Effect of Cold Forming on Low-Temperature Plasma Nitriding and Carburizing Characteristics of Austenitic Stainless Steel

Motoo Egawa,* Yasushi Matsuda, Nobuhiro Ueda, Takumi Sone, Masato Tsujikawa, Kazuhiro Nakata

The cold-rolled specimen of AISI304 and AISI316 were plasma nitrided and carburized at low temperature, and the S-phase layers formed on the surface were investigated. In nitriding on AISI304 and AISI316, the thicknesses of the nitrided layers increased with an increase in rolling reduction. In plasma carburizing, on both steels, the thicknesses of the carburized layers were almost unchanged as the rolling reduction increased. In the nitriding, the growth of the S-phase layer was accelerated by the deformation structure. However, in the carburizing, the growth of S-phase layer was almost constant as the rolling reduction increased.

Introduction

Austenitic stainless steels are widely used in many industrial parts owing to their excellent corrosion resistance. However, the use of austenitic stainless steels is not considered for parts exposed to severe friction because they have low hardness and poor friction and wear properties. Therefore, many attempts have been made to harden the surface of these steels. For example, a conventional nitriding treatment at 773–823 K is well known to increase the surface hardness of the austenitic stainless steels and improve the wear resistance. However, hardening by nitriding is induced by the precipitation of chromium nitrides in the nitrided layer. This leads to a depletion of chromium in the austenitic matrix and thus a significant reduction in corrosion resistance. Therefore, it is important to develop surface engineering techniques that can improve the wear resistance of austenitic stainless steels without the loss of corrosion resistance.

Low-temperature plasma nitriding can produce a new phase with high hardness and good corrosion resistance on austenitic stainless steel surfaces. It does so by the formation of a non-equilibrium supersaturated layer, what is called "S-phase" or "expanded austenite."[1,2] This low-temperature diffusion processing is also effective for carburizing. Despite its very high nitrogen or carbon content, the S-phase has no chromium nitrides and carbides that consume the dissolved chromium in the austenitic matrix. Although many researches[3–8] have been reported in the literature, the nature of the S-phase has not yet been fully characterized. Some papers have reported low-temperature nitriding for commercial stainless steels of AISI 304, 316, 321, and 310S.[1–9] Many of these papers have described research on stainless steels that are solution heat-treated in order to eliminate deformation-induced martensite that forms during the preparation of specimens. However, there are many stainless steel parts that are used without solution heat-treatment subsequent to the cold forming. Therefore, to apply low-temperature plasma processing to parts made of stainless steels, it is important

M. Egawa, N. Ueda, T. Sone
Technology Research Institute of Osaka Prefecture, 2-7-1 Ayumino Izumi-shi, Osaka, Japan
Fax: (+81) 725 51 2749; E-mail: egawa@tri.pref.osaka.jp
Y. Matsuda
Sumitomo Metal Technology Inc., 1 Higashimukoujima-Higashino-chou Amagasaki-shi, Hyogo, Japan
M. Tsujikawa
Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-Cho Nakaku Sakai-shi, Osaka, Japan
K. Nakata
Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka Ibaraki-shi, Osaka, Japan

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to clarify the nitriding and carburizing behavior of the cold-formed structure. In this study, we investigated the effect of cold-formed structure on the thickness of the plasma nitrided layer and carburized layer on the austenitic stainless steels. The austenitic stainless steels used were AISI304 and AISI316 steels. We examined the influence of the difference between the austenite stabilities of the two steels.

