Stainless steel, an Fe-based material with a minimum of 11 wt% Cr content, has corrosion resistance, which is attributed to the formation of Cr- and/or Fe-oxide films, so-called passive films, on the surface. The resistance is related to the chemical composition of the film, which is strongly dependent on the chemical composition of the substrate. The pitting resistance equivalent (PRE) number (\(\approx\) wt% Cr + 3.3 (wt% Mo + 0.5 wt% W) + 16 wt% N) has been used to determine the localized corrosion resistance of stainless steels.1 The larger the PRE number of stainless steel is, the greater is the resistance to localized corrosion.2 The PRE number is related to the contribution of elements to the resistance of a passive film on stainless steel. Alloying with Cr forms non-crystalline Cr\(_2\)O\(_3\) on stainless steel by a direct reaction of Cr with H\(_2\)O and improves the passivation of the stainless steel.3 Alloying with W inhibits localized corrosion by forming insoluble WO\(_3\), which enhances the stability of the passive film.4 Alloying with N decreases local pH by decreasing acidity in the resistance to localized corrosion.5

The liquid-phase ion gun (LPIG), a silver microelectrode covered with a silver chloride layer, was cathodically polarized to generate Cl\(^{-}\) in the vicinity of the stainless steel polarized at 0.4 V\(_{\text{SSE}}\). Contact of the stainless steel surface with the Cl\(^{-}\)-concentrated environment by the LPIG operation induced a rapid increase in anodic current flow through the stainless steel electrode after the induction period \(t\) and consumption of the cathodic electric charge \(Q_d\) by the LPIG microelectrode. Numerical modeling using the LPIG microelectrode current for \(t\) gave a critical Cl\(^{-}\) concentration [Cl\(^{-}\)] needed for the initiation of localized corrosion.

These parameters obtained by LPIG tests showed that type 443J1 stainless steel was superior to type 430 stainless steel in localized corrosion resistance. AES depth profiling of the stainless steel surfaces after the LPIG operation revealed enrichment of Cl in the outermost oxide film as well as decreased film thickness. The mechanism of degradation of the stainless steel surface due to contact with the Cl\(^{-}\)-concentrated solution is discussed. The adsorption of Cl\(^{-}\) on the oxide surface is thought to be a trigger of the oxide degradation.

Stainless steel samples with a surface area of 1.0 cm\(^2\) were mounted in epoxy resin, ground mechanically with SiC paper down to 1500 grit, rinsed with distilled water, and used as specimens. The chemical compositions of the stainless steels are shown in Table I. Stainless steel samples with a surface area of 1 cm\(^2\) were mounted in epoxy resin, ground mechanically with SiC paper down to 1500 grit, rinsed with distilled water, and used as substrate electrodes for LPIG-mode SECM.

### Experimental

**Specimens.**—Types 430 and 443J1 ferritic stainless steels were used as specimens. The chemical compositions of the stainless steels are shown in Table I. Stainless steel samples with a surface area of 1 cm\(^2\) were mounted in epoxy resin, ground mechanically with SiC paper down to 1500 grit, rinsed with distilled water, and used as substrate electrodes for LPIG-mode SECM.

<table>
<thead>
<tr>
<th>Type</th>
<th>Cr</th>
<th>Ti</th>
<th>Cu</th>
<th>C</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
<td>0.03</td>
<td>bal.</td>
</tr>
<tr>
<td>443J1</td>
<td>21</td>
<td>0.3</td>
<td>0.4</td>
<td>0.01</td>
<td>0.01</td>
<td>bal.</td>
</tr>
</tbody>
</table>

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Stainless steel samples with a surface area of 1 cm\(^2\) were mounted in epoxy resin, ground mechanically with SiC paper down to 1500 grit, rinsed with distilled water, and used as substrate electrodes for LPIG-mode SECM.

