

Investigation of the Passive Film Formed on SUS 304 Stainless Steel Exposed in an Urban-industrial Atmosphere

Somrerak CHANDRA-AMBHORN¹, Gobboon LOTHONGKUM¹, Noriko MAKIISHI²,
and Misako TOCHIHARA²

¹Department of Metallurgical Engineering, Faculty of Engineering, Chulalongkorn University

²Technical Research Laboratories, Kawasaki Steel Corporation, Japan

Abstract

SUS 304 stainless steel was atmospherically exposed to different seasons lasting for 7 days and 61 days at the Chiba urban-industrial site in Japan. The pitting potentials of the specimens were determined by an anodic polarization technique. The passive film thickness was evaluated by AES. The chemical compositions of passive film were investigated by XPS. After the 7-day exposure and comparing to the unexposed specimens, the pitting potentials and Cr enrichment, i.e., chromium ion / iron ion, of the specimens increased. The photoelectron intensity ratios of H₂O and OH⁻ per O²⁻ in the passive film decreased and the passive film thickness also decreased. It is then proposed that after the 7-day exposure the pitting potentials increase and relate to the increase in Cr enrichment, whereas H₂O and OH⁻ film is removed from the passive film. After the 61-day exposure and comparing to the unexposed specimens, the pitting potentials and Cr enrichment of specimens increased. However, the photoelectron intensity ratio of H₂O and OH⁻ per O²⁻ in passive film is nearly constant and passive film thickness decreases. This implies that there is a removed of passive film out of the surface and there is a formation of novel H₂O and OH⁻ film. It is then proposed that after a 61-day exposure the pitting potentials will increase and may relate to the increase in Cr enrichment or the novel H₂O and OH⁻ film formed. By considering the change in the mass ratio of nickel ion per iron, chromium and nickel ion with the change in passive film thickness, it seems that this ratio is constant after exposure for 7 days and 61 days.

Keywords : SUS 304 stainless steel, Anodic polarization, XPS, and AES

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Introduction

Due to its corrosion resistance and appreciated surface, stainless steels, for example, the conventional SUS 304 austenitic stainless steel mainly alloyed with 18-wt% Cr and 8-wt% Ni, are used for architectural construction. Passive film investigation has become much more interesting in the last twenty years. Many different analysis results for the atmospherically exposed stainless steels were published. The decrease (Asami and Hashimoto, 1996) and increase (Tochihara, *et al.* 2000) in Cr enrichment in passive film as well as the decrease (Tochihara, *et al.* 2000) and increase (Asami and Hashimoto, 1996) in passive film thickness were reported. In the present study, the changes of pitting potentials, chemical compositions and passive film thickness of SUS 304 stainless steel before and after atmospheric exposure were investigated by using anodic polarization techniques, the XPS and AES analyses, respectively. The relationship between the corrosion resistance represented by the pitting potentials and the change in chemical compositions in passive film and passive film thickness is also discussed.

Experimental Method

Specimens in this study were 2B-finished SUS 304 stainless steel sheets. It was produced by cold rolling, annealing and pickling. Table 1 shows the mass percent compositions of the as-received

SUS 304 stainless steels. Specimens were exposed to the atmosphere at the Chiba urban-industrial site situated 1 km from the seafront. Specimens with the dimension of 100 x 150 x 0.8 cm were fixed on the top surface of specimen holders inclined with an angle of 45° southward. The exposure period was 7 days in January 2001, which was the snowy winter, and 61 days during August 22nd to October 22nd 2000, which was summer.

For the anodic polarization techniques, the specimens were coated by a polymer to leave an exposed area of 1 x 1 cm in a 3.5-g/cm³ NaCl aqueous solution at 30°C. The Ag/AgCl reference electrode was used for pitting potential evaluation. The counter electrode was platinum. The solution was first deaerated by Argon-gas for 30 minutes before the specimen immersion. The corrosion potentials were measured for 10 minutes. The anodic polarization experiments were started from the detected corrosion potentials with a scanning rate of 20 mV/min. The potentials at the current density of 10 $\mu\text{A}/\text{cm}^2$, $V \times 10$, were recorded as the pitting potentials.

