Relationships between Pitting Corrosion Potentials and MnS Dissolution of 5–18 Mass% Cr Steels

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With the increase in the Cr content in the steels, the Cr and Fe concentrations in the inclusions increased and decreased, respectively. The MnS inclusions were found to dissolve in 0.1 M Na2SO4 around 0 V vs. Ag/AgCl (3.33 M KCl). Even though the dissolution potential was independent of Cr concentration, the dissolution morphology was remarkable in that the inclusions in Fe-5Cr dissolved and disappeared. For Fe-12Cr, the Cr-enriched portions remained. In the case of Fe-18Cr, Cr-oxides formed on the inclusion surfaces. The micro-scale polarization was performed in 0.1 M NaCl. At approximately 0.05 V, a large pit was generated at the inclusion of Fe-5Cr, and the inclusion disappeared after polarization. For Fe-12Cr, a stable pit was initiated at 0.13 V, and most of the inclusion remained. No stable pit occurred on Fe-18Cr; however, a meta-stable pitting event was observed in the dissolution potential region of the MnS. Cr and O were detected on the entire surface on the inclusion after polarization. It was suggested that the pitting corrosion resistance at the MnS inclusions of Fe-Cr alloys was related to the inclusion dissolution morphology originating from the difference in the Cr concentration of the inclusions.

The objective of this study is to elucidate the effect of Cr on the pit initiation at MnS inclusions in Fe-Cr alloys. The Cr content in the steel matrix was changed from 5 to 18 mass%, and macro- and micro-scale electrochemical measurements were performed. For spontaneous passivation of Fe-Cr alloys, a minimum Cr content of approximately 12 mass% is known to be required. Fe-5Cr was used as a reference to explore the fraction of Cr in stainless steels. The pitting corrosion resistance was evaluated in 0.1 M NaCl (pH 5.5) and 0.15 M H3BO3-0.0375 M Na2B4O7 boric-borate buffer (pH 8.45) with 0.1 M NaCl because NaCl solutions are usually used for measuring the resistance to pitting corrosion, and also the passivation behavior of steels has been widely studied in boric-borate buffer solutions. The dissolution behavior of MnS inclusions were determined in 0.1 M Na2SO4 (pH 5.8) and the boric-borate buffer solution without NaCl. Chloride-free solutions are required for assessing the anodic dissolution potential of MnS. We focused on the dissolution potential of MnS inclusions, and the relationship between pitting potential and MnS dissolution was examined.

Experimental

Specimens and electrolytes.—Three Fe-Cr alloys were made by vacuum induction melting (50-kg ingot). The chemical compositions of these steels are shown in Table I. To form MnS inclusions, Mn and S were added. The ingots of these steels were hot-rolled to an approximately 70% reduction in thickness, and the steel plates were cut into 15 mm × 25 mm × 3 mm. The specimens were heat-treated at 1123 K for 0.6 ks, and then water-quenched. Before taking any electrochemical measurements, the specimen surfaces were mechanically ground with SiC paper through a 1500 grit and polished down to 1 μm with a diamond paste. Finally, the specimens were cleaned ultrasonically with ethanol. Because non-metallic inclusions are darker in color under an optical microscope than the steel matrix, they are clearly visible in the as-polished condition without etching.

Polarization measurements were performed in 0.1 M NaCl and 0.1 M Na2SO4 solutions. In addition to these solutions, 0.15 M H3BO3-0.0375 M Na2B4O7 boric-borate buffer solutions (pH 8.45) with and without 0.1 M NaCl were used. In the case of the NaCl-containing buffer solution, NaCl was added to 0.15 M H3BO3-0.0375 M Na2B4O7 buffer solution. For 0.1 M NaCl and 0.1 M Na2SO4 solutions, no adjustment of pH values was performed, and the pH values of 0.1 M NaCl and 0.1 M Na2SO4 were 5.5 and 5.8, respectively. The electrolytes were prepared from deionized water and analytical grade chemicals. All measurements were conducted at 298 K under naturally aerated conditions. Temperature was controlled by a water bath.

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Conventional electrochemical measurements were conducted on a working electrode with a surface area of approximately 10 mm × 10 mm. The electrode area was accurately measured by means of a Vernier caliper after polarization measurements. With the exception of the electrode area, the surfaces of the samples were covered with an epoxy resin and subsequently with paraffin. The potential scan rate was 3.8 × 10^{-4} V \text{s}^{-1} (23 \text{mV} \text{min}^{-1}). All potentials cited in this paper are expressed with respect to the Ag/AgCl (3.33 M KCl) electrode (0.206 V vs. standard hydrogen electrode at 298 K).

