1   **Title:**

2   Effect of Atmospheric Aging on Dissolution of MnS Inclusions and Pitting Initiation
3   Process in Type 304 Stainless Steel

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5

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1

2 **Abstract:**

3 Microelectrochemical measurements were performed to ascertain the effects of
4 atmospheric exposure on pitting at MnS inclusion on Type 304 stainless steel. The
5 exposure to air at 298 K and 50% RH for 30 and 90 days improved the resistance of the
6 investigated steel to pitting. The thickness of the oxide film on the inclusions increased
7 with the exposure time, and the dissolution of the inclusion was suppressed during
8 anodic polarization in NaCl and Na₂SO₄ solutions. The 90 days exposure effectively
9 inhibited the trench formation at the MnS/steel boundaries, making the inclusions less
10 active as the initiation sites for pitting.

11

12 **Keywords:**

13 A. Stainless steel; C. Pitting corrosion; B. Polarization; B. AES; B. SEM.

14

15 **Main text:**

16 **1. Introduction**

17 The localized corrosion resistance of stainless steels changes with time after
18 surface polishing and/or polarization, since the composition, thickness, and structure of

1 the passive films on stainless steels change as a function of time ¹⁻⁶. In general, the
2 protective properties of the film increase with time after polishing due to the thickening
3 of the film ^{3,4}. Basically, complex electrochemical processes are involved in the aging of
4 corrosion resistance of stainless steels. Maurice *et al.* studied the structure of passive
5 films of stainless steels using X-ray photoelectron spectroscopy and scanning tunneling
6 microscopy ^{1,2}. They revealed that aging under polarization results in the crystallization
7 of the inner oxide layer in epitaxy with the steel substrate, which is beneficial to the
8 stability of the passive film in air. Therefore, the corrosion resistance of stainless steels
9 varies with time over their service life. The aging is an important subject for corrosion
10 engineering of stainless steels, and a thorough understanding of the aging mechanisms
11 helps in the endeavor to create corrosion resistant surfaces for stainless steels.

12 Over the course of decades of research work into pitting corrosion on stainless
13 steels has revealed a considerable amount of information about pit initiation processes
14 ⁷⁻¹¹. Sulfide inclusions such as MnS readily act as initiation sites of pitting ¹²⁻³⁸. In our
15 previous works ³⁹⁻⁴², we proposed that the pit initiation process at the MnS inclusions in
16 stainless steels is as follows: 1) the inclusion dissolution in chloride solutions leads to
17 the deposition of elemental sulfur on and around the inclusions; 2) the synergistic effect
18 of the elemental sulfur and chloride ions causes the dissolution of the stainless steel

1 matrix at the MnS/steel boundaries, resulting in the formation of trenches; 3) the
2 hydrolysis reaction of Cr^{3+} released from the steel decreases the pH in the trenches, and
3 the electrode potential inside the trenches decreases due to iR -drop; 4) a stable pit is
4 initiated as the local transition from the passive to active state inside the trenches. This
5 pit initiation mechanism suggests that the trench formation at the MnS/steel boundaries
6 is a precursor of pitting in stainless steels. The inhibition of the inclusion dissolution
7 decreases the deposition of elemental sulfur, which improves the pitting corrosion
8 resistance of stainless steels.

9   Oxide films on sulfide inclusions play an important role in the susceptibility to
10 pitting⁴³⁻⁴⁷. Muto *et al.* demonstrated the Cr-containing oxide films were formed on the
11 CrS inclusions and grew with the electrode potential, which suggests it is the oxide
12 films on the CrS inclusions which prevent the anodic dissolution of the inclusions,
13 thereby leading to an increased resistance to pit initiation⁴⁵. The oxide films on MnS
14 and (Cr, Mn)S inclusions were also studied using scanning Auger microanalysis, and it
15 was indicated that the (Cr, Mn)S inclusions are covered with an oxide type film
16 containing Cr and S^{44,45}. Shimahashi *et al.* found that the Ti-oxide enriched layers were
17 formed on TiS and $\text{Ti}_4\text{C}_2\text{S}_2$ inclusions, and these inclusions neither dissolved nor acted
18 as initiation sites for pitting of stainless steel (in the passive and the trans-passive

regions) in 3 M NaCl solution ⁴⁶. However, there is no or little information on the aging effect on the oxide film properties on the sulfide inclusions.