For XPS and AES analyses, specimens with a dimension of 1 x 1 x 0.8 cm were used without polishing. Ultrasonic cleaning and degreasing was done for 2 minutes before the measurement. The chemical composition of the passive film was analyzed by KRATOS AXIS HS. A Al K α monochromatic X-ray, a take-off angle of

90°, and a pass energy of 40 eV was used. The energy axis was horizontally shifted to set the binding energy of C1s at 284.6 eV. A Shirley base line was drawn in order to quantify the integrated peak intensities by using the relative sensitivity factor (RSF) method. The XPS sensitivity factors of Fe, Cr and Ni as well as the measurement accuracy were obtained by pre-experiment using the standard stainless steels specimens. From the pre-experiment and previous data, relative sensitivity factors of Cr and Ni are 0.86 and 1.13 respectively (Chandra-ambhorn, 2001), and that of O (Salmon, 1998) is 2.81. All relative sensitivity factors are normalized by the sensitivity factor of Fe. The relative errors of the XPS measurements of Fe and Cr mass concentration are 2.50 and 0.85 %, respectively. (Chandra-ambhorn, 2001).

To investigate passive film thickness, the sputtering technique was performed with the AES PHI model 595. The electron gun was operated at an acceleration voltage of 10 kV and a beam current

of 1 μA . The ion gun was operated at an acceleration voltage of 2 kV and an ion current density of 20 $\mu\text{A}/\text{cm}^2$. The sputtering times at half of the maximum intensities of O and Fe were averaged to find the sputtering time corresponding to the estimated film thickness. The maximum intensity of Fe was selected at a sputtering time of 9 minutes, at which the intensity of Fe is considered to reach a steady level. The sputtering rate estimated from the sputtering of pure iron was 2.1 nm/min.

Results and discussion

The pitting potentials of SUS 304 stainless steel after exposure for 7 days and 61 days are shown in Figure 1. The average pitting potentials of the unexposed specimen is 394.3 $\text{mV}_{\text{Ag}/\text{AgCl}}$. The pitting potentials increase to 461.7 and 632 $\text{mV}_{\text{Ag}/\text{AgCl}}$ after an exposure for 7 days and 61 days, respectively. It can be seen that the pitting potential increases after exposure.

Table 1 Mass percent compositions of as-received SUS 304 stainless steels

C	Si	Mn	Cr	Ni	Mo
0.062	0.52	1.01	18.32	8.44	0.018

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In the XPS analysis accompanied by the RSF quantification method, the ratio of Cr-ion mass percent per Fe-ion mass percent was used to indicate the degree of Cr enrichment at the specimen surface. Figure 2 shows the ratio in the surface of specimens exposed for a different exposure period. The value of the unexposed specimen is 40.4%. From Table 1, the ratio of Cr

mass percent per Fe mass percent in bulk of the as-received SUS 304 is 25.6 %. It says that Cr enriches in passive film of the as-received SUS 304 stainless steel. The Cr-ion mass percent per Fe-ion mass percent is 51.8 % after the 7-day exposure, and is 81.3 % the after the 61-day exposure period. It is evident that Cr enrichment considerably increases after exposure.

