

## SURFACE LAYER HARDNESS OF AUSTENITIC STAINLESS STEEL VIA LOW TEMPERATURE PLASMA CARBURIZING AND/OR NITRIDING

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**Abstract.** Surface layer hardness and concentration profiles of austenitic stainless steels after plasma carburizing and /or nitriding at 673 K were investigated. Carbon and nitrogen concentration were measured by glow discharge optical emission spectrometry (GDOES) and carbides or nitrides were detected by x-ray diffraction analysis (XRD) and TEM. The state of carbon at the treated surface was investigated by Raman spectroscopy. Separation of carburized layer and nitrided layer was observed in a simultaneous carburizing and nitriding plasma treatment.

### Introduction

Surface improvement for austenitic stainless steel has been investigated to enlarge the application of these series of steel with excellent corrosion resistance [1]. Plasma nitriding is one of the most widely used surface improvement techniques to increase the surface hardness and wear resistance of austenitic stainless steels. However, conventional nitriding at temperature higher than 773 K degrades the corrosion resistance of the steels by the chromium nitrides formation which consumes the dissolved chromium for a passive state.

It has been found that the low temperature nitriding make the surface layer of austenitic stainless steel hard and nitrides free [1]. This surface layer so called S phase has the hardness around 1000 HV and keeps good corrosion resistance of austenitic stainless steel [2-4]. On the other hand, because of the low temperature diffusion treatment, the S phase has thin hardened layer, and steep drop of hardness at the border between hardened layer and substrate as the character of nitriding [5]. These characteristic features affect the mechanical properties of treated austenitic stainless steels.

Low temperature carburizing also forms S phase like layer at the surface of austenitic stainless steels. These carburized layers have gentle drop of hardness but lower surface hardness than that of nitrided S phase [6,7]. Furthermore, low temperature nitriding of austenitic stainless steel shows the push-in effect of dissolved carbon [4, 8-12]. Authors showed that the post nitriding can propel the carburized layer into inner space at low temperature. Such a combination of carburizing and post-nitriding make the surface of AISI 304 grade austenitic stainless steel thick duplex structure [13-16].

It has been reported that the precipitation of chromium carbides or nitrides in 316 steel does not occur at higher temperature than in 304 steel, and the carburized layer of 316 steel has higher hardness than that of 304 steel. The duplex surface layer by combined carburizing and nitriding of 316 steel should be thick and mildly dropping hardness profile. The purpose of this paper is to design the duplex layer surface of 316 by various combinations of carburizing and nitriding.

### Experimental procedures

The substrate materials used in this work was AISI 316 type austenitic stainless steel with the

following chemical compositions (in mass%): 16.99Cr, 10.12Ni, 2.19Mo, 1.00Mn, 0.04C, 0.69Si, 0.029P, 0.004S and balance Fe. Solution-treated steel bars were cut into 25 mm in width, 50 mm in length and 5 mm in thickness. The faces of the plates were then ground and polished to the mirror finish.

Table 1 Plasma process used in this study

Process	Symbol	First process						Second process					
		Temp. (K)	Gas flow ratio (%)				Process time (h)	Temp (K)	Gas flow ratio (%)				Process time (h)
			CH <sub>4</sub>	N <sub>2</sub>	H <sub>2</sub>	Ar			CH <sub>4</sub>	N <sub>2</sub>	H <sub>2</sub>	Ar	
Nitriding	8N	723	-	80	20	-	8	-	-	-	-	-	-
Carburizing	8C	723	5	-	45	50	8	-	-	-	-	-	-
Simultaneous Process	8(C+N)	723	5	80	15	-	8	-	-	-	-	-	-
Sequential Process	4C-4N	723	5	-	45	50	4	723	-	80	20	-	4
	4(C+N)-4N	723	5	80	15	-	4	723	-	80	20	-	4

Plasma thermochemical treatment was performed with a laboratory type apparatus with a DC power source. Each specimen attached with a thermocouple was set in the furnace as a cathode. After evacuation up to  $1.33 \cdot 10^{-1}$  Pa, the mixed gas pressure for each specimen was adjusted to  $6.67 \cdot 10^2$  Pa. All plasma thermochemical treatment in this study was carried out at 723 K. Total respective processing times were 8 h.

Table 1 shows details of each plasma treatment with the specimen symbols. For example, 8N specimen was plasma treated at 723 K with a mixture of 80% nitrogen gas and 20% hydrogen gas for 8 h. The 8(C+N) specimen was treated by plasma carbo-nitriding process for 8 h at 723 K with a mixture of nitrogen, methane, and hydrogen gas. The 4C-4N specimen was processed sequentially, first treated by plasma carburizing for 4 h at 723 K, then treated by plasma nitriding for 4 h at 723 K. In such a sequential process, the gas mixture changes were carried out within 10 s without temperature change.

Microstructures of treated layers were investigated by X-ray diffraction analysis (XRD) using Cu-K $\alpha$  (40 kV, 150 mA) and glow discharge optical emission spectrometry (GDOES).

