Use of Ion Microanalyzer in the Analysis of Passive Layers on Stainless Steel

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Passive layers on various stainless steels were studied with an ion microanalyzer. An argon ion beam was directed on the specimen surface in an oxygen atmosphere. The use of oxygen atmosphere effectively minimized the difference in ion yields of the elements in the oxidized layers and matrices, making it possible to determine these elements with good reproducibility. 18% Cr–8% Ni and 18% Cr–8% Ni–0.4% Ti stainless steel was exposed to neutral water containing 8 ppm oxygen at 289 °C. The passive layers contained larger amounts of iron and smaller amounts of chromium than the matrices.

The remarkable resistance of stainless steel to corrosion in various atmospheres is due to the protective nature of the passive layers on the surface. Studies of passive layers have been carried out by means of electrochemistry,[1] impedance and capacitance measurements,[2,3] ellipsometry,[4,5] and infrared spectroscopy.[2] However, no quantitative analyses can be carried out. In order to clarify the nature of passive layer, it is necessary to determine the concentration of elements in the layer, but passive layers are too thin to make analysis by conventional means possible. Recently, Auger electron spectroscopy (AES)[6] and X-ray photoelectron spectroscopy (XPS)[2,6–8] have been used for the determination of the composition of passive layers. The mean escape depth of Auger electrons or photoelectrons from a surface is about 20 Å or less. Thus these methods can be used for the analysis of surface elements. The compositional depth profiles in a thin layer are obtained by ion bombardment. Since these methods are not quantitative, comparison of variations in the ratio of chromium and nickel to iron in specimens is only used for the analyses of passive layers.

The composition profiles of thin layers can be obtained with an ion microanalyzer (IMA) just as with AES and XPS. A quantitative method using an IMA has been examined with calibration[9] and thermodynamical techniques.[10] However, the techniques were developed for elements in matrices.

An oxidized layer, such as a passive layer, gives off much larger quantities of secondary ions than those of a matrix when argon ions are used as primaries. This is due to the difference in the ion yields of elements in oxidized layers and those in matrix. In order to estimate the difference in the concentration of an element between oxidized layer and matrix, it is necessary that the ion yield of the element is the same in both places.

Oxygen ions have been used as primary ions. Andersen and Hinthorne[11] and Nishimura and Okano[12] reported that the difference in the relative sensitivities of element is smaller in the case of oxygen primary ions than in the case of argon primary ions. This seems to result from the oxidation and temperature rise at specimen surface.

We have carried out bombardment by argon ions in an oxygen-atmosphere in order to minimize the difference in the ion yields of elements in the oxidized layers and matrices. The results are applied to analyses of passive layers on stainless steel.

Experimental

Materials. The specimens used in quantitative study of element concentration in a matrix were Japanese Standards of Stainless Steel. Table 1 gives the composition of the main constituents. The specimens were cut into 5 mm cubes, polished with diamond paste and cleaned ultrasonically in alcohol and ether.

The specimens used for the study of element concentration in passive layers were commercial AISI type 304 and 321 stainless steel. The specimens were treated in neutral water containing 8 ppm oxygen. The temperature and time of passivation treatment were 289 °C and 2000 h, respectively.

TABLE 1. CONTENTS OF MAIN CONSTITUENTS OF STAINLESS STEEL SPECIMENS

Specimen	Concentration (%)				
	Fe	Cr	Ni	Mn	Si
No. 650	82.1	16.45	0.24	0.37	0.66
No. 651	69.7	18.65	8.86	1.73	0.47
No. 652	65.5	17.44	11.79	1.94	0.54
No. 654	53.0	24.71	19.80	1.54	0.70

TABLE 2. WORKING CONDITIONS FOR DETERMINATION

Ionic species	Ar^+
Accel. voltage for primary ions	10 kV
Current density of primary ions	0.1 mA/cm^2
Beam diameter	0.8 mm
Sample chamber pressure	
without oxygen	27 μPa
with oxygen	5.3 mPa
Accel. votage for secondary ions	3 kV

Experimental Procedure. An Hitachi type IMA-2 Ion Microanalyzer was used. Typical working conditions are given in Table 2. Argon ionized by duoplasmatron was accelerated at 10 kV. The current density of the primary ions was 0.1 mA/cm^2, making the analysis of a very thin layer satisfactory. The sputtering rate of the stainless steel was 0.04 nm/s.