**Micro-scale polarization measurements.**—To analyze the effect of Cr addition on the polarization behavior of a small area containing MnS inclusions, the specimen surfaces were masked using a vinyl copolymerized resin. The size of the electrode area was approximately 100 \mu m × 100 \mu m and measured using an optical microscope equipped with an image analysis system. After polarization, the measured current values were converted to current densities. A small acrylic cell was put on the masked specimen to preserve the solution. A small Ag/AgCl reference electrode and a Pt wire counter electrode were set in the acrylic cell. The micro-scale polarization measurements were carried out with a battery-powered potentiostat \cite{21} to control the electrode potential of the micro-scale electrode area. Potentiodynamic measurements were conducted at the same scan rate that was used in the macro-scale polarization measurements (3.8 × 10^{-4} V \text{s}^{-1}). The current signals were measured using an AD-converter with a time interval of 0.5 s, which was the average value of 100 points sampled at 1000 Hz. Details of the experimental setup have been described elsewhere.\cite{21} The micro-scale polarization measurements for each steel were performed at least three times for reproducibility.

**Surface characterization.**—Before and after polarization, the electrode surfaces were observed by an optical microscope (OM) and a confocal laser scanning microscope (CLSM). A field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system was employed to observe and analyze the specimen surfaces. SEM images and EDS data were obtained at an electron accelerating voltage of 20 kV.

### Results and Discussion

#### Inclusion compositions and pitting corrosion resistance.**—The morphology and composition of the inclusions were characterized first. Figure 1 shows the optical microscope (OM) images of the specimen surfaces after polishing without any etching treatment. The small black spots with diameters of less than 5 \mu m were determined to be inclusions. Figure 2 shows the SEM images and the corresponding EDS maps of the inclusions. For all steels, even though small amounts of Cr and O were detected (Si was also detected in the inclusion of Fe-5Cr), the inclusions clearly contain large amounts of both Mn and S. The results of the EDS analysis at points 1, 2, and 3 shown in Figure 1 are provided in Table II. In the EDS analysis, the signals of Mn, S, Cr, O, Si, Al, Fe, and Ni were measured, and their relative concentrations were calculated. At points 1, 2, and 3, the atomic ratios of Mn/S were approximately 1:1, indicating that typical MnS inclusions were formed in the Fe-Cr alloys.

![Figure 1. Optical microscopy images of the as-polished specimen surfaces: (a) Fe-5Cr, (b) Fe-12Cr, and (c) Fe-18Cr.](image)

The five different inclusions for each steel were analyzed by EDS to analyze the effect of Cr content in the steel matrixes on the compositions of the inclusions. The EDS point analysis was performed at the center of the inclusions. Figures 3a and 3b summarizes the Cr and Fe concentrations of the inclusions, respectively. In these figures, the average values and error values (maximum and minimum) were plotted. As seen in Figures 3a and 3b, the Cr concentration in the inclusions increased with the Cr content in the steel matrixes. In contrast, the Fe concentration decreased with the Cr content in the steels. It was suggested that the solubility of Cr in the MnS inclusions increases with Cr content in the steels.\cite{22} Figure 3c indicates the atomic ratio of Mn/S in the inclusions. This ratio is almost independent of the Cr content in the steels, with a ratio of approximately 1, even though the Cr and Fe concentrations in the inclusions depend on the Cr content in the steels. MnS has been reported to have Cr and Fe solubility,\cite{22} suggesting the inclusions should be accurately written as (Mn,Cr,Fe)S. For simplicity, the inclusion investigated in this study is expressed as MnS.

To confirm the effect of the Cr content in the steel matrixes on corrosion resistance in chloride environments, polarization was carried out. Figure 4a shows the macro-scale polarization curves for Fe-5Cr, Fe-12Cr, and Fe-18Cr in the 0.1 M NaCl solution. To plot the potentiodynamic polarization for all steels, the cathodic currents were measured initially, and then the anodic currents were measured. The corrosion potential in the potentiodynamic polarization curve for Fe-5Cr is lower than those of Fe-12Cr and Fe-18Cr. For Fe-5Cr, a large current increase was observed above the corrosion potential. This is likely due to the active dissolution of the steel matrix. In contrast, a passive region with many current oscillations appeared on Fe-12Cr and Fe-18Cr above the corrosion potential. After these meta-stable pitting events, a large current increase was generated. The onset potentials of the large anodic current increasing for Fe-5Cr, Fe-12Cr, and Fe-18Cr were measured at approximately −0.3, 0.15, and 0.3 V, respectively. Figures 4b, 4c, and 4d exhibits the OM images of the electrode surfaces after polarization. For Fe-5Cr, a large round-shaped