Stainless steels are widely used for architectural applications, such as roofing and walls. In atmospheric environments, pitting causes discoloration (rust staining) on the steel surfaces, which compromises the esthetic appearance of architecture considerably.

The pitting behavior of stainless steels in outdoor environments has been extensively investigated through long-term exposure tests ⁴⁸. It is generally accepted that most of stainless steels experience severe corrosion within the first two years in marine environments, and there is a correlation between rust staining resistance and pitting resistance ⁴⁹. Even in atmospheric environments, the sulfide inclusions act as initiation sites for pitting. In this study, we focused on the effect of atmospheric aging on both the dissolution of MnS inclusions and the pit initiation processes in Type 304 stainless steel.

2. Experimental

2.1. Specimens and electrolytes

A commercial re-sulfurized (sulfur addition) Type 304 stainless steel bar with a diameter of 70 mm (a hot-rolled bar) was used in this study. This stainless steel was

1 heat-treated at 1353 K for 0.5 h and quenched in water. Sulfur is one of the main
2 elements improving machinability with the formation of large MnS inclusions elongated
3 in the rolling direction and evenly dispersed in steel matrix. To clarify the effect of
4 atmospheric aging on dissolution of MnS inclusions and pitting initiation process at the
5 inclusions, the re-sulfurized stainless steel containing large MnS inclusions was used as
6 a specimen. The chemical composition of the stainless steel is listed in Table I. The
7 stainless steel used in the present study was the same as that used in a previous study⁴⁷.
8 After the heat-treatment, the stainless steel bar was cut into *ca.* 15 mm × 25 mm
9 coupons parallel to the rolling direction. The specimens were mechanically ground with
10 SiC paper through a 1500 grid, finished with 1 μm diamond paste, and finally cleaned
11 ultrasonically with ethanol. The re-sulfurized stainless steel contains large non-metallic
12 inclusions such as MnS elongated in the rolling direction. The MnS inclusions are
13 clearly visible in as-polished conditions without etching since they are darker than the
14 steel matrix. Prior to taking measurements, the specimens were exposed to air at 298 K
15 and 50% relative humidity (RH) for 1, 30, and 90 days in order to investigate the
16 correlation between the oxide film formed on the MnS inclusions and the pit initiation
17 processes in the stainless steel. An ESPEC SH221 environmental chamber was used to
18 perform the atmospheric exposure tests.

1   Anodic polarization curves were measured in 0.1 M Na₂SO₄, 0.1 M NaCl, and 3 M
2   NaCl solutions. The pHs of the 0.1 M Na₂SO₄, 0.1 M NaCl, and 3 M NaCl solutions
3   were 5.8, 5.8, and 5.1, respectively. All the measurements were conducted at 298 K
4   under naturally aerated conditions.

5

6   2.2. Electrochemical measurements

7   In order to analyze the effect of the exposure period on the polarization behavior of
8   a small area containing a strip-like MnS inclusion, the specimen surfaces were masked
9   using a vinyl copolymerized resin (Sunhayato Corp., Japan), as shown in Fig. 1. The
10   size of the electrode area was about 300 μm × 150 μm. Curing of the resin at room
11   temperature is essentially complete after 1 day. A glass cell was put on the masked
12   specimen to preserve the solution. A small Ag/AgCl reference electrode and a platinum
13   wire counter electrode were set on the glass cell. The reference electrode was calibrated
14   with an Ag/AgCl (3.33 M KCl) electrode before the experiments, and all potentials cited
15   in this paper refer to the Ag/AgCl (3.33 M KCl) electrode (0.206 V vs. standard
16   hydrogen electrode at 298 K). The microscopic polarization measurements were carried
17   out with a battery-powered potentiostat ³⁴ to control the electrode potential of the
18   specimen with the micro-scale electrode area. The potential scan rate was 3.8×10^{-4} V

1 s⁻¹ (23 mV min⁻¹). The current signals were measured using an AD-converter (NI
2 DAQCard-6036E) with a time interval of 0.5 s, which was the average value of 100
3 points sampled at 1000 Hz. Details of the experimental setup has been described
4 elsewhere³⁹.