Experimental Part

The substrate materials were commercial grade austenitic stainless steels: AISI304 (0.06 mass% C; 18.2 mass% Cr; 8.1 mass% Ni; 0.18 mass% Mo) and AISI316 (0.03 mass% C; 16.3 mass% Cr; 10.1 mass% Ni; 2.10 mass% Mo). First the substrate plates were solution heat-treated and then cold rolled at rolling reductions of 31 and 62%. The cold-rolled specimens and non-rolled specimens have dimensions of 25 mm width, 50 mm length, and 2.5 mm thickness. The surfaces of all the specimens were electrolytically polished. The martensite content induced by cold rolling was measured using FERITSCOPE MP30 (made by Fisher Instruments). Plasma nitriding or carburizing was performed with a laboratory-type apparatus with a conventional direct current (dc) power source. After the specimen was mounted on the cathode in a furnace, its vacuum bell jar was evacuated to 1.33×10^{-1} Pa. The specimens were plasma nitrided in a gas mixture of 80% nitrogen and 20% hydrogen for 14.4 10^3 s at the temperature of 673 K, and plasma carburized in a gas mixture of 50% argon, 45% hydrogen, and 5% methane for 14.4 10^3 s at the temperature of 673 K. The pressures of the gas mixtures were adjusted to 667 Pa. Each specimen was mounted on the cathode and heated using glow discharge in the nitriding or carburizing processes without pre-cleaning or pre-heating step. The temperature of the specimen was measured using a thermocouple. After the plasma treatment was finished, the specimen was allowed to cool in the evacuated furnace.

The treated specimens were then characterized by X-ray diffraction for phase identification using Cu Kα radiation and a monochromator. Microstructures were observed using an optical microscope. Glow discharge spectrometry (GDS), using a RIGAKU System 3860, was used to analyze the elemental depth profile of treated specimens.

Results and Discussion

Table 1 gives the martensite contents in the specimens before nitriding or carburizing. In the case of AISI304 steel, the martensite content increased with an increase in rolling reduction. On the other hand, in the case of AISI316 steel, the martensite content hardly increased. This difference is due to the different austenite stabilities. The austenite phase in the AISI316 steel containing over 2 mass% of molybdenum is more stable than that in the AISI304 steel containing only 0.18 mass% of molybdenum. Therefore, while cold rolling at 62% reduction produced a martensite content of 13.6% in the AISI304 steel and it produced a martensite content of only 1.1% in the AISI316 steel.

Figure 1 shows the cross-sectional microstructures of the nitrided and carburized specimens. The thicknesses of

Table 1. Martensite contents in the specimens.

Rolling reduction %	Martensite content %	
	AISI304	AISI316
0	0.0	0.0
31	2.2	0.1
62	13.6	1.1

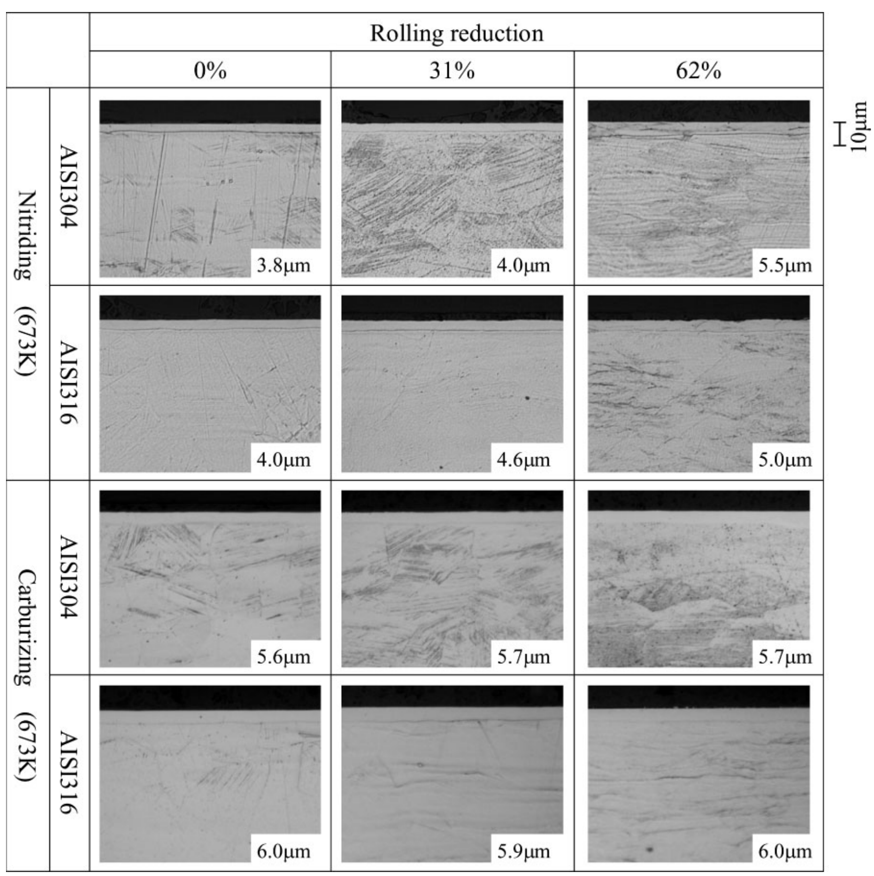

Figure 1. Microstructure of surface layers formed on the stainless steel.

