Observation of Pit Initiation and Growth of Stainless Steel under a Chloride Solution Droplet —Effect of S Content on Pit Initiation, Growth, and Repassivation—^{*1}

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A system was developed based on which the pit growth automatically stops any time after the pit initiation under a chloride solution droplet. The atmospheric pitting corrosion of austenitic stainless steels with various sulfur (S) concentrations was investigated using this system. The results confirm that the initiation sites of pitting corrosion are manganese sulfide inclusions under the droplets regardless of the S concentration. In addition, the growth behavior of the active dissolution area is independent of the S concentration. When these specimens are subjected to wet–dry cycle tests, the probability of pitting corrosion increases with increasing S concentration due to the increase in initiation sites. The onset of pitting corrosion is independent of the chloride concentration. On the other hand, repassivation strongly depends on the S concentration. [doi:10.2320/matertrans.C-M2020869]

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1. Introduction

Stainless steel (SS) exhibits an excellent corrosion resistance due to the formation of a passive film on its surface. Therefore, SS is widely used in various fields such as architecture and railroad coaches. However, pitting corrosion is a significant problem in marine atmospheric environments because pits might cause strength and design deterioration. In this environment, airborne salts are deposited on the SS surface. Subsequently, water droplets containing chloride ions (Cl^-) form on the surface when the relative humidity (RH) rises above deliquescence humidity at night. In contrast, the concentration of Cl^- in the droplet gradually increases with decreasing RH in the daytime. These Cl^- droplets induce the initiation of pitting corrosion.^{1–4)} Temperature, RH, rainfall, and airborne salts are therefore critical environmental factors for the initiation of pitting corrosion of SS in marine atmospheric environments.

Many studies have been conducted to clarify the pitting corrosion mechanism of SS; however, the SS was anodically polarized in an aqueous chloride solution in most of these studies. It is well known that manganese sulfide (MnS) inclusions are the initiation sites for pitting corrosion in SS;⁵⁾ thus, many researchers have paid attention to MnS inclusions. Suter and Webb *et al.*^{6–11)} performed anodic polarization tests on SS containing MnS inclusions using a microcapillary cell (20–1000 μm). They reported that the MnS inclusions become the initiation sites of pitting corrosion because of electrochemical dissolution in the passive region of the SS. In recent years, Chiba *et al.*^{12–14)} developed a unique microelectrochemical measurement system for *in situ* high-resolution optical microscope observations to directly observe the initiation sites of pitting corrosion. They applied this system to SS304 under anodic

polarization in a sodium chloride solution and reported that the initiation sites of pitting corrosion are at the boundaries between the MnS inclusions and SS matrix. Furthermore, it has been suggested that the dissolution of boundaries is due to the synergistic effect of elemental sulfur (S), generated by electrochemical dissolution of MnS inclusions, and Cl^- in the solution and a detailed mechanism of pitting corrosion has been proposed.¹³⁾

As mentioned above, many studies on pitting corrosion of SS are often performed in aqueous solution under anodic polarization. However, the pit initiation and growth mechanism in aqueous solution might differ from those associated with an extremely thin droplet (10 to 100 μm) in an atmospheric environment. In addition, the pit growth mechanism during pitting corrosion based on anodic polarization in an aqueous solution might differ from that of spontaneous corrosion in an atmospheric environment. A pit is initiated when SS is anodically polarized to the pitting potential (E_{pit}) and the pit growth is maintained at E_{pit} or above E_{pit} in the former case. On the other hand, spontaneous pit initiation occurs on the SS surface when the open circuit potential (OCP) increases to E_{pit} or E_{pit} decreases to OCP due to changes in the droplet thickness and/or Cl^- concentration. Immediately after pit initiation, the SS potential shifts into the negative direction (from the passive region to the active dissolution region) and pit growth continues in the active dissolution region. Therefore, we propose a new pitting corrosion test method, which is based on concentrating Cl^- in the droplet by lowering the RH while maintaining the equilibrium at the air/droplet interface rather than on anodic polarization.^{1–4)} This method seems to be much more representative of the actual marine atmospheric environment.