5

6 2.3. Material characterization

7 Auger electron spectroscopy (AES) was carried out using a ULVAC-PHI Model 680
8 to clarify the surface composition of the MnS inclusions and the stainless steel matrix.
9 The accelerating voltage and current of primary electron beam were adjusted to 10 kV
10 and 10 nA, respectively. AES depth profiling was performed by sputtering the specimen
11 surfaces with a 3 kV Ar⁺ ion beam. The thickness of the surface oxide film was
12 estimated according to the sputtering rate of a SiO₂ film on Si. A JEOL JSM-7100F field
13 emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive
14 X-ray spectroscopy (EDS) system was employed to observe the MnS inclusion surfaces
15 at an accelerating voltage of 5 kV and to analyze the chemical compositions of the MnS
16 inclusions at an accelerating voltage of 20 kV.

17

18

3. Results and Discussion

3.1. Inclusion characterization

Figure 2 displays the SEM images of the typical inclusions in the re-sulfurized Type 304 stainless steels exposed to air at 298 K and 50% RH for 1, 30, and 90 days and EDS spectra taken on these inclusions. The relative concentrations of Mn, S, Fe, Cr, Ni, and O are listed in Table II. The surface of the inclusions remained flat after the exposure for 1, 30, and 90 days, indicating that the inclusions did not dissolve under these conditions. The atomic ratios of Mn and S of these three inclusions were almost 1:1, and the concentrations of Fe and Cr were lower than that of Mn. For simplicity, this type of inclusion is referred to as MnS in this paper. The MnS inclusions were observed in grain interior and transgranular locations because the re-sulfurized stainless steel contains large MnS inclusions elongated in the rolling direction. In our previous works^{39,42}, the intersection of the MnS inclusions and the grain boundaries did not act as the initiation sites of pitting.

3.2. Surface films on MnS inclusions and steel matrixes

An AES analysis was carried out to ascertain the effect of the exposure period on the surface compositions of the MnS inclusions and the stainless steel matrix. Figure 3

1 displays the AES spectra (no sputtering) of the steel and the MnS inclusions exposed for
2 1, 30, and 90 days. The squared areas in the SEM images were the locations where the
3 AES spectra were acquired. The spectra on the steel surfaces (Figs. 3a-c) indicate the
4 existence of a passive film which consists mainly of Fe, Cr and a small amount of Ni.
5 No outstanding changes were observed with the exposure period. In Figs. 3d-f, the
6 strong signals of O, especially on the specimen exposed for 30 and 90 days, were
7 observed even on the sulfide inclusions, suggesting that the inclusions were covered
8 with oxide enrichment layer similar to the passive film on the steel matrixes. After the
9 exposure for 1 day, no Fe peak was detected on the inclusion, but Fe peaks appeared
10 after the exposure for 30 and 90 days. Moreover, the intensity of S decreased with over
11 the 30 days exposure period, but the intensity of O increased. It was expected that
12 atmospheric exposure affects the surface composition of the inclusions, as well as
13 surface film thickness. Figure 4 shows the AES depth profiles of the relative
14 concentrations of S, O, Cr, Mn, Fe, and Ni on the MnS inclusions and the steel matrixes
15 exposed for 1, 30, and 90 days. As seen in Figs. 4a-c, the relative concentration of O
16 decreased gradually from the surface to inside the inclusions. It is clear that the oxide
17 enriched layer existed on the inclusions even though the S concentration was around 30
18 at%. This layer is described simply as oxide film hereafter. The thicknesses of the oxide

1 film on the MnS inclusions exposed for 1, 30, and 90 days were determined to be *ca.*
2 0.5, 1.2, and 1.1 nm, respectively, as the medium points between the maximum and
3 minimum concentrations of O. Figure 5 displays the changes in the thickness of the
4 oxide film existing on the MnS inclusions as a function of the exposure period,
5 indicating that the oxide film thickness doubled within the 30-day aging period.

6 From Figs. 4d-f, the oxide film thicknesses on the stainless steel matrix were
7 determined by the same procedure used in the case of the inclusions. The oxide film
8 thicknesses on the steel matrixes exposed for 1, 30, and 90 days were 1.5, 1.5, and 2.2
9 nm, respectively. The estimated oxide films in this study were thinner than the known
10 thickness of passive film in long-term atmospheric exposure tests. Hamada et al.
11 measured the thickness of passive film on Type 304 stainless steel kept in clean air for
12 more than 10 year, and the reported thickness was 3-5 nm⁵⁰. Figure 5 shows the
13 changes in the thickness of the oxide film formed on the steel matrixes as a function of
14 the exposure period. No drastic changes in the thickness or the composition of the oxide
15 film on the steel matrix were observed. From the results presented so far, it was
16 confirmed that the oxide film on the MnS inclusions tends to grow within 30 days,
17 whereas no drastic changes in the film on the steel matrix occur within 30 days. For the
18 oxide film on the inclusions, a signal for Fe was detected after 30 days, suggesting that

1 the oxidation of Fe contributed to the thickening of the oxide film on the inclusion
2 surfaces; however, the changes in chemical states of Mn, S, and Fe in the oxide film
3 with the exposure period have remained unknown.

