Analysis of Film Generated on Various Stainless Steel Surfaces in Soy Sauce by EIS and XPS

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Abstract: This paper was developed the passivation phenomenon for various stainless steels in soy sauce by evaluation for the electrochemical impedance characteristic and the distribution of elements in the specimens measured by X-ray photoelectron spectroscopy. It is possible to show a passivation phenomenon using the electrical equivalent circuit that is assumed consisting of a series connection of two parallel RC circuits and a resistance of solution. By equivalent circuit analysis, the resistance of passive film and the corrosion resistance values of duplex stainless steels are 10 times higher than that of the austenitic stainless steels, the duplex stainless steels are superior in corrosion resistance to the austenitic stainless steels in soy sauce. In stainless steels with higher corrosion resistance, as for the element distribution in the passive film that had been generated to the stainless-steel surface, it was shown that Cr was concentrated to an outermost surface of the film by the X-ray photoelectron spectroscopy (XPS) analysis. And, the thickness of the passive film is thinner. When the high local Cr concentration is generated at the outermost surface of passive firm thus leading to the increase of the film resistance value, its corrosion resistance is enhanced, the corrosion current becomes smaller and corrosion resistance is heightened. The ratio of concentration of Cr is proportional to its film resistance value as well as its charge transfer resistance.

Keywords: electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS), stainless steels, soy sauce, NaCl, pitting corrosion, passivation film.

1. Introduction

Manufacturing plants for soy sauce is exposed to severe corrosive environment of highly concentrated sodium chloride containing various organic compounds. On the top this, the operation in manufacturing process is heat operation that is approximately 368 K. And then, the evaluation of corrosion resistance for stainless steel is the essential factor for equipment which are pitting and crevice corrosion, even stress corrosion cracking in soy sauce in soy sauce environment. On the other hand, many exciting tanks specification is constructed from carbon steel coated with resin. After the resin on the surface of tank is degraded by heat or mechanical damage in production process, aging of resin and the corrosion rapidly destroys the structure of tank. Therefore, tanks specification is shifting from carbon steel with resin to stainless steels due to the stabilization of manufacturing of production process, product quality and cost reduction for plant maintenance in recent years.

However, unfortunately, not very much is known about the corrosion behavior of industrial stainless steels in soy sauce manufacturing plants as compared with the study of corrosion resistance to sodium chlorides and highly concentrated sodium chloride [1-5], although a few reports are available on the immersion test and pitting potential in fermentation of Moromi and storage tank of soy sauce [6-8]. Moreover, not a single study on the corrosive characteristics of stainless steel under such an environment is available.
Therefore, in previous paper [9], the corrosion resistance, morphology of pits after pitting corrosion, the influence on the localized corrosion of components contained of soy sauce of various stainless steels in high concentrated NaCl solution and actual soy sauce environment was investigated an electrochemical polarization method and observation of SEM. In addition, it proposed a new PERn type to the susceptibility of the pitting corrosion of the duplex stainless steel including tungsten, accurately evaluated the pitting resistance of various stainless steels and suggested the design guideline of equipment in case of concentrated NaCl solution containing of various organic compounds such as soy sauce. Moreover, not a single study on the corrosive characteristics of stainless steel under such an environment is available.

On the other hand, electrochemical impedance measurement is avertable method for the monitoring of the corrosion rate of metal and thus the monitoring of corrosion is used under various environments [10]. The application of electrochemical impedance measurement to evaluation of corrosion allows the understanding of the rate of corrosion as well as the property of the passivation film without affecting the metal corrosion state [11, 12].

In our previous research, it reported the polarization characteristic of duplex stainless steels to be a greatly different from the curves at the temperature less than it on the boundary of 368 K. In this paper, immersion tests were conducted on various stainless steels in soy sauce at the temperature of 368 K measured the electrochemical impedance spectra and measured by X-ray photoelectron spectroscopy (XPS) in order to obtain the state of passive film. It was developed the passivation phenomenon for various stainless steels in soy sauce by evaluation for the electrochemical impedance characteristic and the property of passive film.