Regarding the electrochemical measurement for the analysis of the corrosion behavior of metal under the droplet, Stratmann *et al.*^{15–17)} developed a surface potential measurement method using a Kelvin probe (KP) to avoid contact between the reference electrode (RE) and droplet. They obtained the polarization curves of steel under the droplet. Frankel *et al.*¹⁸⁾ measured the anodic polarization curves of SS304L using KP and showed that E_{pit} does not change

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regardless of the droplet thickness. On the other hand, our group successfully measured the corrosion rate of iron (Fe) and zinc (Zn) for various droplet thicknesses using electrochemical impedance spectroscopy (EIS); the results showed that the corrosion rates of Fe and Zn depend on the droplet thickness.^{19,20)} Furthermore, in addition to general corrosion metal (Fe and Zn), EIS was applied to localized corrosion metal (SS), which was exposed to a marine atmospheric environment, the pit initiation was monitored.²¹⁾ The surface condition and corrosion rate of SS were continuously measured using impedance at 10 kHz and 10 mHz, respectively. Tsutsumi *et al.* prepared an electrode assembly embedded in epoxy resin, which consisted of eight SS plates, a silver (Ag) plate, and two Inconel plates.^{1,2)} The Ag and Inconel were used as RE and for the calculation of the droplet thickness, respectively. Pit initiation was successfully monitored with increasing Cl^- concentration during the drying process of the droplet using the potential change of the Ag plate. Based on this method, the pitting corrosion that occurred in many samples could be simultaneously analyzed. This method is extremely useful for the evaluation of the probability of pitting corrosion because pitting corrosion is a stochastic phenomenon. However, because the SS plates are embedded in resin, the samples occasionally suffered from crevice corrosion. Therefore, we improved this method to avoid crevice corrossions in the recent works.^{3,4)}

In this study, we further improved the conventional evaluation system for pitting corrosion in an atmospheric environment. The conventional system was combined with a new system that can automatically stop the pit growth at any time during the pit growth stage. This system was applied to SS304 samples with different S concentrations. The effect of the S concentration on the pit initiation, pit growth, and repassivation behavior of SS304 is discussed in detail.

2. Experimental Procedures

2.1 Pit growth automatic stop test

Austenitic SS304 plates with different concentrations of S (10, 60, 480, 1620, and 3230 ppm) were used as samples in this study. Their chemical compositions are shown in Table 1. They are denoted as 10S, 60S, 480S, 1620S, and 3230S steel, respectively. Figures 1(a)–(e) show optical

Fig. 1 Optical microscope images of austenitic stainless steel with different sulfur concentrations: (a) 10S, (b) 60S, (c) 480S, (d) 1620S, and (e) 3230S steel.

microscope images of the surface of each sample. The black contrast in the images correspond to MnS inclusions. The number and average size of the inclusions increase with increasing S concentration.

These samples were cut into $15 \times 10 \times 5$ mm pieces. The surfaces were polished, first with SiC paper (#2000) and then with diamond paste ($0.25 \mu\text{m}$). Subsequently, they were ultrasonically cleaned in ethanol and Milli-Q ($18.2 \text{ M}\Omega \text{ cm}$) for 10 min, respectively, and used as working electrodes (WEs). The WE fixed to the sample holder shown in Fig. 2 and a 1 M MgCl_2 ($[\text{Cl}^-] = 2 \text{ M}$) droplet with an initial volume (V_0) of $3 \mu\text{L}$ and diameter (d) of 3 mm (height (h) $\sim 0.8 \text{ mm}$) was placed on the surface. An Ag wire ($\phi = 100 \mu\text{m}$), which was placed directly above the WE, was used as RE. This setup was installed in a programmable constant humidity and temperature chamber (IW222, Yamato Scientific Co., Ltd.). Both edges of the WE were covered with $100 \mu\text{m}$ thick insulating tape and both ends of the Ag

Table 1 Chemical compositions (mass%) of austenitic stainless steel samples with different sulfur concentrations.

Elements	C	Si	Mn	P	S	Ni	Cr	Al	Fe
10S	0.05	0.50	1.47	0.025	0.001	8.99	18.45	0.05	Bal.
60S	0.05	0.50	1.47	0.023	0.006	9.00	18.19	0.02	Bal.
480S	0.06	0.50	1.46	0.023	0.048	9.01	18.32	0.03	Bal.
1620S	0.05	0.49	1.41	0.023	0.162	9.04	18.36	0.04	Bal.
3230S	0.05	0.46	1.38	0.024	0.323	9.06	18.24	0.04	Bal.