**Table I. Chemical compositions of stainless steels used (wt%).**
Potentiodynamic polarization.—Potentiodynamic polarization of the stainless steel electrode was performed from a less noble potential than the corrosion potential by −0.05 V to a noble potential at a scan rate of 1 mV s⁻¹ in deaerated 0.15 mol dm⁻³ of Na₂SO₄ solution.

LPIG microelectrode.—An LPIG microelectrode for SECM was prepared by a procedure similar to that reported previously.¹¹ A silver wire (AG-401385, Nilaco) with a purity of 99.99% and a diameter of 500 μm was embedded in a glass capillary with an outer diameter of 1 mm using epoxy resin. A cross section of the silver-glass capillary tip was used as a silver microelectrode. After mechanical polishing with SiC papers down to 4000 grit and rinsing with distilled water, the microelectrode was polarized at 0.3 V against an Ag/AgCl/sat. KCl (SSE) reference electrode in 0.1 mol dm⁻³ NaCl solution at room temperature until a cathodic electric charge of 10 mC was consumed.

LPIG set-up.—An LPIG experiment for evaluating localized corrosion of stainless steel was carried out with an SECM set-up similar to that used previously.¹¹ The electrolyte solution used was 0.15 mol dm⁻³ of Na₂SO₄ solution deaerated by bubbling argon gas before measurements at room temperature. An LPIG microelectrode was positioned above the specimen electrode at a distance of 75 μm. The volume of the electrochemical cell was 100 cm³. A platinum counter electrode with a surface area of 4 cm² and an SSE reference electrode were used. A bipotentiostat (HAL-1512 mM2, Hokuto Denko) was used to polarize both the specimen electrode and the LPIG microelectrode and to pass currents through them independently in the following manner. The potential of the LPIG microelectrode, Eₗₕₖ, was initially kept at 0.3 Vₜₚₑₚₑ for 100 s and was then changed to −0.2 Vₜₚₑₚₑ, whereas the potential of the stainless steel electrode, Eₛₛₑ, was controlled at 0.4 Vₜₚₑₚₑ throughout the experiment. The currents flowing through both electrodes were recorded at a rate of 10 Hz. In all electrochemical tests with an LPIG, the reproducibility was checked more than 3 times with different specimens.

Surface analyses.—The surfaces of the stainless steel specimens polarized at 0.4 Vₜₚₑₚₑ for 100 s with or without the LPIG operation were analyzed by Auger electron spectroscopy (AES; JAMP-9500F, JEOL) with a primary electron beam voltage at 10 keV. The specimen was rinsed with Milli-Q water after removing Na₂SO₄ solution. Ar⁺ sputtering at an etching rate of 0.8 nm min⁻¹ equivalent to silica was used for obtaining a depth profile of the local specimen surface with an electron beam diameter of 30 μm.

Numerical modeling.—The concentration distribution of Cl⁻ generated from the LPIG microelectrode against the specimen substrate electrode was simply considered as a diffusion problem with the stainless steel substrate current measured from the LPIG microelectrode in FEM calculation. A cross section of the silver-glass capillary was modeled with finite element modeling (FEM). A commercial FEM solver, COMSOL Multiphysics 5.0, with a transport of diluted species solver, was used for modeling are 9.31 × 10⁻⁹ and 2.03 × 10⁻⁹ m² s⁻¹, respectively.¹⁶ Current transient obtained in the LPIG experiment with the stainless steel was used to define the quantity of Cl⁻ generated from the LPIG microelectrode in FEM calculation.

Results

Electrochemical reaction of a silver microelectrode.—Electrochemistry of a silver microelectrode with or without a silver chloride layer was reported previously.¹¹ Anodic polarization of a silver microelectrode in a chloride-containing solution and cathodic polarization of a silver-silver chloride electrode correspond to the following reactions:¹⁷

$$\text{AgCl} + e^- \rightleftharpoons \text{Ag} + \text{Cl}^-.$$  [3]

The latter reaction, reduction of AgCl, corresponds to generation of Cl⁻ from the LPIG. Although the diameter of the silver microelectrode used in this study was 500 μm, which is 2.8-times larger than that used previously,¹¹ anodic polarization of the LPIG microelectrode charged by the cathodic polarization with a charge of 10 mC could generate and discharge Cl⁻ with an anodic electric charge of 10 mC.

