

perature was slowly added 12 ml (20 mmol) of a solution of 1.7 M *tert*-butyllithium in pentane. The mixture was allowed to room temperature and stirred overnight and benzene solvent was evaporated off. Then the reaction mixture was dissolved in hexane, lithium chloride and anthracene were filtered off. Procedure as described above was followed by GLC analysis which gave 75% yield of *Z*-, **3a**, and *E*-2-chloro-2-phenyl-3-neopentyl[5,6:7,8]dibenzo-2-silabicyclo[2.2.2]octanes, **3b**. The ratio 91/9 of *Z*-**3a** to *E*-**3b** was determined by $^1\text{H-NMR}$ analysis for the sample which was purified by a preparative GLC. *Cis*-configurational adduct, **3a** was precipitated out from the reaction mixture in hexane at low temperature (*ca.* 0°C). Recrystallization of this crude precipitate in hexane afforded the pure *cis*-adducts (mp. 151-2°C, colorless crystal)

For *Z*-**3a**; $^1\text{H-NMR}$ δ 0.81 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.28-1.45 (m, 3H, CH and CH_2), 4.13 (s, 1H), 4.32 (d, $J=2.1$ Hz, 1H) (benzyl-H), 6.97-7.39 (m, 13H, aryl-H)

For *E*-**3b**; $^1\text{H-NMR}$ δ 0.74 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.14-1.41 (m, 3H, CH and CH_2), 4.13 (s, 1H), and 4.27 (d, $J=2.5$ Hz, 1H) (benzyl-H), 7.11-7.59 (m, 13H, aryl-H); MS: m/e (relative intensity) 404 (3) and 402 (10) (M^+), 179 (14), 178 (96) (anthracene $^+$), 169 (34) and 167 (100) (PhClSiVi^+), 143 (10), 141 (27), 63 (14); Anal. Calcd. for $\text{SiC}_{26}\text{H}_{27}\text{Cl}$: C, 77.48; H, 6.75. Found for a mixture of *E*-**3a** and *Z*-**3b**; C, 77.40 H, 6.78

Trapping Reaction with Methoxytrimethylsilane.

To a solution of 2.4 g (11.8 mmol) of dichlorophenylvinylsilane and 4.2 g (40 mmol) of methoxytrimethylsilane in 80 ml of dry *n*-hexane cooled to -78°C was slowly added 7 ml (11.8 mmol) of 1.7 M *tert*-butyllithium in pentane. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. Lithium chloride which had formed removed by using centrifuge. After the reaction mixture was concentrated by the evaporation of solvent, colorless liquid was obtained which analysis indicated to be 94% silene adducts. The samples for the characterization were purified by a preparative GLC and the ratio 90/10 of **4a/4b** was determined by $^1\text{H-NMR}$.

For **4a(4b)**; $^1\text{H-NMR}$ δ 0.10 (0.06) (s, 9H, $\text{Si}(\text{CH}_3)_3$), 0.38 (0.43) (dd, $J=2.8, 15.7$ Hz (2.5, 6.1 Hz), (1H, SiCH), 0.70 (0.75) (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.44 (1.41) (dd, $J=2.8, 14.4$ Hz (2.5, 14.3 Hz), 1H) and 1.77 (1.70) (dd, $J=5.7, 14.4$ Hz (6.1, 14.3 Hz), 1H) (CH_2), 3.50 (3.46) (s, 3H, OCH_3), 7.38-7.70 (m, 5H, aryl-H); $^{13}\text{C-NMR}$ δ 0.14 (-0.02) ($\text{Si}(\text{CH}_3)_3$), 10.57 (11.48) (CH), 29.31 (29.31) ($\text{C}(\text{CH}_3)_3$), 31.56 (31.67) ($\text{C}(\text{CH}_3)_3$), 36.49 (31.67) (CH_2), 51.10 (50.82) (OCH_3), 127.49, 127.90, 128.18, 130.37, 133.87, 134.25, 134.57 (aryl-carbons); MS: m/e (relative intensity) 313 (20) and 315 (7) (M-15^+), 171 (10), 164 (14), 163 (100), 141 (15), 137 (11), 121 (17), 107 (11), 91 (24), 73 (91), 63 (13), 59 (56), 57 (45); Anal. Calcd. for $\text{Si}_2\text{C}_{16}\text{H}_{29}\text{OCl}$: C, 58.41; H, 8.88. Found for a mixture of **4a** and **4b**: C, 58.63; H, 8.90.