2. Experimental Procedure

2.1 Test Solution

The test solution used is a soy sauce of the composition similar to the previous report. The test solution shall have a volume of 400 mL, the experiment was conducted under atmospheric at constant temperature and static state. Considering the manufacturing processes, the solution temperature is 368 K.

2.2 Specimens

The specimen was used commercially available austenitic stainless steels UNS S30400 and S31600, duplex stainless steels UNS S31803, S32750 and S39274. The chemical composition of these specimens is same as the previous paper [9].

These materials were cut into 15 mm × 15 mm × 2 mm like as flag shape and used as the specimens. The pretreatment of specimen was degreased with acetone after ground with wet Emery paper to #600 and then washed in pure water.

2.3 Electrochemical Measurement

Electrochemical impedance measurements were carried out in a conventional three electrodes system, the working electrode of austenitic and duplex stainless steels, a saturated KCl/Ag/AgCl reference electrode and a platinum counter electrode. The corrosion potential (Ecorr) and the electrochemical impedance spectroscopy (EIS) were monitored by using a potentiostat with connected the frequency response analyzer (FRA). Measured potentials were converted into the potential of standard hydrogen electrode (SHE) at the temperature. After it had been immersed in the test solution for 30 min, the corrosion potential of the specimen was measured as an open circuit potential (Ecorr). AC voltage was applied ±5 mV at Ecorr and EIS was measured from higher frequencies to lower frequencies within the measurement frequency of 10^{-3} to 10^{5} Hz. From obtained the impedance spectra, the electric equivalent circuit was evaluated by the simulation software of ZSimpWin.
2.4 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy was used for analysis of the surface films. It is carefully removed any extraneous matters from the specimen surface using water, etc. The specimen was excited and irradiated the surface with MgK ray source at 15 kV and 200 W. The specimen after tested was conducted in-depth analysis below in the range of 0.8 mm of diameter using Ar etching at the rate of 15 mm/min (1.5 μm/min in term of SiO2).

3. Results and Discussion

3.1 Change of Corrosion Potential in Long-Term Immersion Test

Fig. 1 shows the changes of $E_{\text{corr}}$ for various stainless steels at 353 K and 368 K. In either temperature, the corrosion potential after one hour has shifted to less noble direction about -200 mV. However, the different behavior was shown for the duplex stainless steel according to the temperature. That is, the corrosion potential in UNS2750 and 3927 that contained a lot of chromium and the nickel showed the tendency to increase again though the tendency similar to the austenite was shown in 31803, and the tendency to increase within short time was shown in especially 3927. On the other hand, the corrosion potential in 368 K maintained the decreased potential of about -200 and thus remained stable for a month in the immersion tests. As a result, it is thought that a steady film generates it to the surface of all different stainless steels with the results of the polarization curve.

Brown-colored materials were uniformly adhered to the surface of all the specimens immersed in soy sauce for about a month. The entire surface after the removal of the sediment, however, exhibited a metallic luster, and none of the trace of corrosion was observed, even locally.

3.2 Electrochemical Impedance Characteristics

Within the measured impedance characteristics for all of stainless steels, which were left immersed in soy sauce, both austenitic stainless steels UNS S30400 and UNS S31600 showed a similar impedance spectrum. Fig. 2 shows the change of the impedance ($\log|Z|$) and phase difference ($\theta$) according to the frequencies of UNS S31600. The change of the impedance of UNS S31600 over time shows a constant value of the solution resistance at around the high frequency range of 104 Hz. When the frequency decreases, the $Z$ value starts to increase. A breakpoint in the rise curve was observed at around the 101 Hz and the gradient started to ease off. When left immersed in soy sauce, the $Z$ value of the solution resistance increased, while the position of the breakpoint in the lower frequencies remained almost in the same place and the rise curve
does hardly changed.