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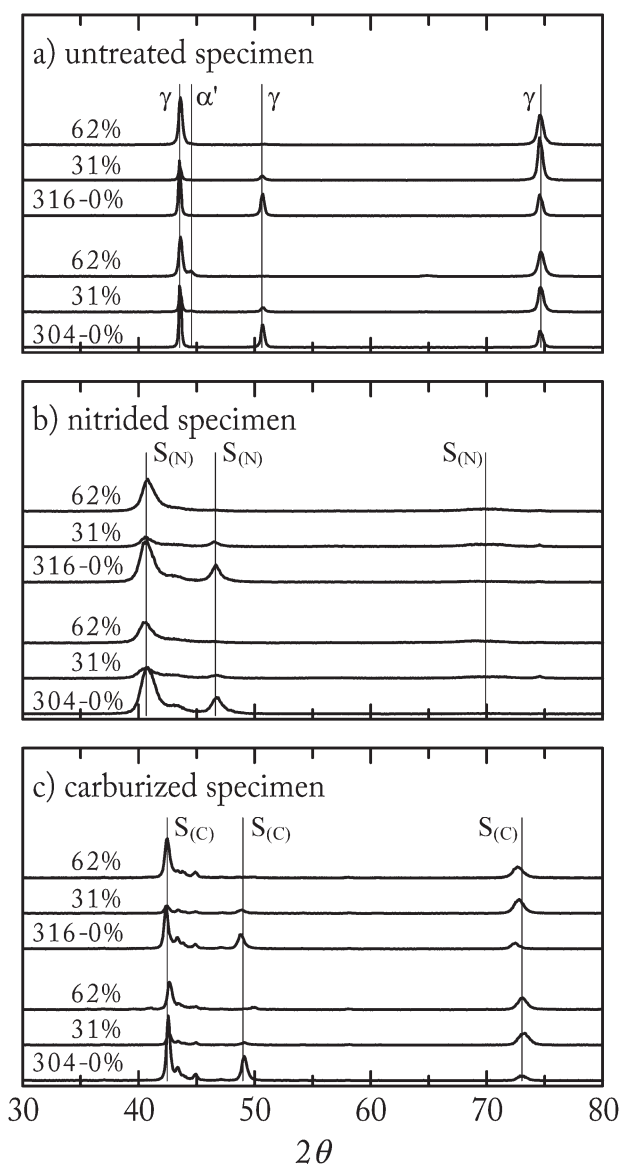
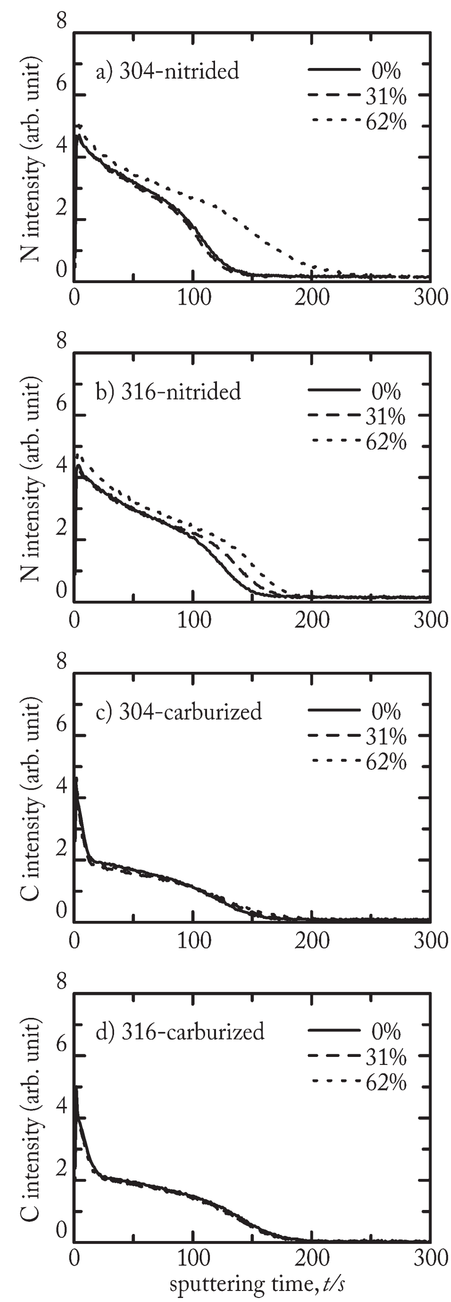
surface layers are also indicated in the figure. The surface layers are resistant to the corrosive attack by the marble's reagent (mixture of equal parts of hydrochloric acid and $CuSO_4$ saturated aqueous solution) such that they appeared 'white' under an optical microscope. For plasma nitriding on the AISI304 and AISI 316 steels, the thickness of the surface layers increased with an increase in rolling reduction. The deformation structure, deformation-induced martensite or dislocations, may accelerate the growth of the nitrided layer. On the other hand, for plasma carburizing on both steels, the thicknesses of the surface layers were almost unchanged as the rolling reduction increased.