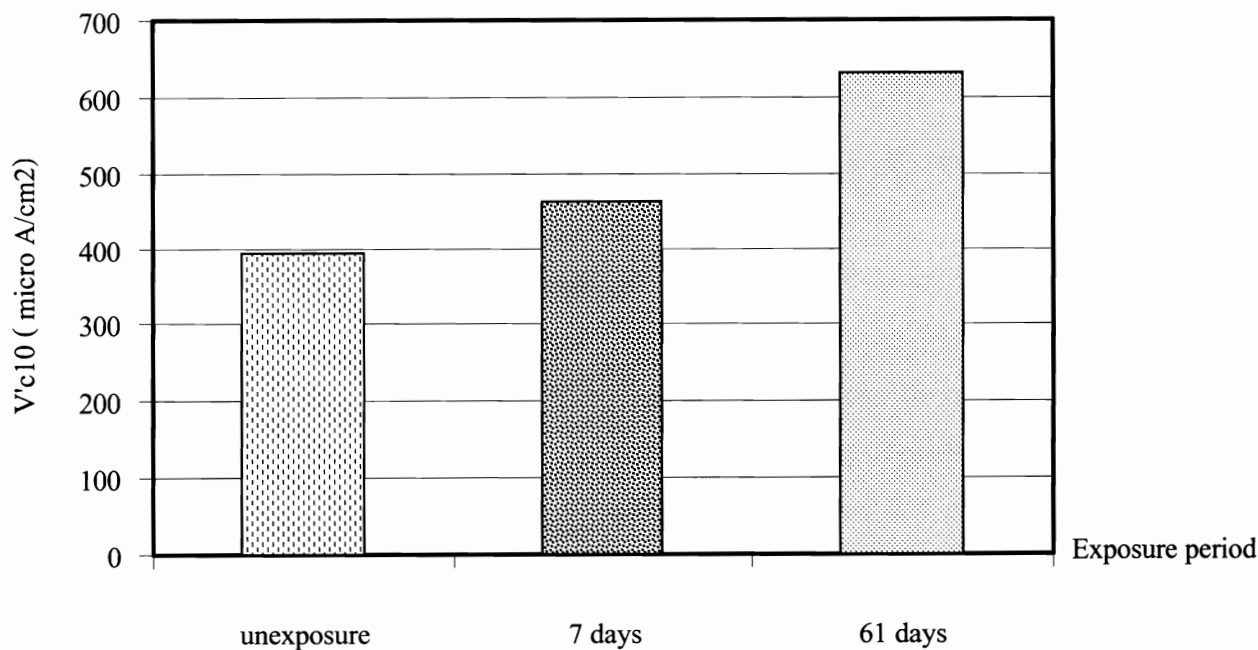


Figure1 Pitting potentials of SUS 304 stainless steel exposed for 7 and 61 days at Chiba urban-industrial site

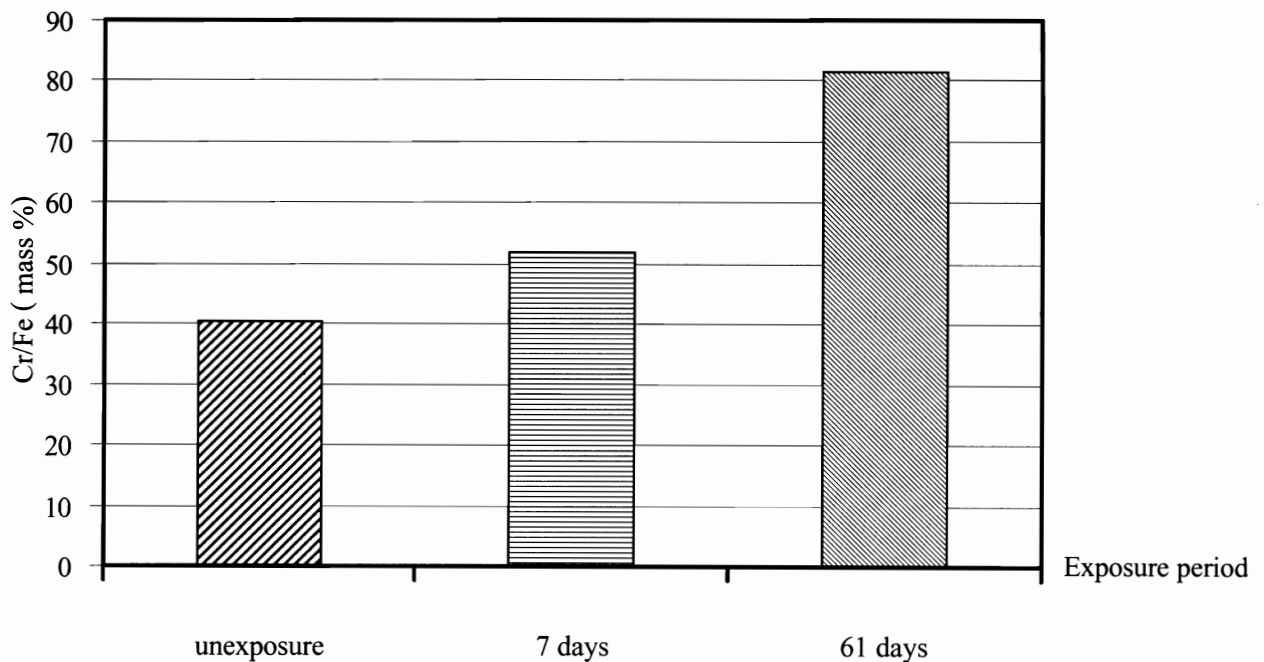


Figure 2 Cr enrichments in passive films of SUS 304 stainless steels at different exposure periods

In the passive film of SUS 304 stainless steel, both nickel oxide and hydroxide were slightly observed in the unexposed specimen. However, only oxide film can be observed after the 7-day and 61-day exposure periods. It is possible that nickel hydroxide in the passive film of an unexposed specimen was deprotonized and changed to nickel oxide after the 7-day exposure. In Figure 3, the mass ratio of nickel ion per iron, chromium and nickel ions (Ni/Fe-Cr-Ni) in the passive film is 1.4%. This is evident, even though the Ni bulk composition is 8.44%. It slightly takes part in passive film, which was 1.4% in the unexposed

specimen. This ratio is 3.2% after the 7-day exposure, and is 2.3% after the 61-day exposure.

