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Low Temperature Plasma Nitriding of High Silicon Duplex Stainless Steel

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The life span, strength, and functionality of metallic materials must be improved. A combination of plasma nitriding with a high silicon duplex stainless steel that was developed as a high strength stainless steel may produce a material with improved wear resistance, high strength, and excellent corrosion resistance. However, traditional plasma nitriding at temperatures ranging from 723 to 823 K, decreases the corrosion resistance of stainless steel. This is because the chromium in the steel reacts with nitrogen to form chromium nitride, and this decreases the concentration of chromium in the matrix, which is necessary for the formation of stable passive layers. Therefore, a low temperature plasma nitriding technique was selected for treating stainless steel. Plasma nitriding below 723 K forms a nitrided layer that is called the S phase. This phase improves the surface hardness without decreasing the corrosion resistance. In this study, a high silicon duplex stainless steel was plasma nitrided at low temperature. In addition to conventional direct current plasma nitriding (DCPN), active screen plasma nitriding (ASPN) was carried out as the plasma nitriding process. ASPN has several advantages, including eliminating the edge effect, arcing, and the hollow cathode discharge that are problems for conventional DCPN. Nitriding was carried out in a direct current plasma nitriding unit at 673 and 723 K for 18 ks at 600 Pa in a gas mixture that was 25% N2 + 75% H2. In ASPN, the specimen was isolated electrically, and an austenitic 304 stainless steel was selected as a screen. After nitriding, the nitrided specimens were characterized with a variety of analytical techniques, including XRD for phase identification, microhardness testing, SEM, EDX, and EPMA for surface and cross-sectional morphological examination, anodic polarization testing for measuring corrosion properties, and pin-on-disc testing to determine the wear properties. All treated specimens were harder than the untreated specimen. The S phase was observed in all treated specimens, and it formed uniformly on the ASPN specimens. The DCPN specimens had superior corrosion resistance, while the ASPN specimens had worse corrosion resistance than the untreated specimen. All treated specimens showed improved wear resistance. In comparing ASPN and DCPN specimens, the ASPN specimens better wear resistance.

Keywords: *high silicon stainless steel, duplex stainless steel, plasma nitriding, active screen plasma nitriding, S phase*

1. Introduction

Stainless steel has good corrosion resistance because the chromium contained in the steel forms a passive layer on the steel surface. Therefore, stainless steel is applied in various applications, such as in chemical and nuclear industries, and as structural material. However, it needs improvement for application in more severe environments. Thus, a number of stainless steels have been developed with good corrosion resistance, mechanical properties, and better wear resistance than conventional austenitic stainless steel, such as AISI304. Conventionally, steel is strengthened by adding carbon; however, adding carbon to stainless steels is difficult. The corrosion resistance decreases when the resulting chromium carbide forms in the grain boundaries. Silicon is considered an impurity when refining steel; however, many researchers have found that adding silicon can strengthen stainless steel, and it does this without decreasing corrosion resistance[1)]. In this study, duplex stainless steel was selected from among the high silicon stainless steels. Duplex stainless steel has a ferritic–austenitic structure. It has good corrosion resistance, similar to that of austenitic stainless steels, with better mechanical properties[2)]. A surface treatment was also applied to this material. The combination of the material itself with the surface treatment provides good corrosion and wear resistance, and good mechanical properties. Plasma nitriding was selected for surface treatment in this study. However, traditional plasma nitriding at temperatures between 723 and 823 K decreases corrosion resistance. Because chromium in steel reacts with nitrogen to form chromium nitride, it decreases the concentration of chromium in matrix, which is necessary for the formation of stable passive layers. Therefore, low temperature plasma nitriding was used. Plasma nitriding treatment of austenitic stainless steel below 723 K forms a nitrided layer called an S phase, which improves surface hardness without decreasing the corrosion resistance[3-5)]. If duplex stainless steel is treated by this technique, the S phase forms on the austenitic phase and some nitrided layer forms on the ferritic phase. The corrosion resistance and surface hardness differ between these phases. The nitriding methods are direct current plasma nitriding (DCPN) and an active screen plasma nitriding (ASPN). In the ASPN process, the specimen is isolated, which resolves the electrical problems seen in the conventional DCPN process, such as the edge effect, hollow cathode discharge, and arcing. Sputtering from the screen occurs in addition to the nitriding process[6-9)]. When the austenitic stainless steel is selected for the screen, the surface composition and structure of nitrided specimens should change to an austenitic structure by sputtering from screen. Consequently, the S phase should form homogeneously and the surface hardness of the specimen would increase.