Fig. 2 Schematic drawing of the experimental setup used in this study.

wire were tightly pulled and fixed to the terminals to maintain a constant gap between the WE and RE (100 μm). A reservoir containing Milli-Q was directly set above the sample holder. By opening the solenoid valve under the PC control, Milli-Q was automatically released on the WE surface. In this experiment, the temperature was maintained at 298 K. The RH was maintained at 95% for the initial 30 min and was then reduced to 35% at a constant rate of 5% h^{-1} . The $[\text{Cl}^-]$ of the droplet is equal to $\sim 2\text{ M}$ at 95% RH.¹⁾ The concentration is almost equal to the initial concentration of the droplet (1 M MgCl_2); hence, the droplet does not dry in the first 30 min. This initial period was employed because the initial surface state (passive film state) of the WE immediately after polishing and cleaning might differ in every experiment; thus, the deviation of the surface state could be minimized by applying this initial period. During the drying process, the potential difference between the WE and RE ($E_{\text{SS-Ag}}$) was measured at an interval of 1 s using an electrometer (HE-104A, HOKUTO DENKO CORP.). The $E_{\text{SS-Ag}}$ is given by the following equation:

$$E_{\text{SS-Ag}} = E_{\text{corr(WE)}} - E_{\text{Ag/AgCl}}, \quad (1)$$

where $E_{\text{corr(WE)}}$ is the corrosion potential of the WE and $E_{\text{Ag/AgCl}}$ is the equilibrium potential of Ag/AgCl determined by the following equilibrium reaction:

This means that the potentials of both the WE and RE change during the drying process. However, we previously reported that the change of $E_{\text{corr(WE)}}$ due to the pit initiation and growth is more significant than that of $E_{\text{Ag/AgCl}}$.³⁾ Thus, the pit initiation and growth can be determined by continuously monitoring $E_{\text{SS-Ag}}$. In this study, the pit initiation was defined as the change in the potential of $E_{\text{SS-Ag}}$ by -0.01 V s^{-1} . The solenoid valve was automatically opened 1–1000 s after the potential change was detected and Milli-Q was released onto the WE surface to stop the pit growth. The initiated pit was observed with a scanning electron microscope (SEM,

JSM-6010LA, JEOL Ltd.) and the inclusions in the pit were analyzed by energy dispersive X-ray analysis (EDX).

2.2 Wet-dry cycle test

The same samples that were used in Section 2.1 were cut into $35 \times 25 \times 5\text{ mm}$ pieces and their surfaces were polished with SiC paper (#1000). The samples were then ultrasonically cleaned in ethanol and Milli-Q for 10 min. Subsequently, three 1 M MgCl_2 droplets with a V_0 of 50 μL and d of 8 mm ($h \sim 1.9\text{ mm}$) were formed on the WE surface at even intervals using a micropipette. For each droplet, Ag wires were used as RE. Insulating tape was used to position them to maintain the distance between the WE and RE at 100 μm . Similar to Section 2.1, the setup was installed in a programmable constant humidity and temperature chamber. The detailed experimental procedure has been previously reported.³⁾ To evaluate stochastic phenomena, such as pitting corrosion, three droplets were dropped on each sample and the samples were subjected to five wet-dry cycle tests twice. In total, 30 test cycles were performed. During the test, the temperature was maintained constant at 298 K and the RH was decreased from 95% to 45% at a constant rate of 5% h^{-1} . Subsequently, it was increased from 45% to 95% at the same rate. The $E_{\text{SS-Ag}}$ of these droplets was monitored during the drying and wetting process using a digital multimeter (2000 MULTIMETER, Keithley Instruments, Inc.) and the RH for the pit initiation and repassivation during the drying process (RH_{pit}) and wetting process (RH_{rep}), respectively, was determined. When the air/droplet interface is in equilibrium, the relationship between the equilibrium relative humidity (RH_{eq}) and equilibrium Cl^- concentration ($[\text{Cl}^-]_{\text{eq}}$) of the droplet can be expressed as follows:

$$[\text{Cl}^-]_{\text{eq}} = -0.000457\text{RH}_{\text{eq}}^2 - 0.0705\text{RH}_{\text{eq}} + 12.71. \quad (3)$$

The $[\text{Cl}^-]_{\text{eq}}$ for pit initiation ($[\text{Cl}^-]_{\text{pit}}$) and repassivation ($[\text{Cl}^-]_{\text{rep}}$) was determined by using eq. (3). The number of pits that formed during the wet-dry cycle test and their morphology were observed using a stereoscopic microscope (SMZ800N, Nikon Instech Co., Ltd.) and optical microscope (LV150, Nikon Instech Co., Ltd.), respectively.