The photoelectron intensities of OH^- and H_2O were grouped and compared to the photoelectron intensity of O^{2-} . The photoelectron intensities of OH^- and H_2O per O^{2-} are shown in Figure 4. The ratio is 2.42 for the unexposed case. It indicates that the photoelectron intensity of OH^- and H_2O is higher than that of O^{2-} . This ratio reduces to 1.34 after the 7-day exposure period, but it is nearly constant (2.41) after the 61-day exposure period. The changes of this ratio and Ni/Fe-Cr-Ni will be later discussed with the change in passive film thickness.

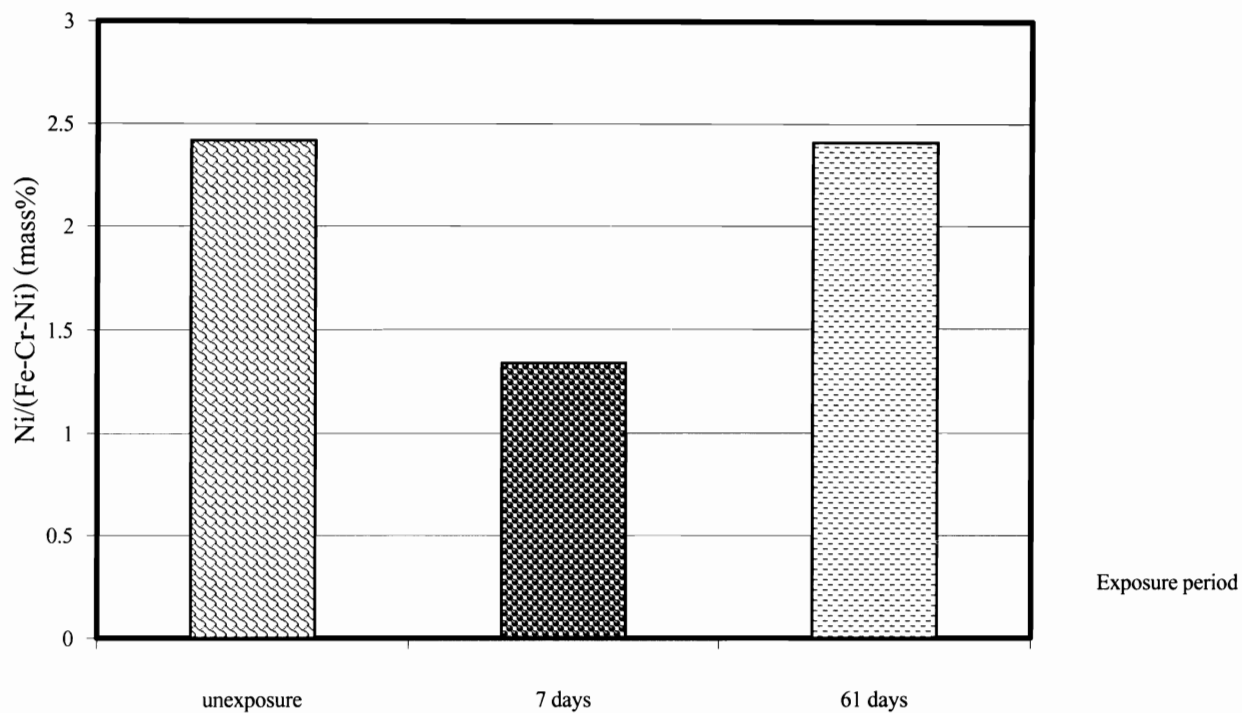
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Figure 3 Ni enrichments in passive films of SUS 304 stainless steel after different exposure periods