Figure 1 shows the apparatus for the introduction of oxygen gas into the sample chamber. Oil particles in oxygen gas were removed by means of a filter. The sample chamber was evacuated with a diffusion pump and liquid nitrogen trap. Pressure of the sample chamber was 27 μPa in the absence of oxygen gas. Oxygen gas was introduced with a pressure of up

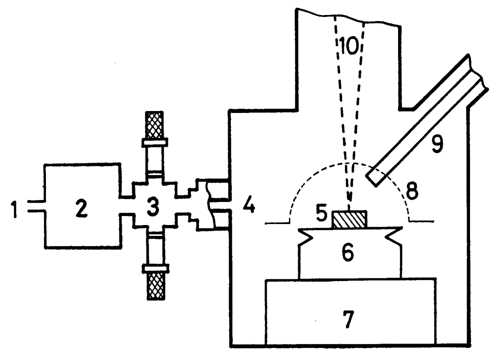

Fig. 1. Apparatus for introduction of oxygen gas into the sample chamber.
1. Oxygen gas inlet; 2. filter; 3. needle valve; 4. sample chamber; 5. specimen; 6. specimen holder; 7. plate for shifting samples; 8. hemispherical shield made of wire gauze; 9. extracting electrode; 10. argon ion beam.

to 5.3 mPa by controlling with a needle valve.

Principle of Quantitative Analysis. The secondary ion current I_X of a specific isotope of element X is given by[9]

$$I_x = \eta_x S_x^+ C_x I_p, \tag{1}$$

where η_X is the transmission coefficient of the instrument between the sample and the collector, $S_X{}^+$ the ion yield of element X, C_X the concentration of element X and I_P the current density of the primary ions. Thus the ratio of the secondary ion current of an element X to a reference element (matrix) R is given by

$$\frac{I_x}{I_R} = S(\text{rel})^+ \frac{C_x}{C_R}, \tag{2}$$

where I_R is the secondary ion current of reference element R, C_R the concentration of a reference element R and $S(\text{rel})^+$ the ratio of the ion yield of element X to a reference element R. This can be used for the determination of the constituents of stainless steel, when a straight line is obtained for I_X/I_R plotted as a function of C_X/C_R.

Results

Effect of Oxygen Atmosphere on Sputtering. Figure 2 shows the texture of the surface of a nickel specimen sputtered by argon ion bombardment. The results were obtained by surface roughness measurement. There is pronounced surface unevenness under a pressure of 27 μPa (without oxygen). On the other hand, the surface resulting from the sputtering in oxygen atmosphere under pressure of 5.3 mPa is very smooth. When the other conditions are the same, the sputtering rates are 0.2 and 0.03 nm/s under pressure of 27 μPa and 5.3 mPa, respectively. The sputtering rate of the stainless steel was 0.04 nm/s under pressure of 5.3 mPa.

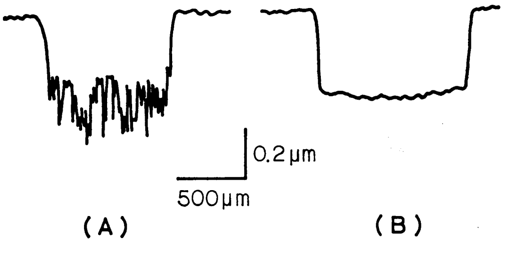

Fig. 2. Texture of surface sputtered by argon ion. Accelerating voltage and current density of argon ion were 10kV and 0.1 mA/cm², respectively. (A) Sample chamber pressure was 27 μPa and nickel bombardment time was 30 min. (B) Sample chamber pressure was 5.3 mPa and nickel bombardment time was 180 min.

The results demonstrate that bombardment by argon ions in oxygen atmosphere is effective for the analysis of a very thin layer such as the passive layers on the surface of stainless steel.

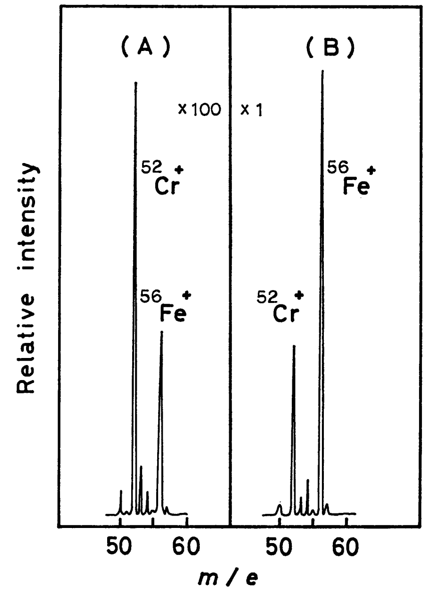

Fig. 3. Mass spectra of chromium and iron ion sputtered from stainless steel. Sample chamber pressure was (A) 27 μPa (without oxygen) and (B) 5.3 mPa(with oxygen).