Meanwhile, the phase angle $\theta$ starts to increase from the 0 degree in the higher frequencies to show a maximum value of 70 degrees at around $10^2$ Hz. After reaching the maximum value, the $\theta$ starts to decrease but it starts to increase again at 100 Hz. When the immersion duration becomes longer, the maximum value at $10^3$ Hz becomes smaller, while hardly any change was found in the phase angle $\theta$ in the lower frequencies than 100 Hz.

The duplex stainless steels UNS S31803 and UNS S32750 as well as the UNS S39274 showed almost identical spectrums change over time. Fig. 3 shows the spectrum of UNS S39274. The constant $Z$ value equivalent to the solution resistance in the higher frequencies was shown and the $Z$ value increased with the elongation of the immersion time. With the decrease of the frequencies, the $Z$ value increased and a breakpoint at around $10^1$ Hz was seen. Its position was seen to have shift to the lower frequencies compared to that of UNS S31600. The phase angle $\theta$ has the maximum value of 75 degrees at $10^1$ Hz. After reaching the maximum value, it lowered down to $10^{-1}$ Hz and started increasing again slightly at the point below $10^{-1}$ Hz. When the immersion time extended longer, the phase angle became smaller in all the frequency ranges.

![Fig. 2](image1.png) **Bode plots of impedance spectra for UNS S31600 in soy sauce at 368 K.**

![Fig. 3](image2.png) **Bode plots of impedance spectra for UNS S39274 in soy sauce at 368 K.**
3.3 Equivalent Circuit Analysis

When a reaction is taking place at the electrode/electrolyte interface covered with films such as passive films, the equivalent circuit can be obtained by studying the passive films under the polarization of Fe [13], Ti [14] and Ag [15]. According to these, $R_{\text{sol}}$ is the sum of the solution resistance and measured circuit resistance of device. An electric double layer capacitance $C_{\text{dl}}$ is found at the electrode interface, namely, films/solution interface, if any reaction occurs at this interface including a charge transfer, its reaction resistance $R_{c}$ will be connected to $C_{\text{dl}}$ in parallel. Moreover, as oxide films generally have semi conducting properties, there exist a film capacitance $C_{f}$, which includes space-charge layer capacitance, which lies between the electrolyte/film interface and the interior of the film, as well as adsorption ion capacitance. There is a charge transfer resistance $R_{f}$ passing through this range, and thus the equivalent circuit in the surface range consists in the parallel circuits of $C_{f}$ and $R_{f}$.

In order to analyze the impedance characteristics obtained in this study, this analysis adopted the equivalent circuit of the above passive films and used the electrical equivalent circuit at the interface of electrodes covered with films [16-18]. Namely, this analysis devised an equivalent circuit [12, 19-21] having an arrangement of $R_{2}$ which is the oxide film resistance to form electrochemical impedance characteristics in soy sauce obtained in the section 3.2 and its electrical capacitance $C_{1}$ as well as charge transfer resistance $R_{3}$, electrical double layer capacitance $C_{2}$ and the soy solution resistance $R_{1}$. Fig. 4 shows such an equivalent circuit. Here, the array of $C_{1}$, $R_{2}$ and $C_{2}$, $R_{3}$ is the opposite to that of the aforementioned passive films of the polarized electrode system. It was reversed the array on the assumption that the passive films in natural immersion might be an ion conductor [19, 21].