X-Ray diffraction patterns of the specimen are given in Figure 2. All diffraction peaks of the untreated specimens are peaks of γ-Fe, except for a weak peak of martensite (α'-Fe) observed in the specimen of AISI304 steel with a rolling reduction of 62%. All nitrided specimens have a series of S(N)-phase peaks, which were broader and at lower 2θ values than those for normal austenite.[1] The peaks corresponding to the nitrides were not observed. The X-ray diffraction patterns of all carburized specimens have typical S(C)-phase peaks,[4] which were at lower angles than were those for normal γ-Fe peaks observed for the untreated specimens.



■ *Figure 2.* X-Ray diffraction patterns of the specimens.



■ *Figure 3.* GDS depth profiles of nitrogen and carbon.

The elemental depth profiles of the nitrided and carburized specimens measured by GDS are given in Figure 3. The nitrogen content in the nitrided specimens and the carbon content in the carburized specimens have similar patterns: there is very high nitrogen/carbon content at the surface, and the content decreases quickly to fair nitrogen/carbon contents within the specimen. In plasma nitriding on the AISI304 steels, the depth of the nitrogen-diffused region increased only at the specimen rolling reduction of 62%. In plasma nitriding on the AISI316 steels, the thickness of the surface layer increased with an increase in rolling reduction. In plasma carburizing of both steels, the depths of the carbon-diffused regions were almost unchanged as the rolling reduction increased. This behavior of the depth of the diffused region is very similar to that of the thickness of the surface layers as shown in Figure 1.

In case of AISI304, it can be seen that the larger the martensite content, the deeper the nitrogen-diffused region. But, in case of AISI316, although the martensite contents were almost constant, the depth of nitrogen-diffused region and the thickness of the nitrided layer were increased. The deformation structure such as dislocations may accelerate the growth of the nitrided layer. On the other hand, for plasma carburizing on both steels, the depth of carbon-diffused region and the thicknesses of the surface layers were almost unchanged as the rolling reduction increased. The difference in the diffusion behavior between carbon and nitrogen is responsible for the S-phase formation mechanism in the austenitic stainless steels.

Conclusion

The experimental results presented in this paper give the structures of low-temperature plasma nitrided and carburized austenitic stainless steels. The steels considered are AISI304 and AISI316 that are cold formed before the plasma treatment. In plasma nitriding on the AISI304 and AISI316 steels, the thicknesses of the nitrided layers increased with an increase in rolling reduction. In plasma carburizing on both steels, the thicknesses of the carburized layers were almost unchanged as the rolling reduction increased. In the nitriding, the growth of S-phase layer on the austenitic stainless steels was accelerated by deformation structure induced by cold forming. However, in carburizing the growth of S-phase layer was almost constant as the rolling reduction increased.

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