Surface Characterization of Stainless Steels Prepared with Various Surface Treatments

By M. Seo* and N. Sato*

The composition depth-profiles of the surfaces of 304 and 316 stainless steels prepared with a variety of surface treatment have been measured by a simultaneous use of argon ion sputter-etching and Auger electron spectroscopy. Chromium was enriched in the surface oxide films, whereas nickel was enriched at the film/substrate interface. The degree of Cr-enrichment in surface films depended on the surface treatment and increased in the following order; mechanical polishing with emery paper in water < chemical etching in mixed acid of 1% HF + 10% HNO₃ < electropolishing in mixed acid of CH₃COOH + HClO₄ (20: 1) < chemical treatment in 10% HNO₃ or chemical passivation in 30% HNO₃. The degree of nickel enrichment at the film/substrate interface increased with increasing degree of chromium enrichment in the film. The surface oxide films on 304 stainless steel were always thicker than those on 316 stainless steel, irrespective of the surface treatments. The aging of specimen for one week in dessicator gave rise to decrease in chromium-enrichment and to increase in film thickness. Discussion was made on the relationship between pitting potential and surface composition of stainless steels.

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I. Introduction

It is well known that the corrosion behavior of metals and alloys strongly depends on the procedure of surface pre-treatment. The corrosion-resistance is closely related to the composition and structure of surface films on metals. However, there is no consistent study on the surface-characterization of metals and alloys prepared with various surface treatments. One of the Technical Subcommittees of the Japan Society of Corrosion Engineering has conducted a collaborative study of surface pretreatment of stainless steels. This work was made as a part of the collaborative study to clarify the surface composition of austenitic stainless steels (304 and 316) prepared with a variety of surface treatments; the depth-

profiling of the surfaces of austenitic stainless steels has been performed with simultaneous use of argon ion sputter-etching and Auger electron spectroscopy (AES).

II. Experimental

1. Specimen preparation

The specimens used are SUS 304 and 316 austenitic stainless steels which have been supplied as standard specimens for corrosion tests from the Japan Society of Corrosion Engineering. The composition of specimens in wt% is listed in Table 1. The specimens were cut into plates of 0.2 × 1.0 × 1.0 cm, annealed in vacuo at 1373 K for 20 min and then quenched into water.

After mechanically pre-polished in air with emery paper (SiC) down to No. 500, the specimens were prepared by the following procedures which have been frequently used in practice:

* Faculty of Engineering, Hokkaido University, Kita 13-jo, Nishi 8-chome, Kita-ku, Sapporo 060, Japan.

Table 1 Chemical composition of stainless steels in wt%.

	Cr	Ni	Mo	Cu	C	Si	Mn	P	S	Fe
SUS 304	18.36	9.23	0.07	0.08	0.051	0.76	0.97	0.027	0.006	balance
SUS 316	17.21	11.20	2.20	0.33	0.049	0.68	1.37	0.032	0.007	balance

(1) Mechanical polishing in distilled water with emery paper of No. 500.

(2) Chemical etching in mixed acid of 1% HF + 10% HNO₃ for 15 min at 323 K.

(3) Electropolishing for 50 s in mixed acid of HClO₄ + CH₃COOH (1:20) at the cell voltage of 50 V and at the current density of $6 \times 10^{-2} \text{ A} \cdot \text{cm}^{-2}$.

(4) Electropolishing for 50 s in mixed acid of H₂SO₄ + H₃PO₄ (2:3) at the cell voltage of 5~8 V and at the current density of $0.5 \sim 1 \text{ A} \cdot \text{cm}^{-2}$.

(5) Chemical treatment in 10% HNO₃ for 30 min at 333 K.

(6) Chemical passivation in 30% HNO₃ for 1 h at 333 K.

The procedures of (2), (3), (4), (5) and (6) were always preceded by the procedure (1).

After these treatments, the specimens were washed with double-distilled water and dried with a jet of nitrogen gas except for the procedure (1) in which the specimens were washed with acetone using ultrasonic techniques.

2. AES measurement and depth-profiling

The specimens prepared with various surface treatments were transferred into the vacuum chamber of Auger apparatus (PHI, 540 A) within 1 h after surface treatments. The Auger chamber was evacuated to a vacuum better than $2.7 \times 10^{-7} \text{ Pa}$. The specimens were cooled down to a temperature of about 120 K by flowing liquid nitrogen continuously into the specimen holder. The sputter-etching of the specimen was performed with a 0.5 kV ion beam having an ion current of about $5 \times 10^{-6} \text{ A} \cdot \text{cm}^{-2}$ at an argon pressure of $6.7 \times 10^{-3} \text{ Pa}$. Under this condition, chromium and iron were sputtered at the same yield from a series of Fe-Cr alloy substrate. The time-variation in Auger spectra of the specimen during sputter-etching was measured by using a primary 2 kV, 40 μA electron beam with a diameter of about 50 μm and a 4 V modulation amplitude at a frequency of 30 kHz. The depth-profiling of the specimen exposed in dessicator for one week after surface treatments was also performed to elucidate the aging effect on the surface composition.