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Stainless Steel Surface Oxidized in Strong Oxidizing Solution

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Stainless steel 304 2B and BA are oxidized in 2.5 M CrO_3 /5.0 M H_2SO_4 solution, and elemental composition and oxidized state of the surface region is analyzed as a function of the surface depth using X-ray photoelectron spectroscopy. It is found that Fe and Cr are preferentially oxidized and diffuse outward following the oxidation. Element Ni, the third major component of the steel is not oxidized and remains deep under the surface. It is also found that the oxidized Fe dissolves considerably into the solution thereby enriching the gas-oxide interface with Cr.

Introduction

Stainless steels are multi-component alloys, and their sur-

face layers have a different elemental composition as a consequence of surface treatment given in the course of rolling the steel. The surface layer so formed protects the bulk from

oxidation much better, thereby giving a higher passivity to the steel¹⁻⁴. This surface can however be oxidized partially to give a brass yellow color if heated in the air above 300-400°C. The surface can be oxidized also by immersing it in a strong oxidizing solution. In this case, some components dissolve into the solution, and the remaining oxidized components in the surface region give diverse beautiful colors according to the extent of oxidation⁵⁻⁷.

The oxidation tendency of the steel is affected by many factors in addition to surface composition, but it shows in general a common feature^{5,6}. When a stainless steel strip is immersed in a strong oxidizing solution, such as acidic chromic oxide solution or permanganate solution, a potential difference develops between the sample strip and an electrically connected inactive counter-electrode. The potential difference increases initially with the immersing time, indicating an increasing oxidation tendency of the steel. The potential difference reaches a maximum and after a short period of time it increases again steadily. The region between the maximum and the minimum is certainly related to a resistive state for the oxidation.

The steadily increasing potential difference beyond the minimum is used as a measure of the degree of surface oxidation^{5,6}. Takeuchi⁸⁻¹⁰ reported that the surface layer becomes oxidized more deeply into bulk as the potential difference increases. Hart^{5,6} used this potential difference in the so called INCO process of stainless steel coloring.

The stainless steel dissolves partially into the oxidizing solution while the oxidation proceeds. The extents of dissolving differ from element to element in a given oxidizing solution. The composition of the surface layer can be controlled to some extent by choosing an adequate oxidizing agent and an acid.

In this work the surface oxidized in $\text{CrO}_3/\text{H}_2\text{SO}_4$ solution is analyzed with X-ray photoelectron spectroscopy (XPS), and the change in elemental composition is studied. The XPS is very effective for this kind of studies since it shows not only the surface elemental composition but can provides information about the chemical state of the elements detected through chemical shift of the electron binding energy. The depth composition profile of the surface region is also investigated by peeling off the surface with Ar ion bombardment.

Experimental

Material. Cold strip of austenite type stainless steel 304 2B and 304 BA are used as samples. The bulk composition is Cr; 17.42%, Ni; 7.42%, C; 0.07%, Si; 0.59%, Mn; 1.02%, P; 0.03%, S; 0.01%, and Fe makes up the rest. The samples are thoroughly washed to remove any organic and inorganic contaminants. All chemicals used are reagent grades without further purification. A solution of 2.5 M in CrO_3 and 5.0 M in H_2SO_4 is used as an oxidizing solution throughout the experiment.

Apparatus. An ultra high vacuum XPS system (ESCA 750, Shimadzu Co., Japan) is used to obtain X-ray photoelectron spectra of the samples. Oxygen, Fe, Cr, and Ni are analyzed. The spectra are calibrated with Ag $3d_{5/2}$ (367.9 eV), Au $4f_{7/2}$ (83.8 eV), Cu $2p_{3/2}$ (932.4 eV) peaks. The pressure inside the ESCA chamber is monitored with BA ionization gauge.

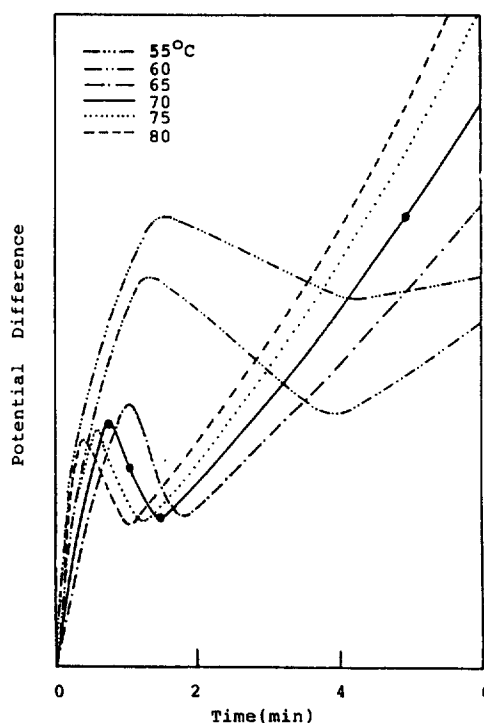


Figure 1. Potential difference between the stainless steel sample and an inert metal(Pt) in 2.5 M/ CrO_3 /5.0 M H_2SO_4 solution, varies with the time and the temperature.