Anodic polarization of stainless steels.—Figure 1 shows polarizations of types 430 and 443J1 stainless steels in 0.15 mol dm⁻³ Na₂SO₄ solution. Corrosion potential of type 443J1 stainless steel is slightly higher than that of type 430 stainless steel due to the higher amount of Cr, which makes the corrosion potential of stainless steel positive.¹⁰ No active-passive transition is observed for the stainless steels, and the anodic current reaches a passive current lower than 4 μA cm⁻² at potentials lower than ca. 0.7 Vₜₚₑₚₑ, implying that the specimen surface is spontaneously passivated before the polarization, probably just after specimen preparation. The passive current of type 430 stainless steel is larger than that of type 443J1 stainless steel, indicating that the passive film formed on type 430 stainless steel is less protective than that formed on type 443J1 stainless steel. At potentials higher than 0.69 Vₜₚₑₚₑ, the anodic current increases and shows a peak at 0.90 Vₜₚₑₚₑ for type 443J1 stainless steel and a peak at 1.09 Vₜₚₑₚₑ for type 430 stainless steel. This is attributed to the trans-passive oxidation of Fe, Cr or Ni in the oxide film and/or stainless steel substrate.¹² At higher potentials, the anodic current shows a trough and increases due to oxygen evolution. In this solution, no localized corrosion occurs on either of the stainless steels.

Current transients of LPIG and stainless steel during LPIG operation.—Figure 2 shows transients of the LPIG current Iₗₕₖ and stainless steel substrate current Iₛₛₑ observed in Na₂SO₄ solution when the LPIG potential Eₗₕₖ was changed from 0.3 to −0.2 Vₜₚₑₚₑ at 100 s while the stainless steel specimen potential Eₛₛₑ was kept at 0.4 Vₜₚₑₚₑ. Before the change of Eₗₕₖ, no anodic current and only a small anodic current flow in the LPIG electrode and specimen electrode, respectively, indicating that the LPIG is in a standby to generate Cl⁻ and that the specimen surface is in a passive state. The Iₛₛₑ at 100 s for type 430 stainless steel is larger than that for type 443J1 stainless steel. After the change of Eₗₕₖ at 100 s, Iₛₛₑ becomes larger because of the generation of Cl⁻. A larger anodic current also starts to flow on stainless steel.
steel specimens. Furthermore, a slightly larger anodic current starts to flow on type 430 stainless steel at 0.72 s after the change of $E_{LPIG}$ ($t = 100.72$ s). Increases in anodic current depending on the type of stainless steel should be correlated with some anodic processes on stainless steel and the operation of LPIG. Although non-faradaic processes including change in electric conductivity and/or capacitance in the interelectrode space due to the Cl$^-$-concentrated environment and/or reorganization of the surface and double layer might be related to the increase in anodic current of the steel, it would be negligible because of the small time constant of the process. Meanwhile, strong dependency of the slightly increased current on the type of steel suggests that some faradaic processes should occur on the stainless steel surface. Degradation of the film is one of the processes and probably competes with the passivity-maintaining process of the surface. In the case of application of an LPIG to passivated pure iron in neutral solution,\textsuperscript{11,12} dissolution of Fe(III) species from the passive film was observed during the initiation of film breakdown by concentrated Cl$^-$ from the LPIG. Fe(III) species diffused to the LPIG were reduced and the so-called feedback phenomenon, repetition of the redox reaction of Fe(III) and Fe(II) between the microelectrode and degrading surface, occurred. If film degradation is initiated on the stainless steel surface due to the concentration of Cl$^-$, some alloying elements in the stainless steel might dissolve. However, the difference in $I_{SS}$ on type 430 stainless steel in Na$_2$SO$_4$ solution is ca. 0.01 mA, which is significantly smaller than that in $I_{LPIG}$, ca. 0.2 mA. Therefore, little feedback of the redox reaction between Fe(III) and Fe(II) species is occurred on stainless steel in this study. Following the slight increase in current of type 430 stainless steel by the LPIG operation, on the other hand, $I_{SS}$ rapidly increases at 12 s after the change of $E_{LPIG}$ change ($t = 112$ s). Type 443J1 stainless steel suddenly allows an increase in anodic current flow at 39 s after the change of $E_{LPIG}$ ($t = 139$ s). These large values of $I_{SS}$ of the specimen electrodes imply the initiation and/or propagation of localized corrosion on stainless steel. In any case, it is considered that the time $t_d$ from the change of $E_{LPIG}$ to the rapid increase in $I_{SS}$ corresponds to an induction period for the initiation of localized corrosion due to the LPIG operation. Additionally, the cathodic electric charge $Q_d$ consumed by the LPIG electrode for $t_d$ is considered to be the amount of Cl$^-$ needed for the initiation of the corrosion. The relations between those parameters concerning the initiation of localized corrosion of stainless steel are discussed later.