### Table I. Chemical compositions of steels (mass%).

|        | C     | Si    | Mn    | P    | S    | Ni    | Cr    |
|--------|-------|-------|-------|------|------|-------|-------|
| Fe-5Cr | 0.0016| 0.29  | 0.91  | 0.018| 0.027| <0.001| 5.0   |
| Fe-12Cr| 0.0012| 0.29  | 0.89  | 0.018| 0.027| <0.001| 12.0  |
| Fe-18Cr| 0.0007| 0.28  | 0.91  | 0.018| 0.027| <0.001| 18.0  |

|        | Mo   | Cu    | Al    | O    | N    |
|--------|------|-------|-------|------|------|
| Fe-5Cr | <0.001| <0.001| 0.001 | 0.0017| 0.0043|
| Fe-12Cr| <0.001| <0.001| <0.001| 0.0020| 0.0046|
| Fe-18Cr| <0.001| <0.001| <0.001| 0.0030| 0.0088|

### Table II. Relative compositions (at.%) of points 1–3 shown in Figure 2.

| Point | Mn | S | Cr | O | Si | Al | Fe | Ni |
|-------|----|---|----|---|----|----|----|----|
| 1     | 39 | 37| 2  | <1| <1 | <1 | 21 | <1 |
| 2     | 45 | 39| 3  | <1| <1 | <1 | 11 | <1 |
| 3     | 46 | 41| 7  | 1 | <1 | <1 | 5  | <1 |
dissolved area (ca. 100 μm in diameter) was observed. In contrast, small pits with a diameter less than 30 μm were generated on Fe-12Cr and Fe-18Cr. In the case of Fe-18Cr, a lacy cover remained over the pit mouth. The Cr addition to steels has been confirmed to improve the localized corrosion resistance of Fe-Cr alloy in 0.1 M NaCl, and the corrosion morphology changes from localized active dissolution to pitting when the Cr content in the steels exceeds 12 mass%.

Chloride ions and pH are important parameters affecting the corrosion behavior of Fe-Cr alloys. It is well-known that chloride ions cause pitting on passive steels and that the stability of passivity increases with pH. Polarization measurements were carried out in the 0.1 M Na2SO4 solution (pH 5.8) and boric-borate buffer solutions (pH 8.45) with and without 0.1 M NaCl. The 0.1 M Na2SO4 solution was used as an example of chloride-free solutions: the pH of this solution was almost the same as the pH of the 0.1 M NaCl (pH 5.5) solution. The boric-borate buffer solutions with and without 0.1 M NaCl were used to estimate the effect of pH on polarization behavior.

Figure 5a shows the macro-scale polarization behavior for Fe-5Cr. The polarization curve in 0.1 M NaCl shown in Figure 4 is presented again as a reference. In 0.1 M Na2SO4, a sharp increase in anodic current density was measured at −0.3 V just above the corrosion potential in potentiodynamic polarization. Figure 5b shows the OM image of the electrode surface after polarization in 0.1 M Na2SO4. In this case, no pit was observed although local dissolution, like the dissolution in 0.1 M NaCl (see Figure 4b), was generated. As Figure 5a shows, the onset potential of large current increase in 0.1 M NaCl is the same as that in 0.1 M Na2SO4, implying that the large current increase observed at −0.3 V in 0.1 M NaCl was due to the initiation of local active dissolution and not to pitting. In the case of low-Cr steels such as Fe-5Cr, it was proposed that localized corrosion readily occurs as local depassivation even in near-neutral pH solutions regardless of the existence of chloride ions.

In the boric-borate buffer solution without NaCl, the steel surface was well passivated, and no pitting was observed. The large increase in current density above 1.0 V is due to the evolution of O2. In the boric-borate buffer solution with 0.1 M NaCl, a sharp increase in current density was measured at −0.06 V. Figure 5c shows the OM image of the electrode surface after the polarization in the boric-borate buffer solution with 0.1 M NaCl. Small pits were observed on the electrode surface after polarization although local active dissolution was generated around the pits. The large current increase at −0.06 V in the boric-borate buffer solution with 0.1 M NaCl is confirmed to originate from pit initiation.
Figure 4. (a) Macro-scale polarization curves for Fe-5Cr, Fe-12Cr, and Fe-18Cr in 0.1 M NaCl at 298 K. Optical microscopy images of the corrosion morphology generated during the anodic polarization: (b) Fe-5Cr, (c) Fe-12Cr, and (d) Fe-18Cr.

Figure 5. (a) Macro-scale polarization curves for Fe-5Cr in 0.1 M NaCl, 0.1 M Na₂SO₄, and 0.15 M H₃BO₃-0.0375 M Na₂B₄O₇ with and without 0.1 M NaCl. Optical microscopy images of the corrosion morphology generated during the anodic polarization: (b) 0.1 M Na₂SO₄ and (c) 0.15 M H₃BO₃-0.0375 M Na₂B₄O₇ with 0.1 M NaCl.