3. Results and Discussion

3.1 Automatic pit growth stop test

Figure 3(a) shows typical changes in the RH and potential ($E_{\text{SS-Ag}}$) for 60S steel during the drying process. The $E_{\text{SS-Ag}}$ gradually increases with the decrease in the RH from the start of the test up to 8.2 h. However, as reported in a previous study,³⁾ the $[\text{Cl}^-]$ in the droplet increases with decreasing RH, which induces the shift of the RE potential in the positive direction. Thus, this potential change does not correspond to the pitting corrosion of 60S steel. Subsequently, $E_{\text{SS-Ag}}$ rapidly shifts in the negative direction at $\sim 8.2\text{ h}$, which is considered to be due to the occurrence of pitting corrosion.

Figure 3(b) is an enlarged view of Fig. 3(a) at $\sim 8.2\text{ h}$ (55% RH). In this study, the time and RH at which the change in $E_{\text{SS-Ag}}$ is -0.01 V s^{-1} were defined as the onset time (t_{onset}) and RH (RH_{pit}) for pit initiation, respectively. In addition, the time when the pit growth automatically stopped (repassivation) by controlling the solenoid valve using the PC and

Fig. 3 Typical changes in the RH and E_{SS-Ag} of austenitic stainless steel for 60S steel (a) from 95% RH to 35% RH, and (b) magnified view of (a) at ~55% RH.

supplying Milli-Q to the sample surface was defined as the end of pit growth (t_{end}). A rapid potential change was observed regardless of the S concentration of the SS during the experiments. Hence, the pit growth time ($\Delta t_{growth} = t_{end} - t_{onset}$) was liberally controlled and the initiated pits were observed after their growth using SEM.

Figures 4(a)–(d) represent the SEM images of pits that formed on the 60S steel surface when Δt_{growth} was 1, 10, 101, and 1000 s, respectively. These images do not show sequential pit growth for one pit and each pit was separately obtained using different samples. Because the pit growth speeds up significantly, they are shown at different magnifications. Only one pit formed under the droplet during the experiment regardless of Δt_{growth} . In each case, a small deep hole with inclusions can be observed in the center part. In addition, traces of active dissolution around the hole can be observed. The inclusions (point A) in the hole in Fig. 4(a) were analyzed by SEM-EDX (Table 2). The chemical composition ratio of Mn to S is approximately 1:1, which indicates that these inclusions are MnS containing chromium and Fe. In addition, because aluminum (Al) and oxygen (O) were also detected, it is highly possible that MnS inclusions are present near the Al_2O_3 inclusions. As described in a previous report,³⁾ the Ag wire used as RE partially dissolves as the Ag complex ions in the high $[Cl^-]$ droplet (~10 M in $MgCl_2$ saturation concentration). These ions react with the MnS inclusions to form AgS on the MnS surface. Thus, Ag was also detected by EDX. It is unclear how the precipitation of Ag affects the pit initiation and growth. However, no suitable RE alternative has been found; therefore, Ag wire was used as RE in this study.

It has been reported that the initiation sites of pits that formed by anodic polarization in the aqueous solution are at the border between the MnS inclusions and SS matrix.^{12,13)} Even in the pit that formed during the drying process of the droplet (non-polarized state), pit initiation most like occurs at the border between the inclusions and matrix because the MnS inclusions remain in the hole. Furthermore, it can be seen that the active dissolution area radially spreads out from the hole in Fig. 4(a). The diameter of the active dissolution

Fig. 4 SEM images of the pit morphology of the 60S steel surface with Δt_{growth} of (a) 1 s, (b) 10 s, (c) 101 s, and (d) 1000 s. Point A indicates the EDS point analysis area.

Table 2 Chemical compositions (at%) of inclusions in the pit on the 60S steel surface with $\Delta t_{\text{growth}} = 1$ s.