A small piece of sample to be studied is put in the ESCA chamber after thorough cleaning. Then the ESCA chamber is evacuated down to 5×10^{-9} torr to remove any contaminants remaining physisorbed on the sample.

Results

The sample of stainless steel strip is immersed in 2.5 M CrO_3 /5.0 M H_2SO_4 solution, and the potential difference developed between the sample strip and inactive Pt plate (the counter electrode) is monitored, using a multimeter (Keithley, 177 microvolt DMM, U.S.A.) connected to a XY-recorder (U-228 unicorder, Denshi Kagaku Co., Japan). The oscillatory behavior of the potential is observed in this work, too. It is found that the higher the temperature of the oxidizing solution the sooner the maximum appears (Figure 1). The surfaces of the oxidized samples and of the as-received samples are analyzed with X-ray photoelectron spectroscopy, and the change in the surface region is also investigated by peeling off the surface with Ar ion bombardment.

As-Received State. The photoelectron spectra of O 1s on the BA strip are shown in Figure 2. Numbers put on the left of the spectra are Ar ion bombardment time (in minutes). A shoulder at 532.0 eV which disappears with the Ar ion bombardment is certainly due to physisorbed H_2O or hydroxide formed at the surface. A strong peak at 530.6 eV is due to atomic oxygens of metal oxide. The intensity of this peak becomes negligible with ca. 5 minutes Ar ion bombardment. The spectra of 2B strip show very similar patterns, and so the results are omitted.

The spectra of Fe 2p show strong oxidized state initially in the BA sample (Figure 3). This peak at a little over 710 eV is replaced gradually with the more intense metallic state

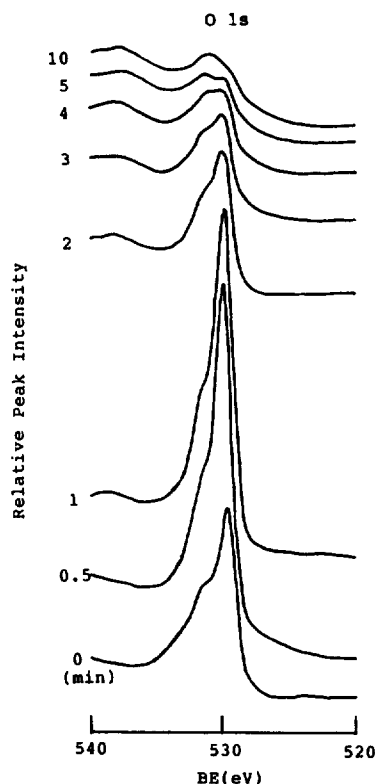


Figure 2. Photoelectron spectra of oxygen in the "as-received" state surface of the stainless steel 304 BA.

peak at 707.0 eV. The replacement is practically completed with about 2 minutes Ar ion bombardment. The stripping rate of the surface with Ar ion bombardment is not determined in this case, but it is estimated to be α . 0.6-1.0 nm min^{-1} . The distinction between two oxidized states of Fe^{2+} (709.8 eV) and Fe^{3+} (710.4 eV) is impossible. The spectra of 2B sample are quite similar except that the metallic state peak appears fairly intensively prior to the bombardment. The spectra of chromium in Figure 4 show a peak at 576.6 eV, and the peak is replaced by the metallic peak at 574.0 eV with the Ar ion bombardment. Nickel, the third major element of stainless steel 304, is buried deep under the surface as revealed by the spectra of Figure 5. It is noteworthy that nickel is not oxidized. Both the 304 BA and 2B show similar spectral behavior, and results for 2B are not shown either.

It is assumed that the peak intensity (*i.e.*, area of the peak) of an element detected is proportional to the amount present, and can be calibrated with the known bulk composition. The elemental composition obtained with this assumption and normalized are plotted against the Ar ion bombarding time in Figure 6 and 7. The oxygen intensity decreases sharply with the bombardment initially in both samples and maintains an almost constant value for a long continues bombardment.