**Parameters of localized corrosion initiation of stainless steels.—** Table II shows parameters of localized corrosion initiation obtained by the LPIG test, including the induction time $t_d$, cathodic electric charge $Q_d$, and concentration of chloride ions [Cl$^-_d$] for initiation of localized corrosion obtained from the LPIG test and numerical modeling in 0.15 mol dm$^{-3}$ Na$_2$SO$_4$ solution.

<table>
<thead>
<tr>
<th>Type</th>
<th>$t_d$ / s</th>
<th>$Q_d$ / mC</th>
<th>[Cl$^-_d$] / mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>430</td>
<td>13 ± 1.1</td>
<td>2.5 ± 0.49</td>
<td>1.3</td>
</tr>
<tr>
<td>443J1</td>
<td>40 ± 8.3</td>
<td>7.0 ± 0.50</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 2. Transients of currents $I_{LPIG}$ and $I_{SS}$ of the LPIG microelectrode and stainless steel substrate electrodes, respectively, in 0.15 mol dm$^{-3}$ of Na$_2$SO$_4$ solution when the electrode potential of the LPIG, $E_{LPIG}$, was changed from 0.3 to −0.2 V$_{SSE}$ while the potential of the stainless steel substrate, $E_{SS}$, was kept at 0.4 V$_{SSE}$.

Figure 3. Change in Cl$^-_d$-concentration [Cl$^-_d$] at the specimen surface calculated numerically from the LPIG current in 0.15 mol dm$^{-3}$ of Na$_2$SO$_4$ solution. [Cl$^-_d$] after commencement of a rapid increase in $I_{SS}$ is plotted by a dashed line.

Figure 4 shows AES depth profiles of specimen surfaces of types 430 and 443J1 stainless steels.
polarized at 0.4 V_{SSB} in Na_2SO_4 solution after the operation of LPIG consuming a cathodic electric charge of 0 or 1 mC. Cl^- concentrations of 0.73 and 0.62 mol dm^{-3} are estimated from Figure 3 for 1 mC consumption of LPIG on types 430 and 443J1 stainless steels, respectively. It is clear from the presence of O with a high atomic concentration that the stainless steel surfaces were covered with oxide films. Assuming that the interface between the oxide film and substrate is located at the transition with a half of the atomic concentration of O, oxide films of both stainless steels formed at 0.4 VSSE in Na_2SO_4 solution have thicknesses of ca. 3 nm. This is in good agreement with the previously reported thicknesses of 2 to 4 nm for passive films on stainless steels in aqueous solutions. A small amount of S is contained in the outermost film of the stainless steels formed on both specimens, while Cl is only observed in the outermost film after the LPIG operation regardless of steel type. The S and Cl apparently originate from the solution and the LPIG, respectively. It is also clear from a comparison of Figures 4a and 4b and Figures 4c and 4d that thicknesses of passive films were ca. 10% smaller when the LPIG was operated and consumed a cathodic electric charge of 1 mC, indicating that the oxide film on stainless steels is thinned by contact with a Cl^-concentrated environment.