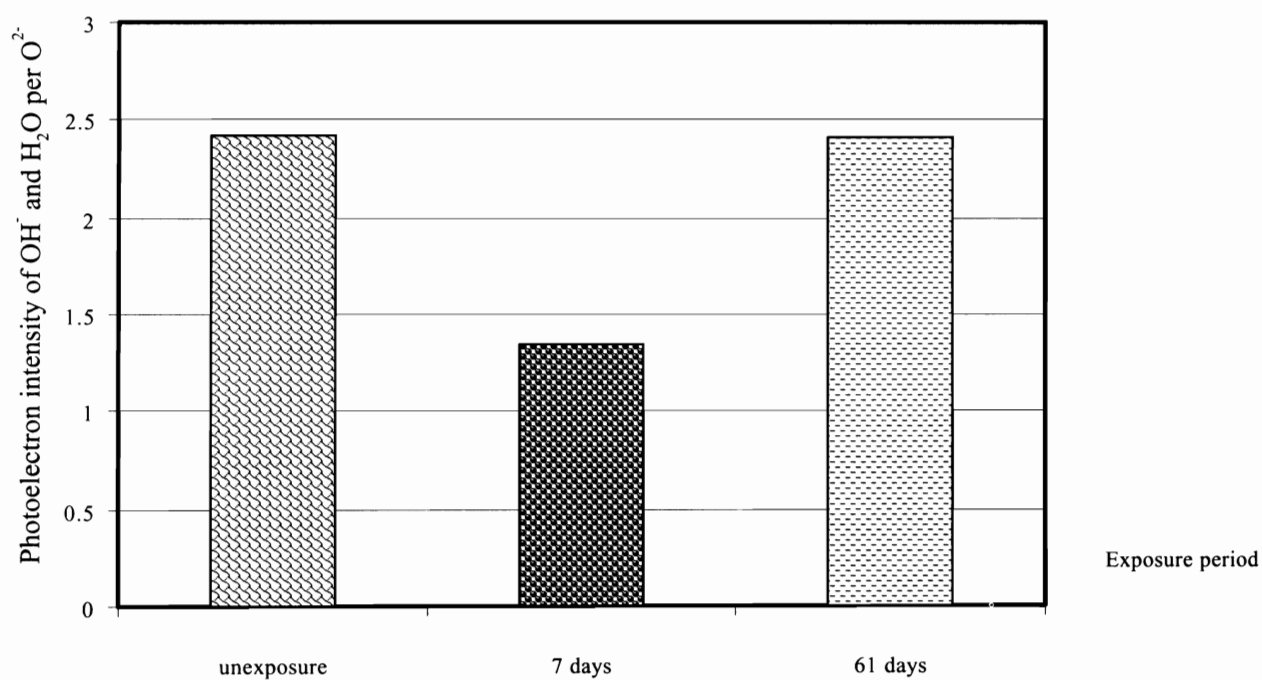


Figure 4 The photoelectron intensity of OH⁻ and H₂O per O²⁻ of SUS 304 stainless steel at the different exposure periods

Figure 5 illustrates the Auger electron intensity emitting from oxygen in the compound form in the passive film and substrate of SUS 304 stainless steel at different exposure periods. The estimated film thicknesses of SUS 304 stainless

steels are 2.6, 1.6 and 2.2 nm for the unexposure, the 7-day and the 61-day exposure periods, respectively. It says that the film thickness decreases after exposure.