In the boric-borate buffer solution with 0.1 M NaCl (Figures 5 and 6), the pitting potentials for Fe-5Cr, Fe-12Cr, and Fe-18Cr were determined at approximately -0.06, 0.23, and 0.39 V, respectively. The pitting potential of Fe-Cr alloys is confirmed to increase with the Cr content in the steels. In Figures 5 and 6, small current peaks were observed at approximately 0 V in 0.1 M Na₂SO₄ and 0.15 M H₃BO₃-0.0375 M Na₂B₄O₇. These current peaks are assumed to originate from MnS dissolution, as explained in the next section.

Dissolution potentials of the MnS.—The first step in elucidating the mechanism of pit initiation at MnS inclusions is to determine the dissolution potentials of the inclusions in 0.1 M Na₂SO₄. Although local active dissolution was generated during the macro-scale polarization of Fe-5Cr in 0.1 M Na₂SO₄, NaCl solutions with near-neutral pH are commonly used in evaluating the pitting corrosion resistance of steels. For this reason, potentiodynamic polarization was performed in 0.1 M Na₂SO₄.

Figure 7a shows the micro-scale polarization curves for a small area with the MnS inclusion in Fe-5Cr in the 0.1 M Na₂SO₄ solution. Figures 7b–7e indicates the CLSM reflectance images of the MnS inclusion and surrounding area before and after polarization. In the case of Fe-5Cr, two current peaks were observed at approximately...
0 V in preliminary research. Thus, potentiodynamic polarization was stopped at $-0.10 \text{ V}$ (specimen A) and $0.18 \text{ V}$ (specimen B). For specimen A, the comparison of the images before and after polarization (Figures 7b and 7c) indicates that little or no dissolution occurred on the inclusion surface. Figure 8a shows the SEM image and the corresponding EDS maps of the inclusions in the micro-scale electrode area for specimen A after polarization shown in Figure 7a. Clearly, the MnS was still intact below $-0.1 \text{ V}$. A comparison of before and after polarization (Figures 7d and 7e) indicates that the dissolution of the MnS surface occurred for specimen B. Figure 8b shows the SEM image and the EDS maps of this inclusion. Almost no Mn or S signal was detected after polarization. It was thus concluded that the small current peak at approximately $0 \text{ V}$ for Fe-5Cr can be attributed to the MnS dissolution. The other peak around $-0.2 \text{ V}$ is probably related to the active dissolution of the steel matrix of Fe-5Cr because the potential region of this current peak is consistent with the onset potential of the large current increase of the macro-scale polarization curve measured in 0.1 M Na2SO4 (Figures 4a and 5a). In the macro-scale polarization for Fe-5Cr in 0.1 M Na2SO4 (Figure 5a), the local active dissolution provided the large current increase. However, only a small current peak was observed in micro-scale polarization. The precise reason is not clear, but this difference was supposed to be caused by the difference of size of the electrode area.

Figure 9 shows the micro-scale polarization curve for a small area with the MnS inclusion in Fe-12Cr in the 0.1 M Na2SO4 solution and the CLSM reflectance images of the inclusion before and after polarization. As shown in Figure 9a, a small current peak was also observed at approximately $0 \text{ V}$, and polarization was stopped at $0.18 \text{ V}$. After polarization (Figure 9c), the surface dissolution of the inclusion was observed. Figure 10 shows the SEM image and the EDS maps for the inclusion shown in Figure 9c. The Mn concentration decreased to less than 12 mass% after polarization compared with the inclusion of the as-polished condition (see Figure 2b). It is confirmed that the MnS dissolution occurred during the anodic polarization up to $0.18 \text{ V}$. The S concentration also decreased to less than 3 mass%. The small current peak at approximately $0 \text{ V}$ is certainly due to the dissolution of the MnS inclusion.

In Figure 10, compared with Figure 8b (Fe-5Cr), clear Mn, Cr, and S signals were detected at the position indicated by the thick arrow. For Fe-12Cr, the Cr concentration in the MnS inclusion was slightly higher than that in the inclusions in Fe-5Cr (see Figure 3). It was demonstrated that the dissolution potential of CrS is located above 0.8 V in NaCl solutions.29 The portion of the Cr-rich region in the MnS inclusion was thought to remain after polarization. Comparing Figures 10 and 2, the Cr concentration in the inclusions increased after polarization. The reason for this is explained as follows. The MnS inclusions in this study should be accurately written as $(\text{Mn,Cr,Fe})\text{S}$.24 The selective dissolution of MnS and FeS is expected to occur during polarization, but CrS is difficult to dissolve because a Cr-containing oxide film formed on the CrS surface.29–31 As a result, the amount of Cr in the inclusions was likely to increase after polarization. Lillard et al. proposed that MnS inclusions are passivated by Cu deposition.32 They analyzed the surface of the MnS inclusion using atomic force microscopy and scanning Kelvin probe force microscopy and found that Cu deposition on the MnS inclusion causes the MnS embrittlement and passivation during pit propagation. However, no Cu-deposition
Figure 7. (a) Micro-scale polarization curves of small areas with MnS inclusions of Fe-5Cr in 0.1 M Na$_2$SO$_4$. (b-e) CLSM reflectance images of the inclusions (b, d) before and (c, e) after polarization. Polarization measurements of specimens A and B were stopped at −0.10 and 0.18 V, respectively: (b, c) specimen A and (d, e) specimen B.