2. Experimental procedure

A high silicon duplex stainless steel was selected for the test. The specimen was cut into sector shapes, 50 mm in diameter and 5 mm thick. Each specimen was polished, starting with #600 emery paper and moving up to 0.05 μm alumina powders. Then, they were ultrasonically cleaned in acetone. Nitriding was performed in a hydrogen–nitrogen atmosphere with a ratio of 25 %N_2 + 75 %H_2 at 600 Pa, at 673 and 723 K by DCPN and ASPN techniques. Henceforth, specimens treated by DCPN and ASPN at 673 and 723 K are called DC673, DC723, AS673, and AS723, respectively. Plasma nitriding equipment has an anodic furnace wall and a cathodic table. For DCPN, the specimen was placed on a cathodic table, which has cathodic

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Table 1 Nominal composition of specimen and screen (mass%).

	Cr	Ni	Si	Mn	Cu	Mo	C	P	S	Fe
Specimen	18.00-20.00	8.50-9.50	3.60-4.40	1.80-2.20	1.00-2.00	1.00-2.00	< 0.03	< 0.03	< 0.03	Bal.
Screen	18.00-20.00	8.00-10.50	< 1.00	< 2.00	-	-	< 0.08	< 0.045	< 0.03	Bal.

potential. For ASPN, the specimen was placed on an electrically isolated table with a quartz rod. The space between the screen and specimen was 10 mm. The screen was made of austenitic 304 stainless steel—the screen was expanded metal with a 55% opening rate. Table 1 shows the nominal composition of the specimen and the screen.

After nitriding, various techniques were used to characterize the structure, composition, corrosion resistance, and physical properties of the untreated and plasma nitrided specimens. Analyses of structure and composition included visual examination, X-ray analysis for nitrided layer identification, and SEM, EDX, and EPMA analysis for surface and cross-sectional structure and chemical composition determination. To analyze the corrosion properties, anodic polarization testing was carried out in a 0.1 N H_2SO_4 bath and the corrosion area was analyzed by EPMA. Analysis for physical properties includes hardness testing of the surface, roughness testing and wear resistance testing. Hardness testing was carried out with a Vickers microhardness tester. Roughness testing was carried out with a stylus profilometer. Wear resistance testing was carried out with a pin-on-disk tribometer. The conditions for wear testing were a running distance up to 2000 m, wear load of 1 N, and an alumina ball for a counter material. The wear friction force was measured. After wear testing, the wear track was analyzed with an optical microscope and stylus profilometer.

3. Results and discussion

3.1 Characterization of the nitrided layer

Visual examination determined that all specimens had a metallic luster and the DCPN specimens had a well-established, non-uniform surface appearance. DCPN specimens changed color from the center to the edge—the center was blue and the edge silver. This phenomenon is known as the edge effect. ASPN specimens were a uniform matt gray over the entire surface. In the ASPN process, as the plasma is not formed directly on the specimen surface, the defects that produce the edge effect are eliminated[6-9].

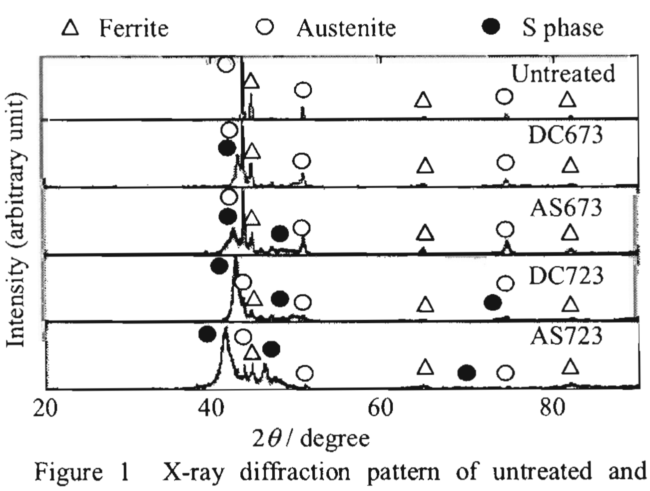

Figure 1 X-ray diffraction pattern of untreated and plasma nitrided specimens.