Using this equivalent circuit ran the simulation on the impedance data obtained in the experiment. Since the capacitive semicircle of a condenser element tends to deform from the true circle in a condenser element, constant phase element (CPE) [21] was employed. In this equivalent circuit, a difference occurred from the measured values in the higher frequency range of $10^4$ to $10^5$ Hz. The simulation curve agreed fairly well with the experimental data when a coil (inductance) was connected in series with $R_{1}$. All the impedance spectra coincided fairly well. As an example of the simulation, Fig. 5 shows a Bode plot (a) and a Nyquist plot (b) of the simulation. In both plots, the simulation curves were corresponding to the experimental data well. As described section 3.1, the surface of all specimens after immersion test was observed none of the trace for corrosion. This means that an ideal passivation phenomenon is taking place in all the stainless steels in soy sauce, which can be shown in the equivalent circuit on a metallic surface with a protective film. Therefore, the obtained impedance data was fitted to the equivalent circuit with the coil connected as shown in Fig. 4 and the parameters of $R_{1}$, $R_{2}$ and $R_{3}$, as well as $C_{1}$ and $C_{2}$ were get for all specimens. The measured cell inductance, which was about $2.0 \times 10^{-6}$ H at the start of the test, gradually became smaller with the

\[ R_{1} : \text{Solution resistance} \]
\[ R_{2} : \text{Resistance of passive films} \]
\[ R_{3} : \text{Charge transfer resistance} \]
\[ C_{1} : \text{Capacitance of passive films with CPE} \]
\[ C_{2} : \text{Double layer capacitance with CPE} \]

Fig. 4  Diagram of electric equivalent circuit for stainless steels in soy sauce.
immersion time. It became about 0 H a month later.

Table 1 shows the impedance parameter obtained with the electric equivalent circuit on the electrode/electrolyte interface for various stainless steels with which it immersed for one month in soy sauce at 368 K.

The soy sauce solution resistance, which was about 0.5 $\Omega \cdot \text{cm}^2$ at the early time of the immersion, gradually increased with the immersion and it was about 4.0 $\Omega \cdot \text{cm}^2$ a month later. This was probably due to that either certain deterioration in the soy sauce component took place or the soy sauce component became deposited on the specimen surface of 368 K.

$R_2$ shows each resistance of the passive film formed in the soy sauce for all stainless steels. The austenitic stainless steels showed a low electric resistance of the order of $10^3 \, \Omega \cdot \text{cm}^2$ during the immersion, while that of UNS S31600 was stable, and that of UNS S30400 fluctuated considerably. The duplex stainless steels showed a stable resistance value of the order of $10^4 \, \Omega \cdot \text{cm}^2$ during the whole immersion test.

The parameter $R_3$ corresponds to the reaction resistance value (corrosion resistance value) concerned with the dissolution of metallic materials in the soy sauce. The reciprocal of this corrosion resistance value is proportional to each the corrosion current, and the steel that has the excellent corrosion resistance is proportional to the corrosion resistance. The value of UNS S30400 gradually decreased after undergoing a wide variation during the immersion period, while that of UNS S31600 remained stable at $10^2 \, \Omega \cdot \text{cm}^2$. The value of the duplex stainless steels remained at the

<table>
<thead>
<tr>
<th>Impedance parameter</th>
<th>Materials</th>
<th>S30400</th>
<th>S31600</th>
<th>S31803</th>
<th>S32750</th>
<th>S39274</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$ (W-cm)</td>
<td>Initial</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1 month</td>
<td>4.2</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5.5</td>
</tr>
<tr>
<td>$R_2$ (kJl-cm$^2$)</td>
<td>Initial</td>
<td>0.7</td>
<td>1</td>
<td>4</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1 month</td>
<td>2~20</td>
<td>1~4</td>
<td>8~20</td>
<td>9</td>
<td>9~10</td>
</tr>
<tr>
<td>$R_3$ (W-cm$^2$)</td>
<td>Initial</td>
<td>50</td>
<td>50</td>
<td>500</td>
<td>900</td>
<td>1,000</td>
</tr>
<tr>
<td></td>
<td>1 month</td>
<td>1~50</td>
<td>50</td>
<td>500</td>
<td>700</td>
<td>1,000</td>
</tr>
<tr>
<td>$1/C_1$ (mF-cm$^3$)</td>
<td>Initial</td>
<td>0.1</td>
<td>0.2</td>
<td>0.25</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1 month</td>
<td>0.13</td>
<td>0.32</td>
<td>0.3</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>$C_2$ (mF-cm$^2$)</td>
<td>Initial</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>1 month</td>
<td>0.35~32</td>
<td>1.3</td>
<td>0.5</td>
<td>0.42</td>
<td>0.38</td>
</tr>
</tbody>
</table>
steady state value of $10^3 \ \Omega \cdot \text{cm}^2$ for the duration of the immersion. When compared the corrosion resistance values of the austenitic stainless steels to those of the duplex stainless steels, the latter ones were 10 times higher than the former ones showing clearly that the duplex stainless steels were superior in corrosion resistance to the austenitic stainless steels in soy sauce.