III. Quantitative Auger Analysis of Surface Composition

The worst difficulty in quantitative Auger analysis of surface oxide films on stainless steels is the measurement of the pure Cr (529 eV) peak from the overlapped peaks of Cr (529 eV) and O (510 eV). As shown schematically in Fig. 1, two possible alternative procedures of *a* and *b* may be proposed as a conventional method for measurement of the Cr (529 eV) peak, whereas as reported by Frankenthal and Thompson⁽¹⁾, the separation of the pure Cr (529 eV) peak can be accomplished by subtracting the pure O (510 eV) peak, observed with a Fe₂O₃ film on iron, from the overlapped peaks of Cr (529 eV) and O (510 eV), assuming that the shape of O (510 eV) is the same for both Fe₂O₃ and Cr₂O₃ films. Figure 2 shows the pure Cr (529 eV) peak (dotted line) separated from overlapped peaks (solid line) for the Fe-20Cr alloy electropolished in mixed acid of CH₃COOH + HClO₄ (20:1). Table 2 shows the surface chromium atomic fraction, X_{Cr}^s , of Fe-20Cr alloy estimated from the different methods described above. The marks of *a*, *b* and *c* in Table 2 represent the

Fig. 1 Two possible alternative procedures, *a* and *b* for measurement of Cr peak (529 eV).

Fig. 2 Separation of pure Cr peak (529 eV) from the overlapped peaks of Cr(529 eV) and O(510 eV). Dotted line shows pure Cr peak (529 eV).

Table 2 Surface chromium atomic fraction X_{Cr}^s of Fe-20 Cr alloy estimated from different methods.

Specimen preparation	X_{Cr}^s		
	<i>a</i>	<i>b</i>	<i>c</i>
No. 1	+	0.28	0.20
No. 2	+	0.24	0.18
No. 3	0.11	0.29	0.26
No. 4	0.19	0.37	0.34

No. 1: Mechanical-polishing with emery paper in air.

No. 2: Mechanical-polishing with emery paper in cyclohexane.

No. 3: Mechanical-polishing with α -Al₂O₃ abrasives in water.

No. 4: Electropolishing (CH₃COOH : HClO₄ = 20: 1)

methods of *a* and *b* in Fig. 1 and that of separation of pure Cr peak in Fig. 2, respectively. The values of X_{Cr} estimated from the method *b* rather than the method *a* are consistent with those estimated from the method *c*. Particularly, the difference of X_{Cr} between the methods of *b* and *c* falls within 8% in the case where the apparent peak height ratio of O (510 eV) to Cr (529 eV), H_O/H_{Cr} measured with the method *b* does not exceed the value of 6.0, whereas the values of X_{Cr} estimated from the method *b* are higher by a factor of more than 25% than those estimated from the method *c* in the case of $H_O/H_{Cr} > 8.0$. Fortunately, the value of H_O/H_{Cr} for the stainless steels prepared with surface treatments used in this study did not exceed 6.0 so that the method *b* was conveniently adopted for the estimation of Cr

content.

The composition profiles in depth of stainless steels were expressed by plotting atomic fraction of alloying component, X_{Me} and atomic ratio of oxygen to total alloying components, $O/\Sigma Me$ versus sputtering time. X_{Me} and $O/\Sigma Me$ can be given by the following equations;

$$X_{Me} = (H_{Me}/\alpha_{Me})/(\Sigma H_{Me}/\alpha_{Me}), \quad (1)$$

$$O/\Sigma Me = (H_O/\alpha_O)/(\Sigma H_{Me}/\alpha_{Me}), \quad (2)$$

Where H_{Me} is the Auger peak height of alloying component, H_O the peak height of oxygen, α_{Me} the relative Auger sensitivity of alloying component and α_O the relative Auger sensitivity of oxygen. For calculations of X_{Me} and $O/\Sigma Me$, the Auger peak heights of Fe (651 eV), Cr (529 eV), Ni (848 eV), Mo (186 eV) and O (510 eV) were measured as a function of sputtering time and the values of $\alpha_{Fe}=1.0$, $\alpha_{Cr}=1.21$, $\alpha_{Ni}=1.05$, $\alpha_{Mo}=1.64$ and $\alpha_O=1.93$ were taken as the corresponding sensitivity factor.

IV. Results and Discussion

Figures 3, 4, 5 and 6 show the composition profiles in depth of the 304 and 316 stainless steels transferred into Auger chamber within 1 h after the surface treatments (2) and (6), respectively. The sputtering time, τ_f required for

Fig. 3 Depth-composition profile of 304 stainless steel transferred into Auger chamber within 1 h after surface treatment (2).

Fig. 4 Depth-composition profile of 316 stainless steel transferred into Auger chamber within 1 h after surface treatment (2).

Fig. 6 Depth-composition profile of 316 stainless steel transferred into Auger chamber within 1 h after surface treatment (6).