Figure 1 shows X-ray diffraction patterns. The analysis was performed on the nitrided surface. The scanning angle (2θ) varied from 20 to 90 degrees. The untreated specimen showed a mixed structure of ferrite and austenite. Nitrided specimens consisted of ferrite, austenite, and an S phase. The S phase is considered to be a supersaturated solid solution of nitrogen in austenite. The S phase intensities of specimens formed at 723 K was stronger than those formed at 673 K, indicating that a formation of the S phase increased with an increasing treatment temperature. Comparing DC723 and AS723, the S phase peaks of AS723 shifted to a lower angle than those of DC723. Based on Bragg's theory ($2d\sin\theta = n\lambda$), this means that AS723 expanded more than DC723, and the S phase of AS723 contained a large amount of saturated nitrogen.

The results of the surface structure analysis are shown in Figure 2 and Table 2. Figure 2 shows the surface structure of untreated and plasma nitrided specimens at 723 K, as analyzed by EPMA. Table 2 shows the chromium and nickel content in the untreated and plasma nitrided specimens, as analyzed by EDX. These results show that all specimens had duplex phases—a Cr-rich phase that is considered ferrite, and a Ni-rich phase that is considered austenite. Comparing DCPN and ASPN specimens, the ASPN specimens showed a uniform surface composition. Moreover, the Cr/Ni ratio in the Cr-rich phase of the surface treated by ASPN was lower than that treated by DCPN. The results suggest that the uniform surface

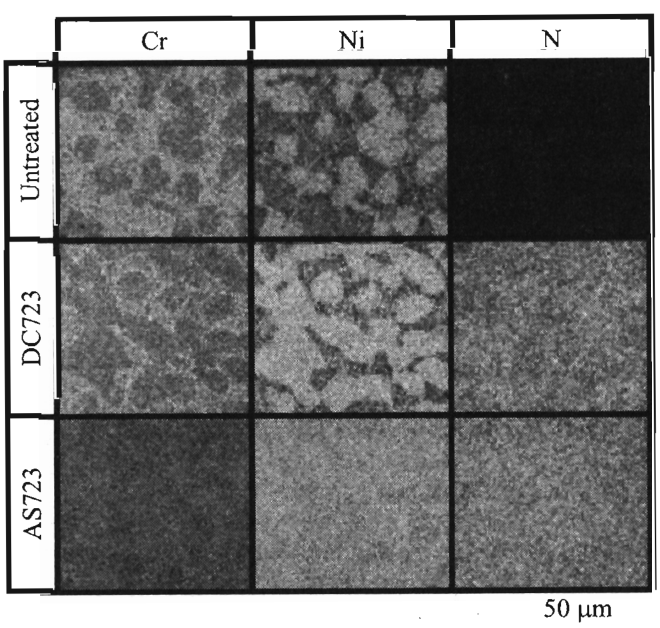

Figure 2 The surface structure of untreated and plasma nitrided specimens at 723 K.

composition resulted from sputtering from the screen of an austenitic 304 stainless steel during the ASPN process.

Figure 3 shows the cross sectional microstructure of DC723 and AS723 analyzed by EPMA. The nitrided layer is observed in each specimen. In DCPN specimens, the layer thickness differed between the Cr-rich and Ni-rich phases. The Ni-rich phase had a thicker layer than the Cr-rich phase. In comparison, in ASPN specimens, the layer thickness was uniform for each phase. The difference in nitrided layer thickness results from differences in the nitrogen solubility limits of ferrite and austenite—austenite has larger solubility limit of nitrogen than ferrite. The specimen treated by the ASPN process has uniform chromium and nickel content in each phase, compared with that treated by the DCPN process, shown in Figure 2. Therefore, the nitrogen easily diffuses from the surface to the matrix in ASPN specimens.

Table 2 Chromium and nickel content in the untreated and plasma nitrided specimen (mass%).

		Cr	Ni	Cr/Ni
Untreated	Cr-rich	22.8	6.2	3.7
	Ni-rich	17.6	10.8	1.6
DC673	Cr-rich	22.9	6.6	3.5
	Ni-rich	19.8	10.3	1.9
AS673	Cr-rich	23.6	7.3	3.2
	Ni-rich	16.4	9.4	1.8
DC723	Cr-rich	26.6	5.2	5.2
	Ni-rich	19.0	10.0	1.9
AS723	Cr-rich	19.5	8.4	2.3
	Ni-rich	16.4	10.0	1.6