For both stainless steels, the atomic concentrations of Fe and Cr (Figures 5a and 5c) are larger in the oxide film formed with the LPIG operation than in the film formed without the LPIG operation, while the atomic concentration of O (Figures 5b and 5d) in the film with the LPIG operation is smaller than that in the film without the LPIG operation. The atomic concentration of Cl in the unsputtered films on both stainless steels is significantly higher than the detection limit. It is clear that the thickness of the film formed on both stainless steels gradually decreases with increase in the electric charge. Since localized corrosion progressed when the LPIG consumed a charge of 2 mC, the thickness cannot be plotted. However, the slope of type 443J1 stainless steel is gentler than that of type 430 stainless steel, indicating that degradation of the passive film formed on type 430 stainless steel occurs more easily than that of the passive film formed on type 443J1 stainless steel.

**Discussion**

The presence of Cl^- in the solution makes the passive film on stainless steel unstable and eventually results in localized corrosion. The degradation of a passive film has been discussed using three major models concerning the role of Cl^-: (i) The adsorption model is associated with the adsorption of Cl^- on the passive film surface. The adsorbed Cl^- accelerates the transfer of metal cations to the solution by forming a metal cation complex on the film, eventually thinning and removing the film. (ii) In the penetration model, the depassivation of steel is due to the penetration of Cl^- through the film to the steel surface. The absorbed Cl^- introduces higher ionic conductive paths in the film, leading to a rapid transfer of metal cations to the solution. (iii) The breakdown model is related to the mechanical stress accumulating in the film. The adsorption of Cl^- on the passive film reduces surface tension, resulting in mechanical breakdown of the passive film. As a result, degradation of the passive film exposed to the solution containing Cl^- is based on the adsorption of Cl^- on passive film surface. By the way, the PRE number has been used to rate the localized corrosion resistance of stainless steels, while the comparison of PRE number does not provide roles of Cl^- in a degradation of passive film before the initiation of localized corrosion on stainless steel. A more quantitative parameter concerning environmental effects of Cl^- should be used for the discussion. As states above, LPIG tests for types 430 and 443J1 stainless steels were carried out in Na_2SO_4 solution. The tests provided information about the induction process until the initiation of localized corrosion on both types of stainless steel.
It is thought that the values of $t_d$ and $Q_d$ directly reflect the induction process of passive film breakdown and/or localized corrosion. The value of $t_d$ is equivalent to incubation time for localized corrosion and the value of $Q_d$ corresponds to the quantity of $\text{Cl}^-$ needed for initiating localized corrosion. The critical $\text{Cl}^-$-concentration $[\text{Cl}^-]_d$ needed for initiation of localized corrosion was obtained by numerical calculation using LPIG microelectrode current during the induction process. These electrochemical parameters are consistent with expectations obtained from the PRE number of stainless steel. Furthermore, AES analyses of the stainless steel surface following the LPIG operation revealed the existence of Cl on the outermost surface and a decrease in film thickness. This indicates that the adsorption of $\text{Cl}^-$ on the oxide film and degradation of the film are caused by contact of the oxide surface with the $\text{Cl}^-$-concentrated solution by the LPIG operation. The adsorbed $\text{Cl}^-$ might support the transfer of metal cations, mainly $\text{Fe}^{2+}$ and/or $\text{Fe}^{3+}$, in the film to the solution by forming a salt and/or complex on the film. Since solubilities of the salts $\text{FeCl}_2$ and $\text{FeCl}_3$ are 3.94 and 4.77 g, respectively, in 1 dm$^3$ water at 298 K, the salt and/or complex spontaneously dissolves in an aqueous solution, suggesting that the presence of $\text{Cl}^-$ at a high concentration in the solution results in dissolution of the film.