Elements	S	Mn	Cr	Fe	Ni	O	Al	Ag
Point A	31.67	32.20	5.95	9.74	—	11.23	6.31	2.90

area (d_{active}) at $\Delta t_{\text{growth}} = 1$ s was determined to be roughly $7.5 \mu\text{m}$. Assuming that the entire surface of the droplet acts as a cathode site, the corroded area (V_{corr}) can be expressed by the following equation:

$$V_{\text{corr}} = \frac{\pi \left(\frac{d_{\text{drop}}}{2} \right)^2 \times i_{\text{cath}} \times \Delta t_{\text{growth}}}{2F} \times \frac{M_{\text{Fe}}}{d_{\text{Fe}}}, \quad (4)$$

where d_{drop} , F , M_{Fe} , and d_{Fe} represent the diameter of the droplet (0.3 cm), Faraday constant (96485 C mol $^{-1}$), molecular weight of Fe (55.845 g mol $^{-1}$), and density of Fe (7.874 g cm $^{-3}$), respectively. Assuming that i_{cath} , which is the oxygen diffusion-limiting current, is 2.0×10^{-5} A cm $^{-2}$, V_{corr} is 5.2×10^{-11} cm 3 when Δt_{growth} is equal to 1 s. As shown in Fig. 4(a), the actual active dissolution area is considerably irregular. Based on the assumption that the shape of the dissolution area is a hemisphere, the active dissolution area can be calculated to be $5.8 \mu\text{m}$ by substituting the value of V_{corr} . Because the calculated value is much closer to d_{active} , it is highly possible that the pit grows to $7.5 \mu\text{m}$ within only 1 s.

As Δt_{growth} increases from 1 s to 10 s, 101 s, and 1000 s, d_{active} increases to 14 , 31 , and $90 \mu\text{m}$, respectively. Figure 5 shows the relationship between d_{active} and Δt_{growth} , which can be expressed as follows:

$$d_{\text{active}} = 6.7 \Delta t_{\text{growth}}^{0.36}. \quad (5)$$

In other words, the increase in the active dissolution area of pitting corrosion is proportional to $\sim 1/3$ power of the time. When Δt_{growth} changes from 1 to 1000 s, the diameter

($d_{\text{small pit}}$) and depth of the small deep hole in the central part ranges from 2.9 to $7.8 \mu\text{m}$ and 2.5 to $5.0 \mu\text{m}$, respectively. The growth of these areas is smaller compared with that of the active dissolution area. Therefore, the initial anodic site should be the small hole immediately after pit initiation. The anodic site then radially spreads from the hole to the outside (active dissolution area) because the pH of the surrounding area of the hole decreases based on the hydrolysis reaction of metal ions dissolved in the hole; as a result, the growth of the small hole (initiation site) stops.

Figure 6 depicts SEM images of the pits that formed on the steel surfaces depending on the S concentration at a Δt_{growth} value of ~ 10 s. Note that only one pit is initiated on the surface in the droplet regardless of the S concentration. A small deep hole in the center of the pit can be observed, similar to the 60S steel (Fig. 4(b)) and the active dissolution area radially spreads around the hole. The MnS inclusions remain inside the holes, except for 10S steel. On the other hand, no inclusions can be identified in the hole of the 10S steel because the inclusions of the 10S steel are extremely small (Fig. 1(a)) and detach from the hole. The diameter of the active dissolution area ranges from 12 to $24 \mu\text{m}$ in all samples and the S concentration does not affect the radial pit growth. In brief, the initiation sites of pitting corrosion are MnS inclusions, even if the S concentration differs. The number and size of the inclusions have almost no effect on the growth rate of the pits during the early stage of pit growth within ~ 10 s.

