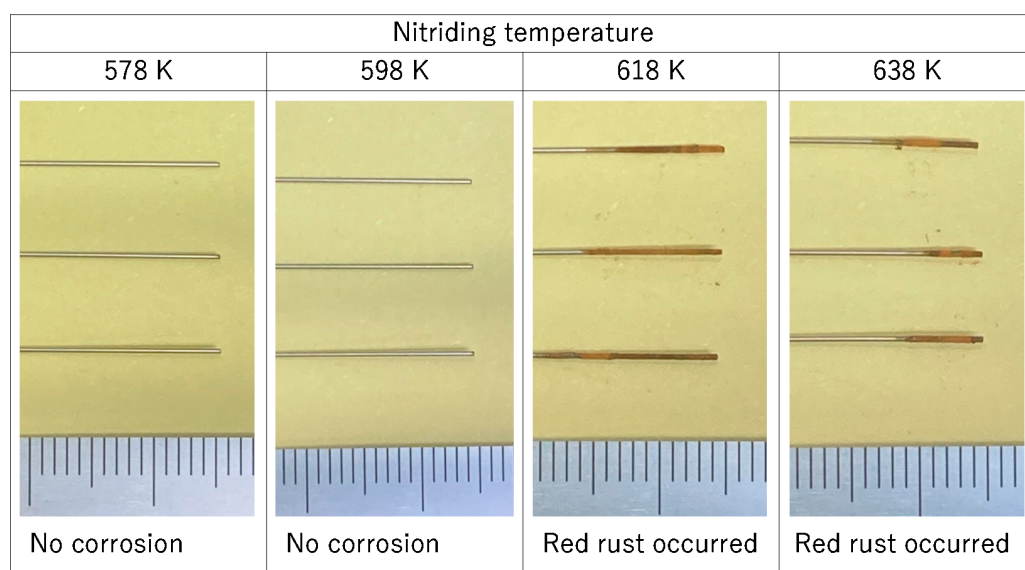


Figure 8. Appearance of samples after salt spray testing for 96 h.

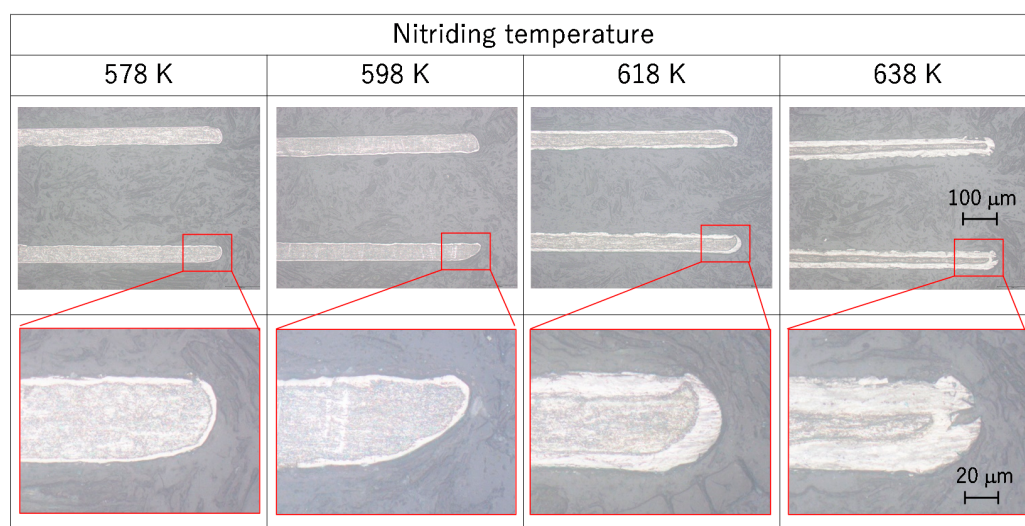


Figure 9. Photographs showing cross sections of plasma-nitrided samples.

4. Conclusions

In this study, low-temperature ASPN was applied to improve the bending rigidity and corrosion resistance of a small-diameter thin pipe composed of austenitic stainless steel. The nitriding layer thickness, layer structure, surface hardness, bending load and corrosion resistance were investigated by varying the nitriding temperature. The results are summarized as follows:

1. An austenitic stainless-steel small-diameter thin pipe was successfully nitrided using low-temperature ASPN.
2. The nitriding layer thickness increased monotonically with the nitriding temperature from 578 to 638 K. The nitriding layer thickness at 638 K was approximately 15 μm .
3. The existence of expanded austenite (S phase) was revealed using the XRD pattern. At high nitriding temperatures of 618 and 638 K, peaks related to the formation of CrN were also observed.
4. The bending load increased with the nitriding temperature because the nitriding layer became thicker and the surface hardness increased.
5. At low nitriding temperatures of 578 and 598 K, the nitrided samples did not corrode in the corrosion test. At high nitriding temperatures of 618 and 638 K, corrosion was

only observed near the tip of the pipe; no corrosion was observed near the center of the pipe.

These results indicated that low-temperature ASPN achieved both flexural rigidity and corrosion resistance in a small-diameter thin pipe composed of austenitic stainless steel. Such results have not been reported thus far. It is expected that the application of plasma nitriding for such applications as medical injection needles will be expanded to provide the required diameter thinness.

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