Fig. 5 Depth-composition profile of 304 stainless steel transferred into Auger chamber within 1 h after surface treatment (6).

removal of surface oxide film, was defined by a point of intersection of two linear lines drawn from the curves of $O/\Sigma Me$ in the figures.

τ_f corresponds to the film thickness if the sputtering rate is not sensitive to the film composition and structure. The enrichment of the chromium component and the depletion of nickel and iron components are always observed in the surface oxide films, but the degree of enrichment and depletion depends on the surface treatments. The degree of Cr enrichment in the film can be represented in

the first approximation by the value of X_{Cr}^s obtained from the uppermost surface without sputtering, as evidenced by comparing X_{Cr}^s with the total amount of enriched Cr estimated from the depth profile.

The enrichment of nickel component is also observed at the film/substrate interface and the degree of nickel enrichment is found to increase with increasing degree of Cr enrichment in the film, as shown in Fig. 7. There was no molybdenum on the uppermost surfaces of 316

Fig. 7 Relation between maximum nickel atomic fraction at the film/substrate interface, X_{Ni}^M , and surface chromium atomic fraction obtained from the uppermost surface layer without sputtering, X_{Cr}^s . The number indicated corresponds to the respective surface treatment.

Fig. 8 Whole Auger results shown in terms of bar-graph for stainless steels transferred into Auger chamber within 1 h after various surface treatments.

stainless steel. The whole Auger results for the stainless steels transferred into the Auger chamber within 1 h after surface treatments were arranged in a bar-graph of Fig. 8. The values of $O/\Sigma Me$ in Fig. 8 designate those of the uppermost surface without sputtering. The values of X_{Cr}^s increases in the order of the following surface treatments; (1) < (2) $\approx$ (4) < (3) < (5) $\approx$ (6). The values of τ_f indicate that the surface oxide films on 304 stainless steel are always thicker than those on 316 stainless steel, irrespective of surface treatments. A bar-graph of Fig. 9 shows the aging effect on the surface composition of stainless steels prepared with the surface treatments (1) and (5). The marks of *h* and *w* in Fig. 9 mean the specimens transferred into Auger chamber within 1 h after surface treatments and the specimens exposed in a dessicator for one week after surface treatments, respectively. The aging of specimen for one week gives rise to a decrease in X_{Cr}^s and an increase in $O/\Sigma Me$ and τ_f . The aging effect is predominant in the surface treatment (1) rather than in (5), suggesting that further-oxidation of the specimen during storage in the dessicator is suppressed by the surface enrichment of Cr.

The pitting potentials of the stainless steels in 3.5% NaCl solution measured by Shibata and Takeyama⁽²⁾ were plotted as a function of X_{Cr}^s in Fig. 10. The pitting potential shifts to noble direction with increasing X_{Cr}^s . The difference of pitting potential between 304 and

Fig. 9 Aging effect on surface composition for stainless steels prepared with surface treatments (1) and (5).

Fig. 10 Relation between pitting potential in 3.5% NaCl solution and X_{Cr}^s . The number indicated corresponds to the respective surface treatment. Pitting potential was measured by Shibata and Takeyama⁽²⁾.

316 stainless steels, however, can not be explained by the difference in surface enrichment of Cr. The aging of the specimen also ennobles the pitting potential in spite of a decrease in X_{Cr}^s . Therefore, some other factors than the surface enrichment of Cr have to be taken into consideration to explain the pitting resistance of stainless steels. At present, the role of molybdenum added to stainless steels in improving the corrosion resistance has not been made clear but an addition of molybdenum is found to reduce the thickness of surface oxide films on stainless steels as shown in Fig. 8. An application of the field-assisted mechanism to the growth of passive films on iron-molybdenum alloy⁽³⁾ has revealed that the decrease in thickness of passive film due to addition of molybdenum is attributed to the formation of passive film with less defective structure. The ennoblement of the pitting potential due to aging may be also attributed to the structural change of surface oxide film as described in XPS studies by Asami and Hashimoto⁽⁴⁾.

V. Conclusion

Chromium was enriched in the surface oxide films, whereas nickel was enriched at the film/substrate interface. The degree of Cr-enrichment in surface films depended on the surface treatments and increased in the following order; mechanical polishing with

emery paper in water < chemical etching in mixed acid of 1% HF + 10% HNO₃ < electropolishing in mixed acid of CH₃COOH + HClO₄ (20:1) < chemical treatment in 10% HNO₃ or chemical passivation in 30% HNO₃. The enrichment of nickel at the film/substrate interface had good correlation with the enrichment of chromium in the surface film. The surface oxide films on 304 stainless steel were always thicker than those on 316 stainless steel, irrespective of the surface treatments.

The pitting potential shifted to noble direction with increasing Cr-enrichment in the surface film. The aging of the stainless steels polished with emery paper in water, however, led to the ennoblement of pitting potential in spite of decrease in Cr-enrichment. To explain the ennoblement of pitting potential due to aging, the structural change of the film, besides the Cr-enrichment must be taken into account.

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