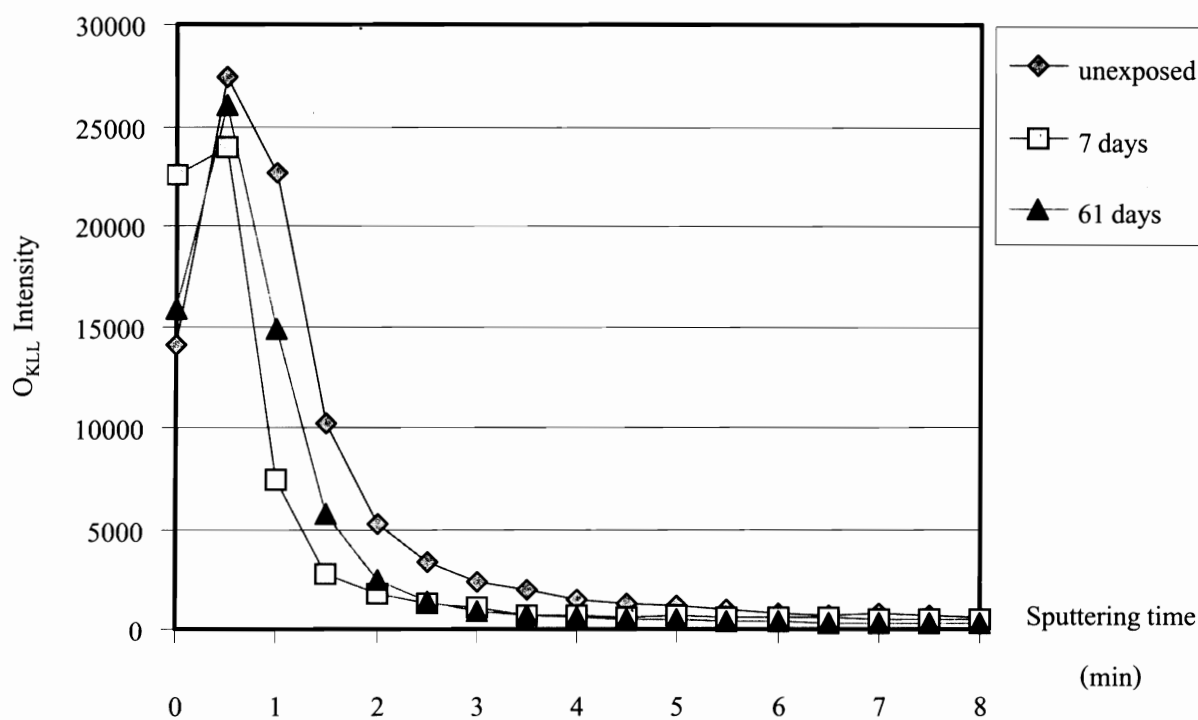


Figure 5 AES depth profile of O_{KLL} Auger electron intensity of SUS 304 stainless steel before and after exposure for 7 and 61 days at the Chiba urban-industrial site

Based on the assumption that the density of passive film in each condition is not markedly different, it may be considered that the passive film thickness decrease due to the reductions of passive film volume and mass. If the Ni content of compounds in the passive film is considered nearly constant and the passive film mass decreases after exposure, the increase in Ni mass percent or Ni/Fe-

Cr-Ni in the passive film should be observed. This is reflected in Figure 3 and Figure 5.

Figure 6 shows the schematic sketch of SUS 304 stainless steel passive films for the unexposure, the 7-day and 61-day exposure periods at the Chiba urban-industrial site. Many workers (Olefjord, *et al.* 1990; and Vito, *et al.* 1992) reported a covering layer of hydroxide on the top

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surface of the passive film. The horizontal dot line indicates the boundary of the hydroxide and oxide layers. The hydroxide means OH^- and H_2O in the passive film in this sketch. From this sketch and previous results, the phenomena can be discussed as follows.

After the 7-day exposure, it may be considered that the Fe ion is dissolved from the passive film to the atmosphere. It results in Cr enrichment as shown in Figure 2. It is also possible that the OH^- and H_2O film, at least that formed on an as-received specimen, is removed from the passive film to the atmosphere. The photoelectron intensity of OH^- and H_2O per O^{2-} is then reduced as in Figure 4. Both the dissolution of the Fe ion and the removing of the OH^- and H_2O film may result in a decrease in the passive film thickness as in Figure 5. By relating pitting potentials to the change in chemical composition of the passive film and passive film thickness, it is then proposed that after 7-day exposure pitting potentials increase and relate to the increase in Cr enrichment.

For the 61-day exposure, a possible reason to explain the increase in Cr enrichment is the same as the 7-day exposure case. It is possible that passive film is removed after exposure. Both the dissolution of the Fe ion and the removing of the passive film may result in the decrease in the passive film thickness as in Figure 5. Because passive film thickness reduces, but the photoelectron intensity of OH^- and H_2O per O^{2-} is nearly constant with respect to the unexposed case, then a novel OH^- and H_2O film must be formed. This formation may occur by two possible ways. The first is the transformation of oxide to be hydroxide. The second is the growth of novel OH^- and H_2O film on the top surface. By relating the pitting potentials to the change in chemical composition of passive film and passive film thickness, it is then proposed that after a 61-day exposure, pitting potentials increase and may relate to the increase in Cr enrichment or the novel OH^- and H_2O film formed after exposure