3.2 Corrosion properties

Figure 4 shows the anodic polarization curve, which indicates that DCPN specimens exhibited better corrosion resistance than the untreated specimen, while ASPN specimens had poor corrosion resistance. It is well known that existing ratio of the phase is effective for corrosion resistance in duplex stainless steel[10]. The phase ratio of the ASPN specimen was changed by sputtering from the stainless steel screen. The corrosion area of all of specimens was analyzed by EPMA. On the ASPN specimen, a concentration of carbon was observed at grain boundaries. This is considered sensitization. Carbon contents were higher in the screen (AISI304) than in the specimen (high silicon duplex stainless steel). Furthermore, the screen might contain a large amount of carbon when it was produced by machining. Therefore, it changed the surface structure, and the sensitization resulted in a decrease of corrosion resistance for ASPN specimens.

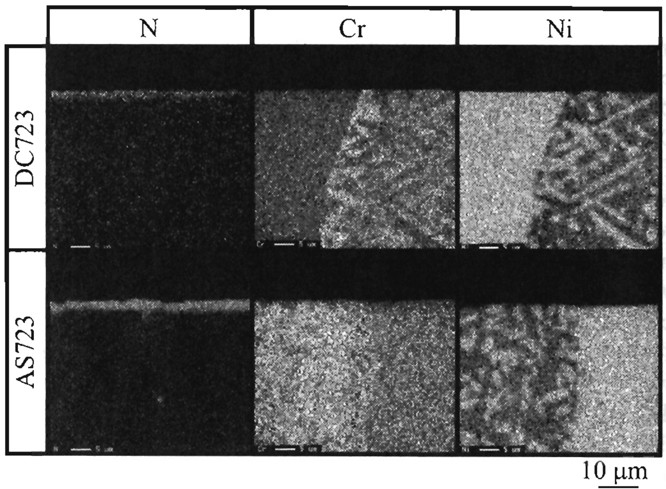

Figure 3 The cross sectional microstructure of plasma nitrided specimens at 723 K.

3.3 Physical properties

Figure 5 shows the results of hardness and roughness testing. All treated specimens were harder than the untreated specimen. All specimens had hard and soft phases, which were considered to be ferrite, austenite, and those nitrided. Comparing ASPN and DCPN specimens showed that ASPN specimens had a harder surface. In particular, AS723 had hardness of over 1000 HV, and the hardness was similar in each phase. This means that the S phase on AS723 was formed uniformly compared with the others. Similarly, nitriding increased the roughness.

Figures 6 and 7 show the results of wear testing. Figure 6 shows wear track profile. The untreated specimen had poor wear resistance, as evidenced by the wear loss area. In comparison, nitrided specimens exhibited considerably less wear. This confirmed that plasma nitriding can effectively improve the wear resistance of high silicon duplex stainless steel. Figure 7 shows durable distance of nitrided layer that was determined from change of the coefficient of friction. In comparing DCPN and ASPN specimens, ASPN specimens had better wear resistance. It is considered that the nitrided layer affected the wear resistance. The S phase layer formed on AS723 was more uniform and thicker than that formed on DC723.

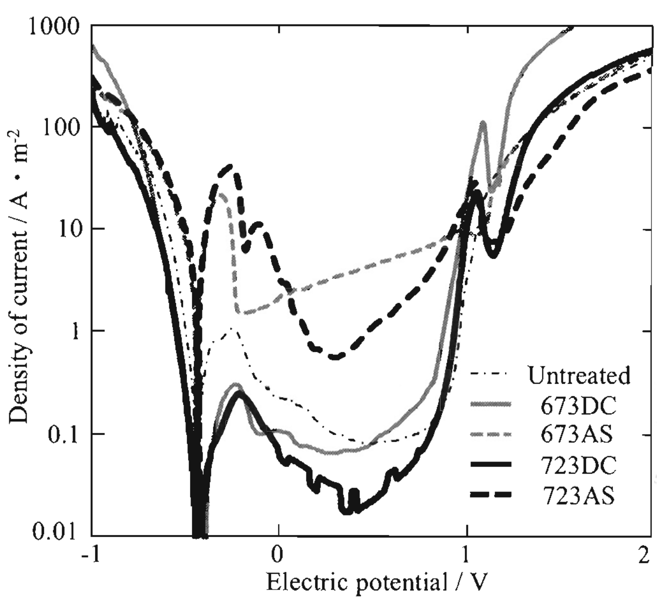

Figure 4 The polarization curve of untreated and plasma nitrided specimens.