Figure 8. SEM images and corresponding EDS maps of the inclusions after the polarization shown in Figure 7: (a) specimen A and (b) specimen B.

Figure 9. (a) Micro-scale polarization curve of a small area with MnS inclusion of Fe-12Cr in 0.1 M Na$_2$SO$_4$. CLSM reflectance images of the inclusion (b) before and (c) after the polarization.

The Si and O signals indicate that there are small residuals containing Si and O, which are probably included in the MnS inclusions. Si-oxides were generally formed as deoxidation products in the melting process of steels, and non-metallic inclusions such as MnS often nucleated at the oxides in the solidification process. It is therefore likely that Si-oxides appeared after the dissolution of the MnS inclusions.

Figure 11 shows the micro-scale polarization curve for a small area with the MnS inclusion for Fe-18Cr in the 0.1 M Na$_2$SO$_4$ solution and the CLSM reflectance images of the inclusion before and after polarization. In this polarization, the potential scan was stopped at 0.07 V just above a very-small current peak at approximately 0 V. After polarization, the surface of the inclusion dissolved as seen in Figure 11c. In Figure 12, the SEM image and the corresponding EDS maps of the inclusion shown in Figure 11c are given. The concentrations were confirmed by the EDS analysis after polarization in this work (Cu concentration was less than 1 mass%).
of Mn and S decreased to less than 10 mass%, implying that the MnS inclusion dissolved during the anodic polarization up to 0.07 V. For Fe-18Cr, it was concluded that the MnS dissolution proceeded at approximately 0 V.

In Figure 12, a part of the MnS remained, and the existence of Cr and O was observed on the entire surface of the inclusion. A Cr-oxide film was reported to grow on the CrS inclusions as the electrode potential increased. Since the Cr concentration in the inclusions of Fe-18Cr is higher than that of Fe-5Cr and Fe-12Cr (see Table II), the entire surface of the inclusion was likely to have been covered by a Cr-oxide film.

In this study, it was difficult to analyze the dissolution behavior of Fe from the (Mn,Cr,Fe)S inclusions because the Fe signal from the steel matrix cannot be eliminated as the thinning of the inclusion by the dissolution. However, it would appear that Fe dissolves simultaneously with Mn and S. Williams et al. observed many MnS inclusions included Fe-enriched regions, presumably FeS. They proposed that the trigger process for pitting is FeS dissolution. Further study is still needed to clarify the role of FeS on initiation processes of pitting.

The results thus far indicate that the MnS dissolution of Fe-Cr alloys occurs at approximately 0 V. It is also interesting that the dissolution potential region is independent of the Cr content in the steel matrix, but the MnS dissolution morphology is quite different for each steel. For Fe-5Cr, the inclusion readily dissolved entirely during anodic polarization as shown in Figure 8b. However, for Fe-12Cr, the Cr-enriched portion of the inclusion remained. In the case of Fe-18Cr, the existence of Cr and O was observed on the entire surface of the inclusion, as presented in Figure 12. The dissolution behavior shown in Figures 8b, 10, and 12 suggest that the dissolution morphology is determined by Cr concentration in the MnS inclusions. On the other hand, the dissolution current peak during polarization appears at the selective dissolution potential of MnS from the (Mn,Cr,Fe)S inclusions. This is the reason why the dissolution potential region of the MnS inclusions is independent of the Cr concentration in the inclusions, but the MnS dissolution morphology is quite different.

In this study, the MnS dissolution in Fe-Cr alloys was found to occur at approximately 0 V. Regarding Type 304 austenitic stainless steel (18Cr-8Ni), MnS inclusions have been reported to dissolve at approximately 0.3 V in Na$_2$SO$_4$ and NaCl solutions. Although the precise reason for this difference is unclear, one possible explanation is the difference in the Cr concentration in MnS inclusions between Type 304 stainless steel and the Fe-Cr alloys used in this study. It was reported that the Cr concentration in MnS inclusions for Type 304 stainless steel is approximately 10 at.%. In contrast, the Cr concentrations for Fe-5Cr, Fe-12Cr, and Fe-18Cr were 2.0, 3.5, and 6.5 at.%, respectively. Baroux reported that the sulfide solubility in 0.02 M NaCl decreases by the addition of Cr to MnS, and that the pitting potential at the sulfide inclusions increases in the same way.
The Cr in MnS inclusions is expected to inhibit the dissolution by the formation of a Cr-oxide film on the inclusion.\textsuperscript{29,33,37} Systematic studies are needed to confirm the above speculation.