3.2 Wet-dry cycle test

Figures 7(a) and (b) show the representative change in RH and $[\text{Cl}^-]$ in the droplet calculated by using eq. (3) and $E_{\text{SS-Ag}}$ of 60S steel during wet-dry cycle test, respectively. From the start of the test until 7.3 h, $E_{\text{SS-Ag}}$ gradually increases with decreasing RH. This potential shift is considered to be due to the Cl^- condensation, as described in Section 3.1. Subsequently, $E_{\text{SS-Ag}}$ suddenly shifts into the negative direction due to the pit initiation. The onset time of pit initiation (t_{onset}) is the same as that defined in Section 3.1 and the RH and $[\text{Cl}^-]$ during pit initiation are defined as RH_{pit} and $[\text{Cl}^-]_{\text{pit}}$, respectively. The $E_{\text{SS-Ag}}$ value becomes constant (approximately -0.1 V) under the active dissolution potential for ~ 8 h and then moves into the noble direction due to the repassivation of the pit during the wetting process. The repassivation time of the initiated pit is defined as t_{rep} when $E_{\text{SS-Ag}}$ reaches 0 V during the transition of the potential toward the noble direction and the RH and $[\text{Cl}^-]$ during the repassivation are defined as RH_{rep} and $[\text{Cl}^-]_{\text{rep}}$, respectively.

Figure 8 exhibits one of the examples of changes in $E_{\text{SS-Ag}}$ and RH when (a) 60S steel and (b) 3230S steel are subjected to five wet-dry cycle tests. The highlighted area in the figures

Fig. 5 Diameters of the active surface area (d_{active}) and deep small pit ($d_{\text{small pit}}$) as a function of the pit growth time (Δt_{growth}).

Fig. 6 SEM images of the pit morphology of the (a) 10S, (b) 480S, (c) 1620S, and (d) 3230S steel surface at Δt_{growth} of ~ 10 s.

Fig. 7 Typical change in the $E_{\text{SS-Ag}}$ of 60S steel during the RH cycle, (a) RH change and chloride concentration $[\text{Cl}^-]$ calculated from the RH change using eq. (3) and (b) potential change of $E_{\text{SS-Ag}}$ of 60S steel. Definitions of RH_{pit} at the onset of pitting corrosion (point “ t_{onset} ”) and RH_{rep} at the onset of repassivation (point “ t_{rep} ”).

Fig. 8 Changes in $E_{\text{SS-Ag}}$ for (a) 60S and (b) 3230S steel exposed to five RH cycles between 95% and 45%. The highlighted area indicates the growth period of pitting corrosion (Δt_{growth}).

corresponds to the pit growth time. The pit growth time increases with increasing S concentration of the SS. Figure 9 shows optical microscope images of pits that formed on the (a) 60S and (b) 3230S steel surfaces during the five wet–dry cycle tests. In addition, Figs. 9(c)–(e) are magnified images of the pit (Fig. 9(b)) that formed on the 3230S steel surface. First, as shown for 60S steel (Fig. 8(a)), the potential shifts in both the negative and positive directions occur in each cycle

of the wet–dry cycle tests. Because the number of potential fluctuations is consistent with the number of initiated pits observed on the 60S steel surface (Fig. 9(a)), a sharp decrease and increase in the potential results in the initiation and repassivation of a pit, respectively. The results of the wet–dry cycle test show that five pits form on the 60S steel surface during five cycles. However, because pitting corrosion is a stochastic phenomenon, the probability of pitting corrosion (P_{pit}) will be discussed later. Second, the

Fig. 9 Optical microscope images of pits on (a) 60S, and (b) 3230S steel after exposure to five RH cycles. The dotted white circles indicate the pit positions. The magnified pit morphologies observed on 3230S steel are shown in (c), (d), and (e), respectively.

potential fluctuation can also be observed for 3230S steel. However, in the first cycle, although a negative shift of the potential to the initiation of the pit can be observed in the drying process, the positive potential shift due to pit repassivation does not occur in the wetting process and E_{SS-Ag} remains below 0 V. Even in the initial stage of the drying process in the second cycle (high RH region), E_{SS-Ag} remains below 0 V without repassivation; a potential shift due to repassivation can be observed at the end of the wetting process. After the test, four pits were observed on the 3230S steel surface (Fig. 9(b)), which corresponds to the number of potential fluctuations monitored by the Ag wire shown in Fig. 8(b). However, one of the four pits (Fig. 9(c)) grows significantly more than the others. In other words, it is highly possible that the initiated pit did not repassivate in the wetting process during the first cycle and continued to grow in the second cycle, resulting in large pit formation. This phenomenon is only noticeable when the S concentrations of SS is high.