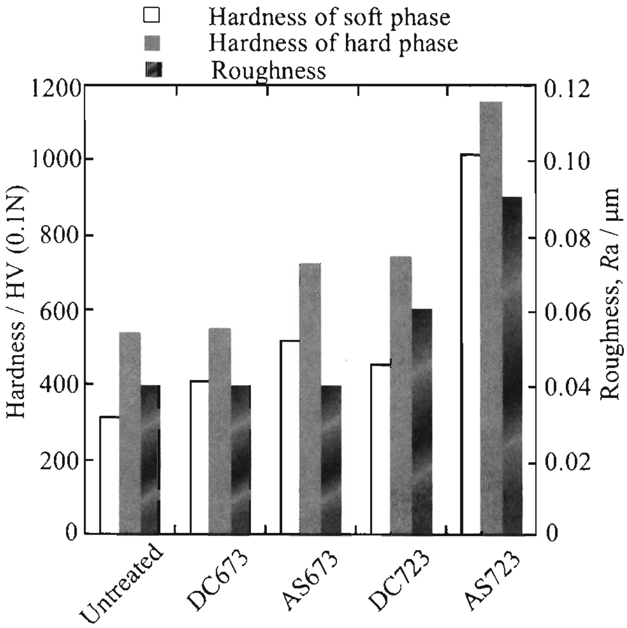

Figure 5 Hardness and roughness of untreated and plasma nitrided specimens.

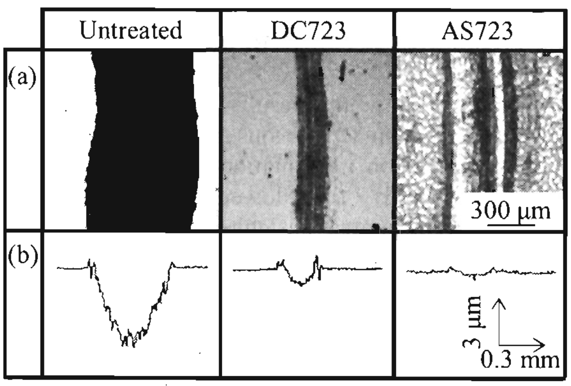

Figure 6 Wear track profile: (a) structure of the wear track, and (b) a cross sectional profile of the wear track of untreated and plasma nitrided specimens at 723 K.

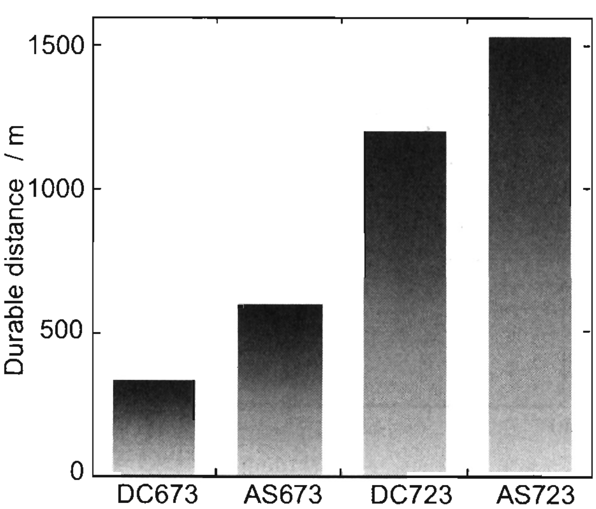

Figure 7 Durable distance of plasma nitrided specimens.

4. Conclusions

High silicon duplex stainless steels were plasma nitrided. Direct current plasma nitriding (DCPN) and active screen plasma nitriding (ASPN) with an AISI304 screen at 673 and 723 K were selected as the plasma nitriding conditions. The results of this study are as follows:

(1) An edge effect was observed on DCPN specimens, not on ASPN specimens.
(2) S phase was observed on all treated specimens and a formation of the S phase treated at 723 K increased compared with that treated at 673 K in both treatment conditions. Moreover, S phase formed uniformly on ASPN specimens.
(3) DCPN specimens had good corrosion resistance, while ASPN specimens had poor corrosion resistance, compared to the untreated specimen.
(4) The hardness of specimens treated at 723 K was higher than that treated at 673 K, and ASPN specimens were harder than DCPN specimens.
(5) All treated specimens had better wear resistance than the untreated. Wear resistance of specimens treated at 723 K was better than that treated at 673 K, and ASPN specimens had better wear resistance than DCPN specimens.

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