In the macro-scale polarization curves presented in Figures 5a and 6, small current peaks are observed at approximately 0 V in Na\textsubscript{2}SO\textsubscript{4} and 0.15 M H\textsubscript{2}BO\textsubscript{3}-0.0375 M Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} solutions. From the discussion in this section, these current peaks are suggested to be the dissolution of the MnS inclusions. In this study, there was no pH-dependence in the MnS dissolution potentials, but the dissolution reaction of MnS usually contains H\textsuperscript{+} as follows:\textsuperscript{38}

\[ 2\text{MnS} + 3\text{H}_{2}\text{O} \rightarrow 2\text{Mn}^{2+} + \text{S}_{2}^{2-} + 6\text{H}^{+} + 8\text{e}^{-} \quad [1] \]

The reason for “no pH-dependence” is unclear; however, there is a possibility that the H\textsuperscript{+}-consuming reactions, such as a disproportionation reaction:\textsuperscript{39}

\[ \text{S}_{2}^{2-} + 2\text{H}^{+} \rightarrow \text{S} + \text{SO}_{2} + \text{H}_{2}\text{O} \quad [2] \]

proceed along with the MnS dissolution.

For the polarization curve of Fe-5Cr in the boric-borate buffer solution without NaCl and for Fe-12Cr in 0.1 M Na\textsubscript{2}SO\textsubscript{4}, additional current peaks were seen at 0.15 V. The reason for these current peaks was not determined by the micro-scale polarization measurements. However, it is possible that the Fe\textsuperscript{2+} ions released from the inclusions and steel surface are oxidized to Fe\textsuperscript{3+} and provide the additional current peak above the MnS dissolution potential region.

**Pitting corrosion at the MnS**—To elucidate the role of the MnS dissolution in pit initiation, polarization measurements were performed in 0.1 M NaCl. Figure 13 shows the comparison of the micro-scale polarization curves for a small area with the MnS inclusion of Fe-5Cr in the 0.1 M NaCl and 0.1 M Na\textsubscript{2}SO\textsubscript{4} solutions. The polarization curve measured in 0.1 M Na\textsubscript{2}SO\textsubscript{4} shown in Figure 7 is indicated again as a reference. Figures 13b and 13c presents the CLSM reflectance images of the electrode area before and after polarization in 0.1 M NaCl. From the comparison of the CLSM images before and after polarization (Figures 13b and 13c), a pit was clearly initiated at the MnS inclusion. After polarization, the MnS inclusion disappeared, and a pit was observed at the position where the inclusion was located. Figure 13d shows the SEM image of the area surrounded by the blue lines shown in Figure 13c. The EDS point analysis was performed at points 4–6, and the results are summarized in Table III. No signal of S was detected inside and outside the pit. In the case of Fe-5Cr, it is likely that the MnS inclusions dissolved completely or fell out by the corrosion. In 0.1 M NaCl, a metastable pitting event was generated at 0.03 V, and a stable pit was initiated at 0.05 V. Clearly, these pitting events are generated in the potential region of the MnS dissolution. Therefore, the dissolution of the MnS inclusion is directly related to the initiation of pitting. When MnS dissolution begins during polarization, bare steel surfaces are exposed to the solution. For Fe-5Cr, active dissolution was observed in 0.1 M Na\textsubscript{2}SO\textsubscript{4} (pH 5.8) as shown in Figure 5a. In contrast, no active dissolution occurred in the boric-borate buffer solutions (pH 8.45). The depassivation pH for Fe-5Cr is located between pH 5.8 and 8.45. In the case of 0.1 M NaCl, the solution pH is supposed to be below or near the pH of depassivation. Moreover, the repassivation ability of Fe-5Cr is relatively low. The active dissolution of the steel matrix is likely to start from the exposed steel surfaces and become pitting as local active dissolution.

In the boric-borate buffer solution with 0.1 M NaCl, stable pitting was generated on Fe-5Cr at −0.06 V, as shown in Figure 5a. The pitting potential is located in the potential region of a small current peak at approximately 0 V in the boric-borate buffer solution without 0.1 M NaCl. As already mentioned, this small current peak is probably due to the dissolution of the MnS inclusions. In the boric-borate buffer, it is also suggested that the MnS inclusion dissolution brings about the initiation of pitting.