$C_1$ shows the electrical capacitance of the films to be formed in soy sauce. The reciprocal of $C_1$ is said to be proportional to the thickness of the formed films [20]. UNS S30400 showed a considerable variation. The values of other specimens remained relatively stable.

When it is assumed that a film is formed with the same kind of composition and similar electrical properties, its thickness is apparently like; UNS S39274 < UNS S31803 < UNS S32750 = UNS S31600 < UNS S30400.

For the change over time of $C_2$ corresponds to electrical double layer capacitance. UNS S30400 showed an exorbitantly deviated value in the change over time of $C_2$ in 10 to 20 days after the immersion. The reason why is not clear. The electrical capacitance of other samples showed stable values for the duration of the test, except UNS S32750 whose value considerably varied immediately after the immersion. All specimens were stable, however, in the order of 500 $\mu \F \cdot \text{cm}^2$ from the 15th day onward.

3.4 In-depth Analysis of a Film

Fig. 6 shows an in-depth profile of the elements contained in the corrosion product films (passive films) formed in soy sauce after tested. The elements subjected to analysis are Cr2p, Ni2p, Fe2p, Mo3d and W4f, which are contained in respective types of stainless steels. Fig. 6 also shows O1s as a corrosion product. The sputtering time ($t_s$) in Fig. 6 shows the in-depth direction from the outermost surface of the specimens. Its absolute depth, however, is unknown.

For the distribution of Cr2p, Cr concentration increased at around the surface layer except UNS S30400 and Cr concentration in its vicinity was distributed in the depth direction in order of UNS S39274 < UNS S32750 < UNS S31803 < UNS S31600.

Thus it can be seen that UNS S39274 had the highest Cr concentration at the surface layer, while in UNS S30400 Cr was more distributed in the middle layer than in that of the Meanwhile, for the distribution of
Fe2p, the concentration of Fe increased inversely in response to this Cr distribution from around the outermost surface in order of UNS S39274 < UNS S32750 < UNS S31803 < UNS S31600. For the distribution of Cr2p, Cr concentration increased at around the surface layer except UNS S30400 and Cr concentration in its vicinity was distributed in the depth direction in order of UNS S39274 < UNS S32750 < UNS S31803 < UNS S31600.

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Then, for the distribution of Ni2p, hardly any Ni was found in the outermost surfaces of all specimens and it was distributed in UNS S39274 and UNS S32750 at a depth of around 2 min and at a deeper depth than 2 min in UNS S31803 and UNS S31600. In the particular case of UNS S30400, a strikingly high Ni concentration is found at the middle layer of 4 min. It can be seen that the distribution of this Ni concentration agrees with that of Cr as well as that of the lower part of Fe concentration. It was seen that those of Mo3d and W4f increased moderately from the surface layer to the depth direction.