To evaluate the effect of the S concentration of SS on the pit initiation, P_{pit} was calculated by using eq. (6) and all results of the wet-dry cycle tests:

$$P_{pit} = \frac{N_{pit}}{N_{total}}, \quad (6)$$

where N_{pit} and N_{total} indicate the number of initiated pits and wet-dry cycles, respectively. However, the number of cycles is regarded to be one when the pit growth straddled two cycles, as shown in Fig. 8(b). The number of repassivated pits in the wetting process was defined as N_{rep} , and the pit repassivation probability (P_{rep}) was calculated as follows:

$$P_{rep} = \frac{N_{rep}}{N_{pit}}. \quad (7)$$

Figure 10(a) shows the correlations between the S concentration of SS and P_{pit} and P_{rep} . The P_{pit} value is ~60% when the S concentration of SS is 10 ppm and increases sharply with increasing S concentration. Finally, P_{pit} reaches 100% when the S concentration is above 1000 ppm. This means that pits were initiated in all cycles of the wet-dry cycle tests.

Fig. 10 (a) P_{pit} and P_{rep} as well as (b) $[Cl^-]_{pit}$ and $[Cl^-]_{rep}$ vs. the sulfur concentration of austenitic stainless steel.

Furthermore, P_{rep} decreases with increasing S concentration of SS and the initiated pit is less likely to be repassivated.

By substituting the measured RH_{pit} and RH_{rep} values into eq. (3), $[Cl^-]_{pit}$ and $[Cl^-]_{rep}$ during pit initiation and repassivation, respectively, were calculated. The results were plotted against the S concentration, as shown in Fig. 10(b). Due to the stochastic nature of pitting corrosion, $[Cl^-]_{pit}$ varies, to some extent, even in the same sample; however, it mostly ranges from 5.5 to 8.5 M and a dependency on the S concentration cannot be observed. Therefore, as the number

of MnS inclusions increases with increasing S concentration, the probability of MnS inclusions, which are the initiation sites of pitting corrosion, in the droplet also increases, which enhances the probability of pitting corrosion. On the other hand, $[Cl^-]_{rep}$ decreases with increasing S concentration, which implies that repassivation is less likely to occur with increasing S concentration. Due to the expansion of the active dissolution area (Fig. 6), the amount of MnS inclusions increases in this area with increasing S concentration. Because the initial volume of the droplet is constant regardless of the S concentration, the number of MnS inclusions in the active dissolution area might change the environment in the droplet and thus may affect the repassivation behavior. Webb *et al.*²²⁾ observed the evolution of HS^- from MnS inclusions on a SS surface immersed in 0.1 M Na_2SO_4 (pH = 2) and proposed that MnS chemically dissolves in low-pH solution based on the following equation:

Because the pH of the active dissolution area decreases due to the hydrolysis reaction of the dissolved metal ions, the MnS inclusions in the active dissolution area chemically dissolve and HS^- forms due to the expansion of the area. Because the acid dissociation constant (pK_a) of HS^- is 7.02²³⁾ the ratio of H_2S and HS^- can be expressed by the following equation:

$$\frac{[H_2S]}{[HS^-]} = 10^{7.02}[H^+]. \quad (9)$$

In other words, HS^- that forms by chemical dissolution almost changes to H_2S in a low-pH environment. Based on previous reports,^{24–26)} H_2S promotes the destruction of the passive film on the SS surface and shift of the pitting potential to the negative direction, suggesting that H_2S that forms by the chemical dissolution of MnS inclusions might inhibit the repassivation of SS. In the future, a more detailed study of the effect of the S concentration on the repassivation behavior will be performed.

4. Conclusions

The corrosion behavior of austenitic SS with different S concentrations was investigated using automatic pit growth stop and wet-dry cycle tests. The findings are as follows:

- (1) We established an electrochemical measurement system based on which the pit growth automatically stops and pits with a growth time of 1 to 1000 s (after initiation) can be observed using SEM. The system was applied to SS with different S concentrations. The results confirm that the initiation sites of pitting corrosion are MnS inclusions and that the growth behavior of the active dissolution area does not change regardless of the S concentration.

- (2) As the S concentration increases, the probability of MnS inclusions in the droplet and thus the probability of pitting corrosion increase. In addition, the chloride ion concentration does not differ when pits are initiated because the initiation sites of pitting corrosion are MnS inclusions regardless of the S concentration in SS. On the other hand, the repassivation of the initiated pits strongly depends on the S concentration and becomes difficult when the S concentration increases.

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