On the other hand, it has been reported that passive films formed on various ferritic stainless steels in aqueous solutions generally have an n-type semiconductive property. Figure 8 shows schematic electron energy diagrams of the degradation process of a passive film during the operation of LPIG. In a solution without $\text{Cl}^-$ (Fig. 8a), an oxide film that is composed of metal cations from the substrate and oxygen anions from the aqueous solution forms on the substrate, and it is subjected to an electric field and limits the anodic current flow. That is, the substrate is in a passive state. When the oxide film is in contact with the $\text{Cl}^-$-concentrated solution by the operation of LPIG (Fig. 8b), however, $\text{Cl}^-$ adsorbs on the film because $\text{Cl}^-$ has about two times higher ability to adsorb on metal cation at film/solution interface than $\text{SO}_4^{2-}$ or $\text{O}_2^{-}\text{.}^{39}$ Salt and/or complex of chlorides forms in the outermost film and support the removal of metal cations in the film, resulting in an increase in the field applied to the film under a...
potentiostatic condition. This process affects further migration of cations and anions in the film. The dissolution of salt/complex competes with the repair of oxide film. In the case in which the dissolution rate is smaller than the repair rate, the film sustains the electric field and limits the current flow as a passive state. However, the film repaired is not completely as same as that before the dissolution. In that case, larger passive current might flow. When the dissolution rate is larger than the repair rate (Fig. 8c), in contrast, the thickness of the oxide film decreases and/or lead to form donor states, which are cation interstitials and/or anion vacancies, in the film. The damaged part experiences a higher electric field than the undamaged part. The migration of both anions and cations in the film is accelerated locally. The bands in the thin film become steep through these processes. Competitive reactions also lead to form surface states at the film/solution interface. They can provide additional paths of electric charge transfer in the space charge layer. When the oxide film allows an extraordinary electron transfer from surface states to the substrate through the conductive path of the oxide film, the dissolution of salt/complex is accelerated more and more since the electric charge transfer is more rapid than the ionic charge transfer for the oxide repair reaction. This process of film degradation corresponds to film breakdown or depassivation and proceeds until the film disappears.

Chromium oxides are superior to iron oxides for corrosion resistance in a Cl−-containing solution. The enrichment of chromium oxides in the oxide film formed on stainless steel improves the localized corrosion resistance. A series of film degradation processes due to Cl− adsorption on the film, i.e., formation of a chloride salt/complex and acceleration of substrate oxidation should be dependent on the concentration of Cr in the oxide film as well as the concentration of Cl− at the film-solution interface. It is implied that the formation of chloride salt/complex is suppressed on chromium-rich oxides or the repair of oxide film is accelerated by portion of Cr content in stainless steel. It was confirmed in this study that the larger portion of Cr and/or the smaller portion of Fe in the oxide film formed on type 443J1 stainless steel than those in the film on type 430 stainless steel provide superior localized corrosion resistance.

Conclusions

Localized corrosion resistance of types 430 and 443J1 ferritic stainless steels polarized at 0.4 VSE in 0.15 mol dm−3 of Na2SO4 solution was evaluated by using the LPIG technique. As the LPIG microelectrode was cathodically polarized to generate Cl−, the localized corrosion was initiated on both stainless steels. AES of stainless steel surfaces following the LPIG test revealed enrichment of Cl in the outermost layer of the oxide film and decreased film thickness due to contact with the Cl−-concentrated solution by the LPIG. Adsorption of Cl− on the oxide film is thought to be a trigger of the dissolution and degradation of the passive film. The parameters obtained by the LPIG test, i.e., induction period τ, cathodic electric charge Qc and critical Cl− concentration [Cl−]c, needed for the initiation of localized corrosion, are closely related to the PRE number of the stainless steel. The LPIG technique, which provides quantitative parameters concerning the role of Cl− during the induction period, is useful for investigating the initiation of localized corrosion of stainless steels.

Acknowledgments

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References