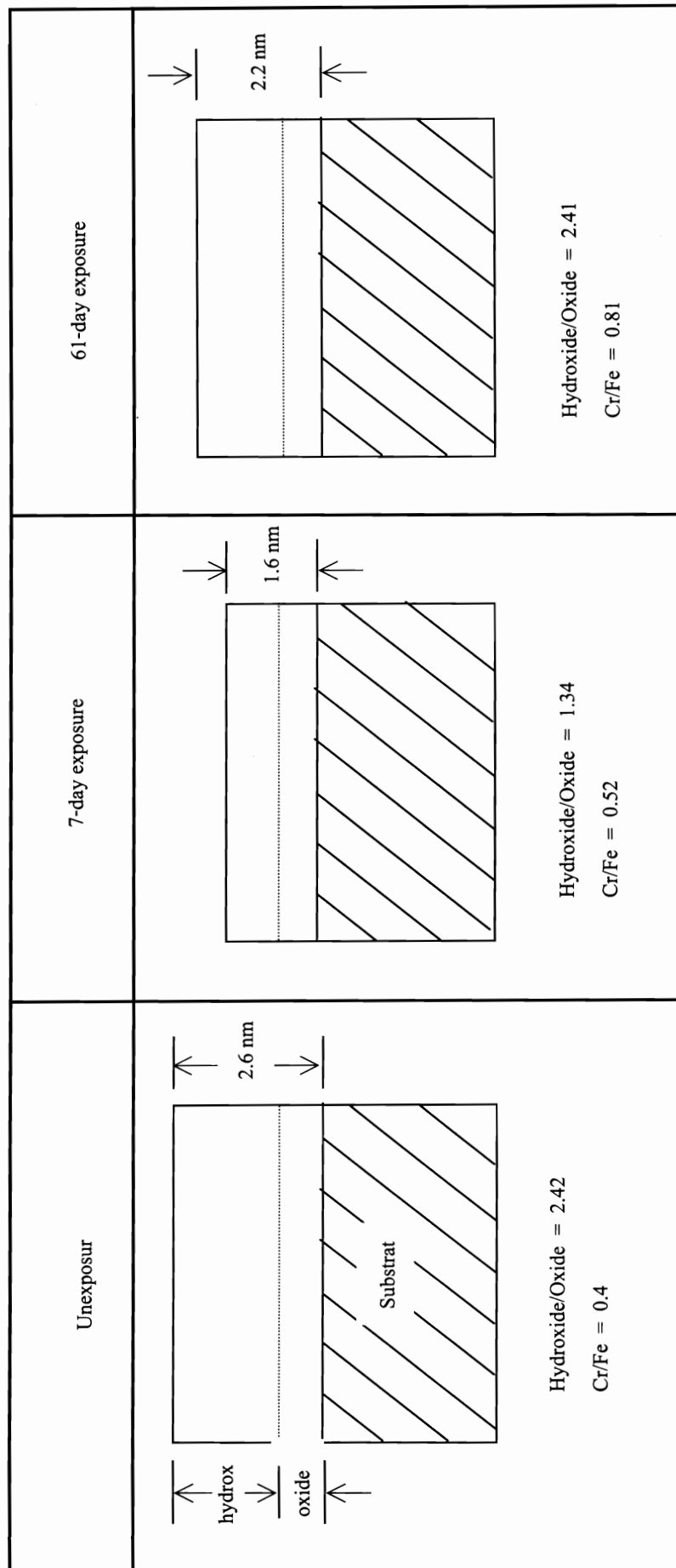


Figure 6 Schematic sketch of the change in construction of passive film of SUS 304 stainless steels

Conclusions

The SUS 304 stainless steel was exposed for 7 and 61 days to the Chiba urban-industrial atmosphere. The anodic polarization technique, the XPS and AES analyses were used to investigate the passive films. The following conclusions can be drawn:

1. The pitting potentials and Cr enrichment of the specimen exposed for 7 days and 61 days are higher than those unexposed.

2. A small amount of Ni is found in the passive films. Its content seems to be constant after exposure.

3. By comparing to the unexposed case, after the 7-day exposure period, the photoelectron intensity ratio of H_2O and OH^- per O^{2-} in passive film decreases, but it is nearly the same ratio after the 61-day exposure period.

4. The passive film thickness of the specimen exposed for 7 days and 61 days decreases after exposure.

5. After the 7-day exposure, it is proposed that the pitting potentials increase and relate to the increase in Cr enrichment.

6. After the 61-day exposure, it is proposed that the pitting potentials increase and may relate to the increase in Cr enrichment or the novel OH^- and H_2O film formed after exposure.

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