## Results and discussion

### Layer Morphology and Elemental profiles of Carbon and Nitrogen

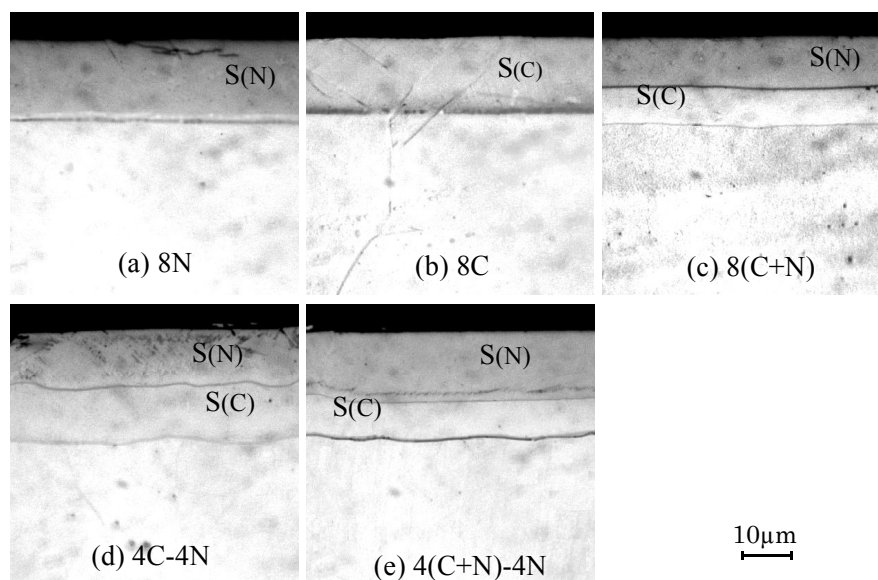


Fig. 1 Features of plasma treated surface layers

The morphological appearance of the processed 316 steel specimens are shown in Fig. 1. The three combined processed specimens, 8(C+N), 4C-4N and 4(C+N)-4N, have duplex layers irrespective of whether they were processed sequentially or simultaneously.

The elemental depth profiles of plasma-processed specimens for carbon and nitrogen are shown in Fig. 2. The carbon push ahead effect of incoming nitrogen [14] is shown clearly in Fig. 2(c), (d) and (e). Even in Fig. 2(a), dissolved carbon is accumulated at the front of nitrified layer. Large amount of carburized carbon accumulated beyond the nitrified layer in combined process. However, some carbon remains in the nitrified layer of 4C-4N. A small peak of carbon is at the sub-surface layer. This small peak in (d) is due to the dissolved carbon in  $\epsilon$ -phase ( $Fe_{2-3}N$ ) [13]. Simultaneously carburized and nitrified specimen 8(C+N) in Fig. 2(c) shows accumulation of carbon beyond the nitrified layer as in (d), but carbon concentration at the surface is also observed.

From XRD analysis shown in Fig. 3, the carburized specimen and nitrified specimen show a typical S phase by carbon and nitrogen. The  $\theta-2\theta$  diffraction pattern of 4C-4N is fundamentally the sum of the nitrified specimen's and the carburized specimen's patterns. However, in the pattern of 8(C+N), the peaks that were inferred to indicate S phase do not show the separated manner of  $S_{(N)}$  and  $S_{(C)}$ . They are positioned between  $S_{(N)}$  and  $S_{(C)}$  in the 8(C+N) pattern. Some chromium carbides were suspected in the 8(C+N) specimens.

### Hardness Profile

Fig. 4 shows these five specimens' hardness depth profiles. The 8C specimen has the maximum hardness of about 770 HK, which is far lower than the hardness of other specimens about 1050 HK. Comparison of the hardness profile of the 8C specimen with that of the 8N shows that the nitrified layer of the 8N specimen has a hard layer with an abrupt layer-core interface, while the carburizing produces a gradually decreased hardness profile.