4 5 3.3. Pitting potential of area with MnS inclusions

6 In order to clarify the effect of the exposure period on the pitting potentials of the
7 areas with the MnS inclusions in the stainless steel, the anodic polarization curves of a
8 micro-scale electrode area containing a strip-like MnS inclusion were measured in 3 M
9 NaCl. Figures 6a-c show the microscopic anodic polarization curves. The anodic
10 polarization measurements were repeated five times on the different specimens exposed
11 for 1 day (control sample), and stable pitting at MnS inclusions was observed in all
12 times (100%). For the specimens exposed for 30 and 90 days, the anodic polarization
13 was performed two times on different specimens, and no pit was initiated in all times
14 (100%). Typical polarization curves were displayed in Fig. 6. The polarization
15 measurements were started at -0.2 V. Cathodic current flowed initially, and anodic
16 current was measured above around -0.05 V. The corrosion potentials tended to shift to
17 anodic direction as the time of aging increased. The anodic polarization curves indicated
18 a broad current peak in the passive region of stainless steel around 0.3 V regardless of

1 the exposure period, which was anywhere between 1 and 90 days. Suter et al. studied
2 the dissolution behavior of MnS inclusions during potentiodynamic anodic polarization
3 measurements in 1 M Na₂SO₄ and 1 M NaCl solutions with a microelectrochemical
4 technique and an atomic force microscopy (AFM) ²⁴. They demonstrated that the
5 dissolution of MnS inclusions results in a broad current peak at around 0.3 V in an
6 anodic polarization curve, and the pit initiation at MnS inclusions occurs in the potential
7 range of the dissolution of MnS inclusions. In the anodic polarization curve of the
8 specimen exposed for 1 day (Fig. 6a), a lot of current spikes due to the initiation of
9 metastable pits and a sharp increase in current density due to the initiation of a stable pit
10 were measured in the potential range of the dissolution of the MnS inclusion. The
11 potential control was interrupted immediately after the stable pit initiation at 0.35 V. In
12 contrast, as shown in Figs. 6b and 6c, no stable pit was initiated on the specimens
13 exposed for 30 and 90 days. In the polarization curves of the specimens exposed for 30
14 and 90 days, only one current spike due to the initiation of a metastable pit was
15 observed around 0.3 V, which was in the potential range of the MnS inclusion
16 dissolution. The anodic polarization was then stopped at around 0.6 V. Figures 6d-i
17 exhibit the optical microscope images of the MnS inclusions before and after the
18 polarization, and Figs. 6j-l display SEM images of the MnS inclusions after the

1 polarization. The color of the MnS inclusions had changed from light gray to brown
2 after the polarization (Figs. 6d-i). Although the surface of the inclusions dissolved
3 during the polarization, almost all of the inclusions remained after the polarization (Figs.
4 6j-l). As seen in Fig. 6g, in the case of the specimen exposed for 1 day, metastable pits
5 and one stable pit were initiated at the MnS/steel boundary. For the specimens exposed
6 for 30 and 90 days, one metastable pit appeared at the boundary as shown in Figs. 6h
7 and 6i. It was confirmed that the initiation site of the pitting is at the MnS/steel
8 boundary, regardless of the exposure period. It is interesting to note that the long term
9 exposure (over 30 days) improves resistance of the investigated stainless steel to pitting
10 initiated at the MnS inclusions. It is expected that the oxide film on the inclusion
11 surfaces became thicker, leading to an improvement in the pitting corrosion resistance.

12

13 3.4. MnS inclusion dissolution

14 It was expected that the oxide film on the MnS inclusions would suppress the
15 anodic dissolution of the MnS inclusions. As mentioned above, the MnS dissolution
16 product, elemental sulfur, has been shown to be one of the triggers for the pit initiation
17 on stainless steels. The inclusion dissolution is an essential factor in determining the
18 formation of the elemental sulfur. The anodic polarization curves of a micro-scale

1 electrode area containing a strip-like MnS inclusion were measured in 0.1 M Na₂SO₄
2 (Fig. 7).