Figure 14 indicates the micro-scale polarization curves for a small area with the MnS inclusion of Fe-12Cr in the 0.1 M NaCl and 0.1 M Na\textsubscript{2}SO\textsubscript{4} solutions. The polarization curve measured in 0.1 M Na\textsubscript{2}SO\textsubscript{4} shown in Figure 9 is presented again. Figures 14b and 14c shows the CLSM reflectance images of the inclusion before and after polarization in 0.1 M NaCl. During anodic polarization in 0.1 M NaCl, a stable pit was initiated at 0.13 V. This pitting potential was close to the dissolution potential region of the MnS inclusions. As shown in Figure 14a, a small current peak was observed at approximately 0 V.

| Table III. Relative compositions (at.%) of points 4–6 shown in Figure 13. |
|---|---|---|---|---|---|---|---|---|---|
| Point | Mn | S | Cr | O | Si | Al | Fe | Ni |
| 4 | 1 | <1 | 6 | <1 | 1 | 93 | <1 | |
| 5 | 1 | <1 | 6 | <1 | 1 | 93 | <1 | |
| 6 | 1 | <1 | 6 | <1 | 1 | 93 | <1 | |

Figure 13. (a) Micro-scale polarization curves of a small area with MnS inclusions of Fe-5Cr in 0.1 M NaCl and 0.1 M Na\textsubscript{2}SO\textsubscript{4}. CLSM reflectance images of the electrode area (b) before and (c) after the polarization in 0.1 M NaCl shown in (a). (d) SEM image of the pit shown in (c).
in 0.1 M Na₂SO₄. Also in the case of Fe-12Cr, stable pit initiation seems to be associated with the MnS dissolution.

In Figure 14c, a stable pit is seen to be generated at the boundary of the steel matrix and the inclusion. This result is consistent with data already published in the literature.19-23,33 Suter and Böhn applied a micro-capillary cell to study the pit initiation behavior at a MnS inclusion in Type 304 stainless steel. They found that the boundary of the steel matrix and the inclusion is mainly attacked in NaCl solutions. Figure 15 shows the SEM image and the corresponding EDS maps of the inclusion after polarization in 0.1 M NaCl shown in Figure 14a. It is seen that a part of the MnS remains even after anodic polarization. In contrast, the whole of the MnS dissolved in the case of Fe-5Cr in 0.1 M NaCl (see Figure 13) because the Cr concentration in the MnS inclusions in Fe-5Cr is lower than in Fe-12Cr. In Figure 15, clearly the pit was initiated at the boundary of the MnS and the steel matrix. Moreover, the trench (micro-crevice) was generated at the boundary, and the pit is thought to have initiated at this trench. Many researchers demonstrated that the boundaries of the inclusions and steel matrix act as the initiation sites for pitting, and trenches were often observed.21,22 Chiba et al. proposed that the trench was formed at the boundary of MnS inclusions and steel matrix (Type 304 stainless steel) due to the depassivation of the steel matrix at the boundary, and the stable pit was initiated inside the trench as a local active dissolution.21,22 In this study, it was not possible to determine which mechanism was more important.

In Figure 16, the micro-scale polarization behavior for a small area with the MnS inclusion of Fe-18Cr in the 0.1 M NaCl and 0.1 M Na₂SO₄ solutions is shown. In this figure, the polarization curve measured in 0.1 M Na₂SO₄ (Figure 11) is presented again. Figures 16b and 16c shows the CLSM reflectance images of the inclusion before and after polarization in 0.1 M NaCl. In this case, no stable pit was initiated. In the dissolution potential region of the MnS inclusion, only a metastable pitting event was observed. Polarization in 0.1 M NaCl was repeated seven times on different specimens, but no stable pit was observed. However, stable pits were generated in the macro-scale polarization (Figure 4). The difference is thought to originate in the number of the inclusions in the electrode area. Pitting is a statistical phenomenon, and the corrosion resistance of the MnS inclusions depends on their composition and the morphology. In the macro-scale polarization, many inclusions exist in the electrode area, and any one of them acts as the initiation site for stable pitting. However, only one inclusion was randomly selected in the micro-scale polarization. If...
the micro-scale measurements are repeated many times, stable pits are thought to be initiated even in the micro-scale measurements.

Figure 17 shows the SEM image and the corresponding EDS maps of the inclusion after polarization in the 0.1 M NaCl solution shown in Figure 16a. The dissolution of the inclusion surface is observed, but no trench at the boundary of the MnS and steel matrix was generated, probably due to the relatively high passivation ability of Fe-18Cr steel matrix compared to Fe-12Cr. Additionally, the high Cr concentration in the inclusions is thought to contribute to the resistance against the trench formation. However, further studies are needed to determine the reason for the absence of trench generation at the inclusions in Fe-18Cr.