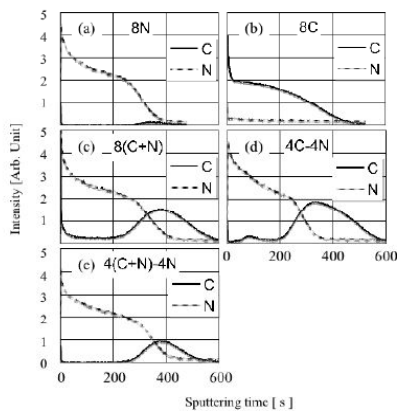


Fig. 2 GDOES depth profiles of N and C

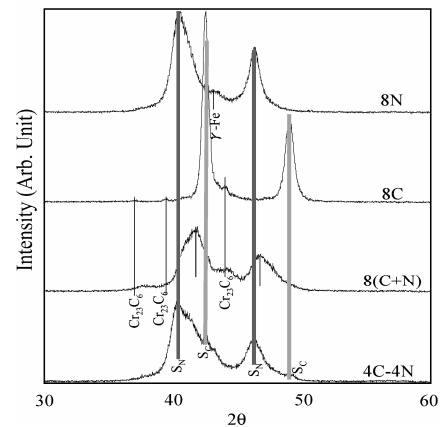


Fig. 3 XRD analysis of treated surface

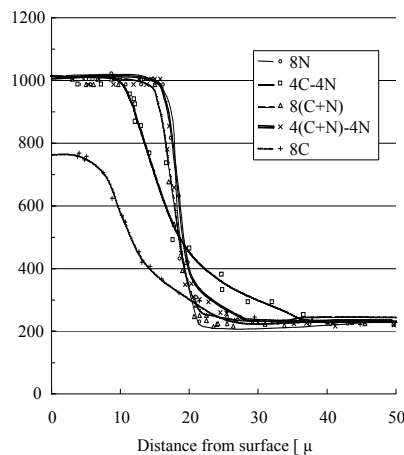


Fig. 4 Depth profiles of Knoop hardness

Three combined carburized and nitrided specimens, 8(C+N), 4C-4N and 4(C+N)-4N, show a similar tendency to bulge in hardness profiles at inner carburized layer as shown in Fig. 1 (c), (d) and (e) as  $S_{(C)}$  definition. The most gradual decrease in hardness from 1050 HK level to substrate hardness was displayed by 4C-4N specimen. The hard surface layer thickness of 4C-4N specimen was about 70 % of that of nitrided-only specimen 8N, because of the half nitriding duration. However, the largest bulging of hardness at inner layer was achieved.

### Conclusions

The surface structure of AISI 316 austenitic steel was controlled by combinations of low temperature plasma nitriding and plasma carburizing. A plasma-carburized layer of carbon was pushed ahead by post-plasma-nitriding. It accumulated in the front of the nitrided layer. This formed duplex surface layers with different hardness. The possibility of surface material design has been extended by the control of the location of carbon-S phase by the combined carburizing and nitriding at low temperature.

### References

- [1] M. Tsujikawa, S. Noguchi, N. Yamauchi, N. Ueda, A. Okamoto, T. Sone, PLASMA PROCESSES & POLYMERS, (2007), accepted.
- [1] K. Ichii, K. Fujimura, T. Takase, Netsu Shori 25(4) (1985) 191.
- [2] Z. L. Zhang and T. Bell, Surf. Eng. 1(2) (1985) 131.
- [3] K.-T. Rie and E. Broszeit, Surf. Coat. Technol. 76-77 (1995) 425
- [4] N. Yamauchi, N. Ueda, K. Demizu, A. Okamoto, T. Sone, K. Oku, T. Kouda, K. Ichii, K. Akamatsu, Proc. Int. Current Status Seminar on Thermochemical Surf. Eng. Osaka (2000) 247
- [5] T. Bell and Y. Sun, Proc. Int. Current Status Seminar on Thermochemical Surf. Eng. Osaka (2000) 275
- [6] Y. Sun, X.Y. Li and T. Bell, Surf. Eng. 15 (1999) 49
- [7] Y. Sun, X.Y. Li and T. Bell, Mater. Sci. Tech. 15 (1999) 1171
- [8] M. P. Fewell, P. Garlick, J. M. Priest, P. T. Burke, N. Dytlewski, K. E. Prince, K. T. Short, R. G. Elliman, H. Timmers, T. D. M. Weijers and B. Gong, Proc. Int. Current Status Seminar on Thermochemical Surf. Eng. Osaka (2000) 177
- [9] M. J. Baldwin, S. Kumar, J. M. Priest, M. P. Fewell, K. E. Prince and K. T. Short, Thin Solid Films 345 (1999) 108
- [10] X. Li, Y. Sun and T. Bell, Z. Metallkd. 90 (1999) 901
- [11] D. L. Williamson, P. J. Wilbur, F. R. Fickett and S. Parascandola, Proc. Int. Current Status Seminar on Thermochemical Surf. Eng. Osaka (2000) 333
- [12] C. Blawert, B. L. Mordike, G. A. Collins, K. T. Short, Y. Jiraskova, O. Schneeweiss and V. Perina, Surf. Coat. Technol. 128-129 (2000) 219
- [13] M. Tsujikawa, T. Sone, N. Yamauchi, N. Ueda, Y. Hirose, Surface & Coatings Technology, 193/1-3 (2004), pp. 309-313.
- [14] M. Tsujikawa, D. Yoshida, N. Yamauchi, N. Ueda, T. Sone, Materials Transactions, 46(4) (2005) 863-868.
- [15] M. Tsujikawa, N. yamauchi, N. Ueda, T. Sone, Surface & Coatings Technology, Vol 200/1-4 (2005), pp 507-511.
- [16] M. Tsujikawa, S. Noguchi, N. Ueda, N. Yamauchi, T. Sone, Surface & Coatings Technology, Vol 201/9-11 (2007) pp 5102-5107.
- [17] N. Ueda, N. Yamauchi, M. Tsujikawa, T. Sone, Surface & Coatings Technology, Vol 201/9-11 (2007) pp 5487-5492
- [14] A. Leyland, D. B. Lewis, P. R. Stevenson and A. Matthews, Surf. Coat. Technol. 62 (1993) 608

**PRICM 6**

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