Oxidized State. The 304 BA and 2B samples are oxidized to various degrees in the solution of 2.5 M CrO_3 /5.0 M H_2SO_4 at 70°C, and then the photoelectron spectra are obtained as with the as-received samples. Figures 8, 9, 10, and 11 are the plots of peak intensity versus Ar ion bombardment time for samples which are oxidized until the potential shows

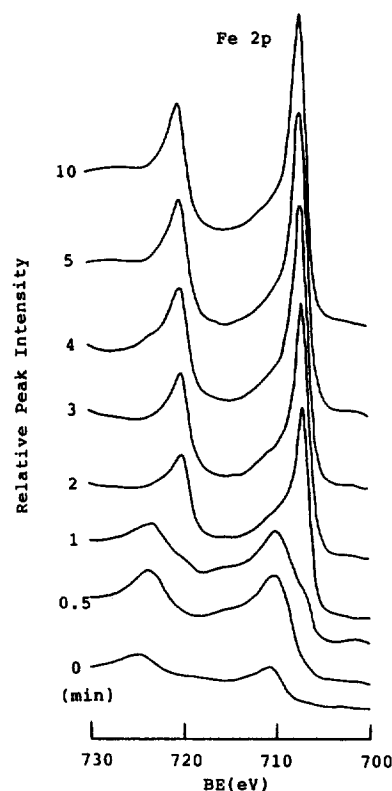


Figure 3. Photoelectron spectra of iron in the "as-received" state surface of the stainless steel 304 BA.

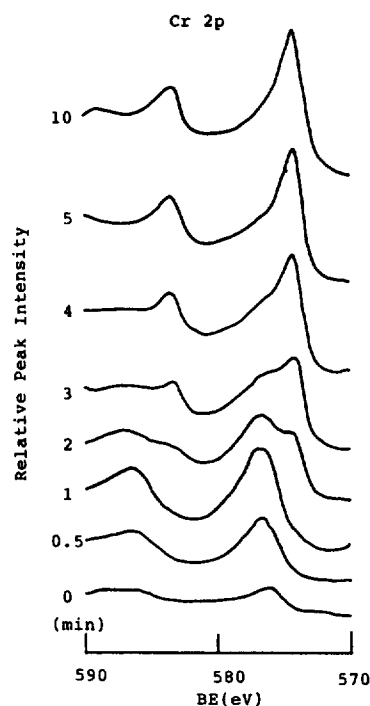


Figure 4. Photoelectron spectra of chromium in the "as-received" state surface of the stainless steel 304 BA.

the maximum, the negative slope over the maximum, the minimum, and the increasing slope over the minimum in Figure 1, respectively.

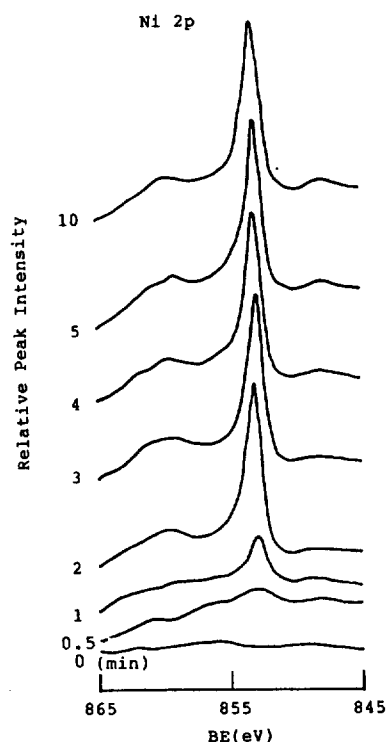


Figure 5. Photoelectron spectra of nickel in the "as-received" state surface of the stainless steel 304 BA.

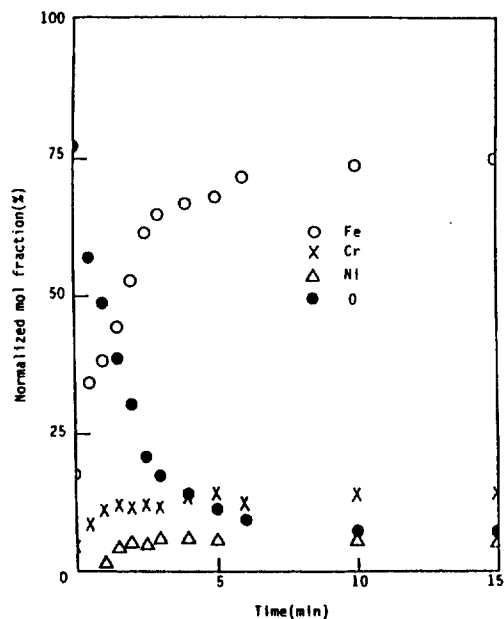


Figure 6. Elemental composition of the surface layer of the stainless steel 304 BA versus Ar ion bombarding time.