In Figure 6, for both Fe-18Cr and Fe-12Cr, the small current peaks due to MnS dissolution appear at the same potential region. However, the pitting potential for Fe-18Cr in the boric-borate buffer solution with 0.1 M NaCl is higher than that of Fe-12Cr. This difference is likely due to the repassivation ability of the steel matrix and the dissolution behavior of the MnS inclusions. When the bare steel surface was exposed to the solution due to the MnS dissolution, the repassivation ability of the steel matrix is thought to determine subsequent reactions, that is, whether active dissolution or passivation occurs at the boundaries of the inclusions and steel matrix. If dissolution rate is high and repassivation rate is low, a stable pit is thought to be generated as local active dissolution. In contrast, only metastable pitting events are seemed to be observed on the steels with high repassivation ability. Moreover, it was supposed that the S-containing species released from the MnS inclusions retard the repassivation reaction and promote the active dissolution of the steel matrix. Brossia and Kelly demonstrated that the MnS dissolution forms aqueous sulfide, which increases the corrosivity of the solution on and around inclusions. In this study, the MnS inclusions were found to dissolve around 0 V. Even though the dissolution potential was independent of Cr concentration, the dissolution morphology was remarkable in that the inclusions in Fe-5Cr dissolved and disappeared. For Fe-12Cr, the Cr-enriched portions remained. In the case of Fe-18Cr, Cr-oxides was observed to form on the entire surface of the inclusion. The dissolution amount of S-species from the MnS inclusions was expected to decrease with increasing Cr concentration of the inclusions. Additionally, the Cr concentration in the inclusions increased with the Cr content in the steels. It was suggested that the pitting corrosion resistance at the MnS inclusions of Fe-Cr alloys was related to the inclusion dissolution morphology originating from the difference in the Cr concentration of the inclusions. More extensive research is required to determine the quantitative contribution of the inclusions dissolution and to fully identify the role of Cr in pitting corrosion resistance of Fe-Cr alloys.

Conclusions

1. MnS inclusions containing small amounts of Cr and Fe existed in 5–18 mass% Cr steels. The Mn/S ratio was approximately 1 and independent of the Cr content in the steels. With the increase in the Cr content in the steels, the Cr and Fe concentrations in the inclusions increased and decreased, respectively.
2. In 0.1 M NaCl (pH 5.5), the onset potentials of the large anodic current increase for Fe-5Cr, Fe-12Cr, and Fe-18Cr were measured at approximately −0.3, 0.15, and 0.3 V, respectively.
large current increase for Fe-5Cr was the initiation of local active dissolution and not pitting because the pH of 0.1 M NaCl is estimated to be below or near the depassivation pH for Fe-5Cr. For Fe-12Cr and Fe-18Cr, typical pits appeared after polarization.

3. In 0.15 M H$_3$BO$_3$-0.0375 M Na$_2$B$_4$O$_7$ boric-borate buffer solution (pH 8.45) with 0.1 M NaCl, the pitting potentials for Fe-5Cr, Fe-12Cr, and Fe-18Cr were determined to be approximately −0.06, 0.23, and 0.39 V, respectively.

4. MnS inclusions in 5–18mass% Cr steels dissolved at approximately 0 V in 0.1 M Na$_2$SO$_4$ (pH 5.8) and 0.15 M H$_3$BO$_3$-0.0375 M Na$_2$B$_4$O$_7$ boric-borate buffer solution (pH 8.45). The potential region of the MnS dissolution was independent of the Cr content in the steels; however, the inclusion morphology after polarization in 0.1 M Na$_2$SO$_4$ was quite different for each steel. The inclusion of Fe-5Cr readily dissolved entirely. For Fe-12Cr, the Cr-enriched portion of the inclusion remained even after polarization. In the case of Fe-18Cr, Cr and O were detected on the entire surface of the inclusion.

5. In micro-scale polarization of a small area with the MnS inclusion of Fe-5Cr in 0.1 M NaCl, a large pit was generated at the inclusion, and the inclusion disappeared. The MnS inclusion dissolution and the exposure of bare steel surfaces were expected to be directly related to the initiation of pitting.

6. During micro-scale polarization of a small area with the MnS inclusion of Fe-12Cr in 0.1 M NaCl, the MnS dissolution began at approximately 0 V, and a stable pit was initiated at 0.13 V. Rather than dissolve entirely, most of the inclusion remained. A trench (micro-crevice) was generated at the boundary of the MnS/steel, and a pit was initiated at the trench.

7. For Fe-18Cr, no stable pit was initiated during micro-scale polarization for a small area with the MnS inclusion in 0.1 M NaCl. In the dissolution potential region of the MnS, only a metastable pitting event was observed.

8. The pitting corrosion resistance at the MnS inclusions of Fe-Cr alloys was thought to be related not only to the repassivation ability of the steel matrices but also to the dissolution behavior and morphology of the MnS inclusions.

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