Effect of Oxygen Atmosphere on Intensity of Secondary Ions. Figure 3 shows the mass spectra of chromium and iron ions. The pressure in the sample chamber is 27 μPa (without oxygen) for the specimens on the left side and 5.3 mPa (with oxygen) for the specimens on the right side. The specimen contained 82% Fe and 16% Cr. The peaks of $^{52}Cr^+$ and $^{56}Fe^+$ in the case with oxygen are *ca.* 40 and 240 times that in the case without oxygen, respectively. The other elements contained in stainless steel also show the same tendency. However, the peak height multiple differs from one element to the other. The relative ion yield of each element as compared to iron was calculated in the cases of pressure 27 μPa and 5.3 mPa. Table 3 gives the results where the secondary

TABLE 3. RELATIVE ION YIELD OF EACH ELEMENT TO IRON

Element	Relative ion yield[a)]	
	(A)	(B)
Fe	1.0	1.0
Cr	8.6	2.7
Ni	0.3	0.4
Mn	5.6	2.1
Si	1.8	0.4

a) Sample chamber pressure 27 μPa for (A) (without oxygen) and 5.3 mPa for (B) (with oxygen).

ion intensity of each element is divided by the concentration and the value of each element is divided by the value of iron. The relative ion yield of elements is in the range 0.3—8.6 for 27 μPa, and in the range 0.4—2.7 for 5.3 mPa. The results show that the introduction of oxygen into the sample chamber causes increase in the sensitivity of elements and decrease in the difference in the relative ion yield of elements.

Selection of Reference Element. Iron is used as a reference element for analyses of steels containing more than 90% Fe. Thus the secondary ion peak of iron does not vary even when the secondary ion peak values of other elements vary. However, in the analysis of stainless steel containing less than 80% Fe, the percentage varies from specimen to specimen, and neither iron nor any other element can be used as a reference element.

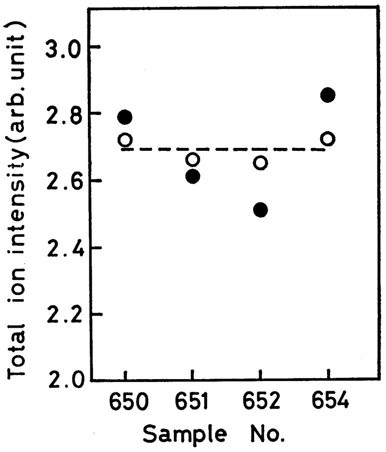

Fig. 4. Variations in total ion intensity with different specimens. Sample chamber pressure was (●) 27 μPa (without oxygen) and (○) 5.3 mPa(with oxygen).

Equation 2 cannot be used without a reference element. The secondary ion peak values of all the elements in steel are summed and the value obtained is assumed to be a composite reference. Figure 4 shows variations in the sums of the secondary ion peak values (total ion intensity) with different specimens. The total ion intensity varies widely with specimen when no oxygen is introduced into the sample chamber, but varying very little when it is introduced.

Figure 5 shows the relation between the ratio of secondary ion peak value to total ion intensity and concentration. A linear relation is obtained in an oxygen atmosphere. The total ion intensity could be used as a reference. The reproducibility of the method when the total ion intensity is used as a reference is given in Table 4.

Analysis of Passive Layers. Figure 6 shows the variation of total ion intensity below the surface of a specimen with a passive surface layer. In the case without oxygen, there is a large difference in total ion intensity between the passive layer and the matrix, while in an oxygen atmosphere, total ion intensity is the same for both. Consequently, the calibration curve shown in Fig. 5 can be used in the quantitative analysis of sub-surface concentration profiles in specimens with passive surface layers.

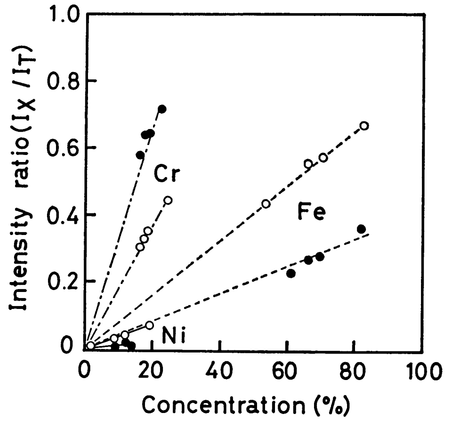

Fig. 5. Relation between the ratio of secondary ion intensity to total ion intensity and concentration. Sample chamber pressure was (●) 27 μPa(without oxygen) and (○) 5.3 mPa(with oxygen). —·—·—: Chromium,- - - -: iron,——: nickel.