Discussions

The X-ray photoelectron spectra of as-received samples show an intense O 1s peak which lasts until about 5 minutes Ar ion bombardment (Figure 2). The O 1s intensity thereafter keeps a considerable residual intensity for a continued bombardment. This experimental finding is consistent with the known facts that the stainless steel has an oxidized layer on the surface already in the as-received state, and that the

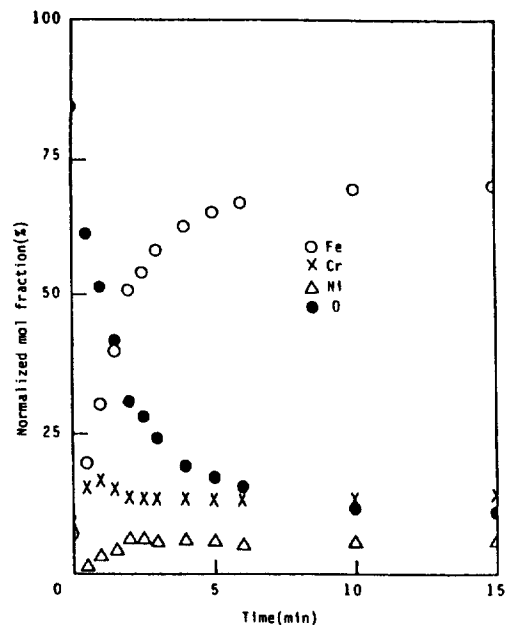


Figure 7. Elemental composition of the surface layer of the stainless steel 304 2B versus Ar ion bombarding time.

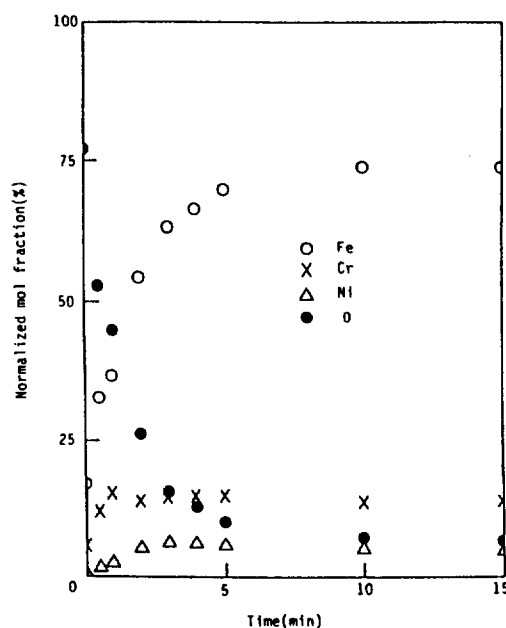


Figure 8. Elemental composition of the surface layer of the stainless steel 304 BA versus Ar ion bombarding time. The sample is oxidized in 2.5 M CrO_3 /5.0 M H_2SO_4 solution at 70°C until the potential reaches the maximum.

elemental composition of this surface layer is different a little from that of the bulk. The oxidized samples in 2.5 M CrO_3 /5.0 M H_2SO_4 solution have far thicker oxidized layer as can be seen in Figures 8, 9, 10, and 11. With 5 minutes immersion in the oxidizing solution, O 1s peak maintains high intensity until about 200 minutes Ar ion bombardment.

Fe 2p peak shifts from the oxidized state to the metallic state at the depth where O 1s peak intensity is still high. Cr is oxidized more deeply into the bulk than iron. The same phenomena hold in all of the oxidized samples. On