As above, the Cr distribution fairly matches the O distribution, and the Fe shows an inverse result. The factor of these tendencies for various distributions is considered the effect of alloy element. In stainless steel, Cr is concentrated in passivation film on the surface of the metal by selective dissolved of steel, and thus stainless steel has excellent corrosion resistance [22]. Especially, Cr is alloy component to have localized corrosion inhibitor in the presence of activated dissolution in acid solution and chloride ion [22]. It has been known that in solution around pH-neutrality, Cr in alloy easily passivates due to oxidizing action of H+ ions or dissolved oxygen, forms CrOOH coating on the metal surface, and improves corrosion resistance [22]. When the passive films were formed on the metal surface by selective dissolved of Fe in soy sauce, Cr and O was concentrated at the surface layer of metal. The Cr distribution fairly matched the O distribution, and the Fe showed an inverse result. The dissolution of UNS S30400 was most advanced with the Cr concentration occurring in the depth in a similar manner to the Ni distribution. It is understood that the amount of Fe has decreased due to its elution. The dissolution progresses was in order of UNS S30400 > S31600 > S31803 > S32750 > S39274, and the thickness of the respective passive films increased. For this tendency of distribution, it is considered that UNS S30400 is not contained Mo in alloy. It has been known that Mo in alloy has excellent corrosion resistance in
hydrogen chloride and chloride solution without an oxidizer [23], and Mo in alloy forms film such as MoOCl₂ [24]. It is considered that Mo in alloy indicates the effect of the corrosion resistance in soy sauce.

On the other hand, it is known that Ni in alloy contained in UNS S30400, passivates in acid and alkaline environment, forms Fe(OH)₂ or NiOOH coating on the metal surface, and improves corrosion resistance [25]. The impedance parameter of UNS S30400 fluctuated considerably in Table 1. It is considered that the factor of fluctuations is the effect of dissolution of the passive film to form by Ni in soy sauce.

3.5 Passivation Phenomenon

Fig. 7 shows the relationship between puttering time $t_c$ with the highest Cr distribution in Fig. 6 and the impedance parameters of $R$ and $C$. When the thickness of passive film is increased, $R_2$ and $R_3$ value decreased, $C_1$ and $C_2$ were stable.

Meanwhile, Fig. 8 shows the relationship between the content ratio of Cr, Ni, and Mo in the film and the chemical composition of the substrate materials. In Fig. 8, it is obtained the content ratio of the respective elements in $t_c$ same as Fig. 7 and expressed it in percentage. The straight line with a 45-degree angle shows that the ratio between the content and the chemical composition in the passive film is 1:1. Cr amount in the passive film was 2 times more concentrated than the composition of the substrate materials. It showed that the ratio between Ni and Mo was almost 1 to 1. It is considered that the soundness passive film is formed in all the stainless steels in soy sauce at the point of the highest Cr distribution. As above, it is suggested that the Cr is most influence element to improve corrosion resistance in the alloy element of stainless steel in soy sauce.

From the observation of Fig. 6, the XPS analysis of the passive film generated in 368 K in soy sauce clearly shows that Cr distribution differs according to the types of stainless steels. In Table 1, with an increase of $R_2$ and $R_3$, the Cr concentration at the outermost surface of the film became narrower and denser. When the Cr concentration at the outermost surface of the film becomes less dense, it tends to extend its distribution in the depth direction. Namely, it is reasonable to think that UNS S39274 with a high local Cr concentration at the outermost surface was the most excellent in corrosion resistance. As such, only its surface was dissolved, allowing the formation of a passive film. With the deterioration of the corrosion resistance, the Cr distribution extended in the depth direction, which seemed to be a result of the progress of dissolution. The dissolution progress was in order of UNS S31600 > UNS S31803 > UNS S32750 > UNS S39274, and the thickness of the respective passive films increases with the dissolution progress. The Cr distribution fairly...
matched the O distribution, and the Fe showed an inverse result. As above, the dissolution of UNS S30400 is most advanced with the Cr concentration occurring in the depth in a similar manner to the Ni distribution. It is understood that the amount of Fe had decreased due to its elution. It is considered that the deference of dissolution between the austenitic stainless steel (UNS S30400, S31600) and the duplex stainless steel (UNS S31803, S32750, S39274) is effect by the amount of Cr in alloy. As above, it is considered that Cr improves corrosion resistance in soy sauce. The deference between UNS S31803 and S32750 is considered by the amount of Cr and Mo in alloy, the respective amount of Cr and Mo in UNS S32750 is bigger more than those of UNS S31803. For UNS 32750 and S39274, the amount of Mo in UNS S32750 is higher than UNS S39274. Thus, although it is considered that the ratio of dissolution for UNS S32750 is lower than that of UNS S39274, namely, UNS S32750 has superior corrosion resistance. However, its result was revised between UNS S32750 and S39274. For this reason, it is considered that Mo has little effect on the corrosion resistance, or W in alloy, which UNS S32750 does not contain, affect on the corrosion resistance. On the one hand, it is known that in an acidic aqueous solution, W in alloy continuously forms oxide films such as $W \rightarrow WO_2 \rightarrow W_2O_5 \rightarrow WO_3$, due to electrochemical oxidation or oxidation by an oxidizer, thus exhibiting excellent corrosion resistance [26, 27]. Additionally, according to the report by Ogawa [28] et al., similar to Cr, and Mo, W is effective in increasing corrosion resistance in soy sauce environment.