TABLE 4. REPRODUCIBILITY OF IMA METHOD

No.	With oxygen (%)			Without oxygen (%)		
	Fe	Cr	Ni	Fe	Cr	Ni
1	69.7	18.62	9.00	70.9	18.95	9.00
2	70.0	18.60	9.22	71.3	18.43	8.32
3	69.7	18.60	9.22	70.9	18.95	7.71
4	70.0	18.60	8.93	69.5	19.00	8.18
5	70.1	18.62	9.20	68.1	19.38	8.85
6	69.6	18.65	9.20	70.4	18.48	9.71
7	69.6	18.62	9.00	69.3	19.00	7.82
8	70.0	18.65	9.21	72.3	18.33	7.88
9	69.7	18.62	8.90	69.3	18.95	8.53
10	69.7	18.65	8.92	69.1	18.76	9.12
Av.	69.8	18.62	9.08	70.1	18.82	8.52
Std. val.	69.7	18.65	8.86	69.7	18.65	8.86
Std. dev.	0.19	0.21	0.14	1.2	0.31	0.63
C. v. (%)	0.27	0.11	1.5	1.7	1.6	7.4

Analyses were carried out with specimen 651, Table 1.

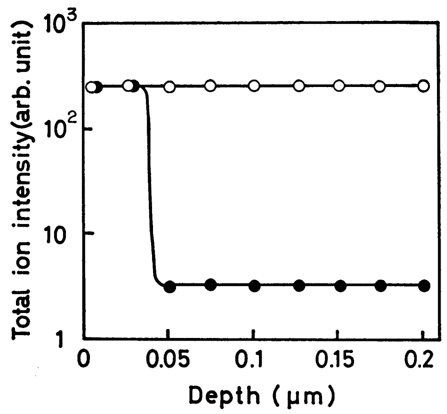

Fig. 6. Sub-surface variations in total ion intensity in specimens with passive surface layers. Sample chamber pressure was (●) 27 μPa(without oxygen) and (○) 5.3 mPa(with oxygen).

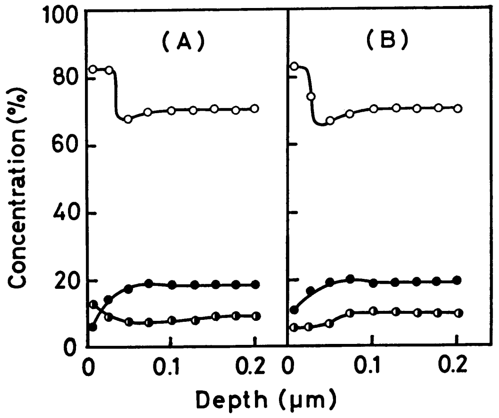

Fig. 7. Indepth concentration profiles for (A) 304 and (B) 321 stainless steels treated in neutral water containing 8 ppm oxygen. Specimens were treated for 2000 h at 289 °C.
○: Fe, ●: Cr, ◑: Ni.

The present method has been used to determine the concentration profiles in the surface layer of 304 and 321 stainless steel specimens treated in neutral water containing 8 ppm oxygen. Figure 7 shows the results obtained with specimens treated at 289 °C for 2000 h. The passive layers on the surfaces of 304 and 321 stainless steel are about 20 and 10 nm in thickness, respectively. These layers contain a larger amount of iron and a smaller amount of chromium than the matrices of the same steel.

It was found by carbon furnace atomic absorption spectrometry that iron, chromium, and nickel dissolve in water in a concentration of 239, 320, and 48.7 ppb, respectively. The concentration ratios of chromium and nickel to iron are 0.24 and 0.18 in matrices and 1.34 and 0.20 in water, respectively. The amount of nickel in water was nearly equal to that in the matrices, but the amount of chromium in water was much greater than that in matrices.

Thus, the decrease in the amount of chromium in passive layers corresponds to the increase in the amount of chromium in water.

A number of studies have been carried out on the composition of the passive film on 18% Cr–8% Ni stainless steel. Castle and Clayton[8] analyzed the passive film by X-ray photoelectron spectroscopy. They reported that the passive film prepared in low temperature (313 and 353 K), neutral, de-oxygenated water has a duplex layer structure, the outer layer being rich in iron and inner layer rich in chromium. A duplex layer structure was reported by Kowaka and Nagata,[13] and Bittel *et al.*[14] They prepared the passive layer in steam at temperatures 600—650 °C[13] and 1200—1300 °C, and analyzed the cross section of passive film with an electron probe microanalyzer. The results show that the passive layer consists of an outer layer of hematite rich in iron and inner layer of spinel and fcc metal rich in chromium.

Our result shows that the passive layer is rich in iron, corresponding to the composition of the outer layer.

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