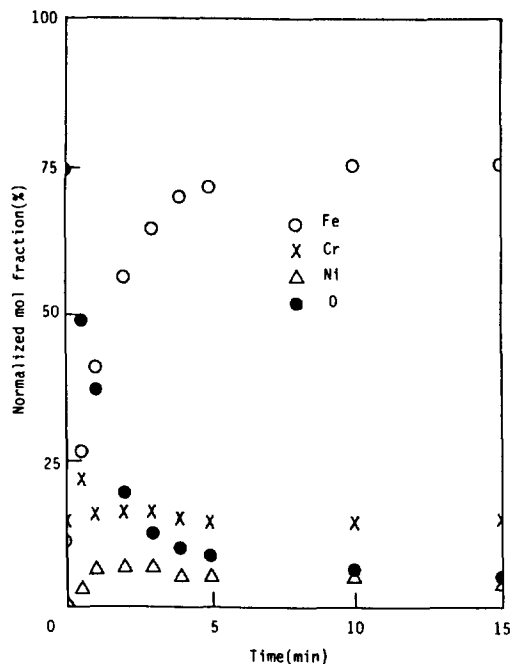


Figure 9. Elemental composition of the surface layer of the stainless steel 304 BA versus Ar ion bombarding time. The sample is oxidized in 2.5 M CrO_3 /5.0 M H_2SO_4 solution at 70°C until the potential reaches midway between the maximum and the minimum.

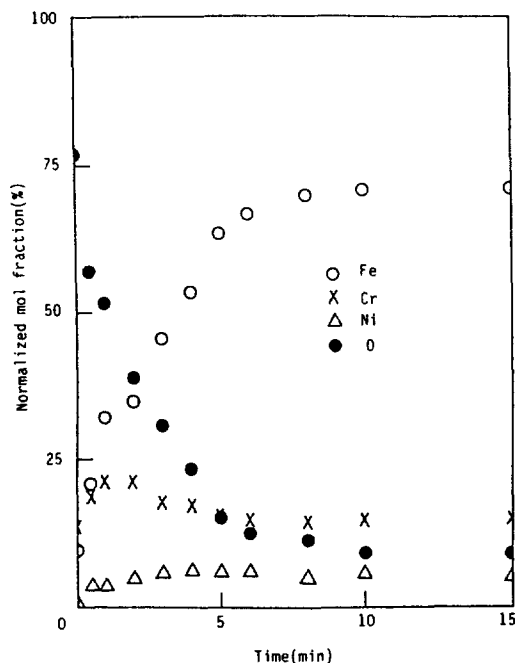


Figure 10. Elemental composition of the surface layer of the stainless steel 304 BA versus Ar ion bombarding time. The sample is oxidized in 2.5 M CrO_3 /5.0 M H_2SO_4 solution at 70°C until the potential reaches the minimum.

the other hand, Ni 2p peak is detected in the interior where O 1s peak diminished to the residual intensity. These sug-

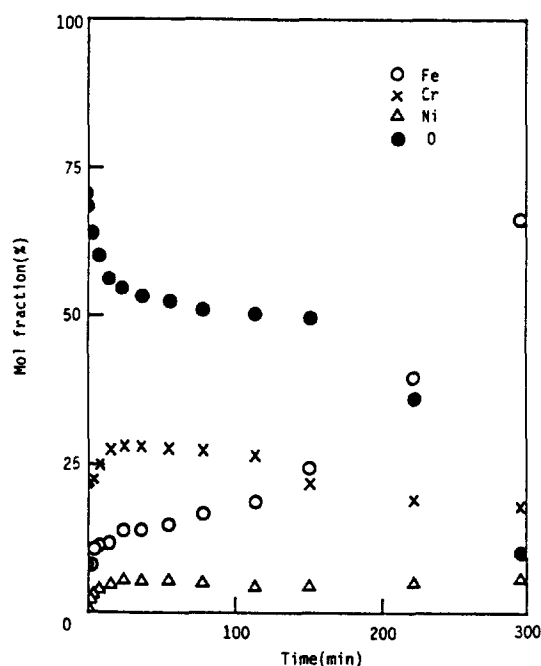


Figure 11. Elemental composition of the surface layer of the stainless steel 304 BA versus Ar ion bombarding time. The sample is oxidized in 2.5 M CrO_3 /5.0 M H_2SO_4 solution at 70°C until the potential passes beyond the minimum.

gest that the surface elements diffuse outward on oxidation, the rate being in the order of $\text{Fe} > \text{Cr} > \text{Ni}$. It is not certain whether the residual O 1s peak is a result of a partial inward diffusion of oxygen or an impurity introduced previously in the course of the alloying process.

It is interesting to note that the relative abundance of Cr in the gas-oxide interface increases as the degree of oxidation is increased. The cause of low Fe concentration, in spite of its higher relative diffusion rate, is believed to be due to its dissolution into the solution. When the oxidation potential difference passes over the minimum, the Cr concentration exceeds the Fe concentration in the gas-oxide interface. A further systematic work is necessary to be able to relate this compositional change to the color developing in the surface.

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