The reciprocal of electrical capacitance of $C_1$ is said to be proportional to the thickness of a film when it is electrically analogous [12], which agreed with this experimental result. The XPS profiles of this study showed, however, that the more corrosion resistant was the surface, the thinner was the thickness of the passive film. It is suggested that the electrochemical properties of the passive film is different and prove to be right for

the assumption that the passive films in natural immersion might be an ion conductor for equivalent circuit as mentioned in section 3.2.

Fig. 9 shows the relationship between the amount of elements contained in the passive films and $R_2$ as well as $R_3$. The Cr content hardly changes irrespective of the type of stainless steels. In those films with high $R_2$ and $R_3$, there is a tendency that fewer Ni and more Fe are found. This means that when a passive film is formed, a film with higher corrosion resistance is not likely to be affected any more by corrosion, while that with lesser corrosion resistance exhibits progress of dissolution and elution of Fe component, and increasing the Ni proportion as a result.

From the above, it can be concluded that when the high local Cr concentration is generated at the outermost surface thus leading to the increase of the film resistance value, its corrosion resistance is enhanced, or that is, the corrosion current becomes smaller and corrosion resistance is heightened.

4. Conclusions

The electrochemical impedance characteristics of various stainless steels immersed in soy sauce and the element distribution in a passive film through the XPS analysis were evaluated in this study. It is analyzed the
obtained impedance spectra of the passive films using the equivalent circuit in order to acquire their film resistance and electrical capacitance as well as the corrosion resistance and electrical double layer capacitance on the metallic interface. As a result, the conclusions may be drawn:

An electric equivalent circuit concerning the interface of the electrode and electrolyte in the soy sauce is shown in the series circuit where two parallel circuits of resistance of passive film and the electrical double layer capacitance had been combined.

The resistance of passive film and the corrosion resistance values of duplex stainless steels are 10 times higher than that of the austenitic stainless steels, and the duplex stainless steels are superior in corrosion resistance to the austenitic stainless steels in soy sauce.

It is said that the reciprocal of electrical capacitance of a film is proportional to the thickness of the film when it is electrically analogous. The XPS analysis, however, shows that the more corrosion resistant is the stainless steel, Cr is concentrated at the outermost surface of the film and the thinner is the thickness of the passive film.

When the high local Cr concentration is generated at the outermost surface of passive firm thus leading to the increase of the film resistance value, its corrosion resistance becomes smaller and corrosion resistance is heightened.

The concentration of Cr around the outermost surface of passive firm is proportional to its film resistance value as well as corrosion resistance value.

From these results, the material used in a high concentration and high temperature sodium chloride environment should use the duplex stainless steels.

References


[17] M. Kissi, M. Bouklan, B. Hammouti, M. Benkaddour, Establishment of equivalent circuit from electrochemical