3   Figures 7a-c show the microscopic anodic polarization curves of the specimens
4 exposed for 1, 30, and 90 days measured in 0.1 M Na₂SO₄. The polarization was started
5 at -0.2 V and interrupted at around 0.6 V. Figures 7d-i display the optical microscope
6 images of the MnS inclusions before and after the polarization, and Figs. 7j-l display
7 SEM images of the MnS inclusions after the polarization. The color of the MnS
8 inclusions had changed from light gray to brown after the polarization (Figs. 7d-i). The
9 surface of the inclusions slightly dissolved during the polarization (Figs. 7j-l). The
10 dissolution of the MnS inclusions brought about a broad peak in the current density in
11 the passive region of the stainless steel around 0.3 V²⁴. The estimated passive current
12 densities on the steel matrix are indicated by the broken lines in Figs. 7a-c. The total
13 electric charges passed during the MnS inclusion dissolution were calculated subtracting
14 the passive currents on the steel matrix. For instance, the current of the MnS dissolution
15 was calculated from the anodic current in the range from *ca.* 0.25 to 0.45 V subtracted
16 the estimated passive current on the steel matrix (the broken lines in Figs. 7a-c). The
17 area of MnS inclusions was estimated from the number of pixels in bitmap images of
18 the electrode surfaces using a digital image processing (Table III). Thus, the obtained

1 electric charges for the specimens exposed for 1, 30, and 90 days were 8280, 3730, and
2 3330 C m⁻², respectively. In these calculations, the values were normalized by the area
3 of the MnS surfaces.

4 The same experiments were also carried out in a weak chloride solution (0.1 M
5 NaCl), in which no stable pit was initiated at the MnS inclusions. Figures 8a-c show the
6 microscopic anodic polarization curves of the specimens exposed for 1, 30, and 90 days
7 measured in 0.1 M NaCl. Figures 8d-i exhibit the optical microscope images of the MnS
8 inclusions before and after the polarization, and Figs. 8j-l display SEM images of the
9 MnS inclusions after the polarization. As was the case in 0.1 M Na₂SO₄, the color of the
10 MnS inclusions changed from light gray to brown (Figs. 8d-i), and the surface of the
11 inclusions slightly dissolved after the anodic polarization in 0.1 M NaCl (Figs. 8j-l). The
12 current spikes due to the initiation of metastable pitting were measured in the potential
13 range from 0.3 to 0.5 V, which was the dissolution potential range of the inclusion ²⁴.
14 The metastable pits were initiated not only at the MnS inclusions shown in Figs. 8g-i,
15 but also at small (diameter < 1 μm) MnS inclusions found within the electrode areas
16 (Figs.8m-r). From the same procedure used in the case of 0.1 M Na₂SO₄, the electric
17 charges passed for the inclusions dissolution were calculated. The results for the
18 inclusions on the specimens exposed for 1, 30, and 90 days were 22300, 5280, and

1   13100 C m⁻², respectively.

2   Figure 9 presents the changes in the electric charge of the MnS inclusion
3   dissolution as a function of the exposure period. As seen in Fig. 9, even though the
4   dissolution amount of the MnS inclusion on the specimen exposed for 90 days doubled
5   compared with that exposed for 30 days, the dissolution amount of the MnS inclusions
6   on the specimens exposed for 30 and 90 days was obviously suppressed to less than half
7   that for the specimen exposed for 1 day. The wide range of scatter in the dissolution
8   amount of the MnS inclusions was considered to come from the difference in the
9   morphology (shape and size) and composition of the MnS inclusions used in this
10   experiment. Webb et al. detected thiosulfate ions at a location 20 μm above a MnS
11   inclusion during an anodic polarization measurement with a Pt wire microelectrode into
12   an electrochemical microcell⁵¹. Thiosulfate ions are assumed to be MnS inclusion
13   dissolution products. Chiba et al. found out the deposition of elemental sulfur on and
14   around the MnS inclusions after anodic polarization in 3 M NaCl solution with a
15   microscope Raman spectroscopy⁴⁰. The elemental sulfur was likely to be produced by
16   disproportionation reaction^{52,53} and/or reduction reaction⁵⁴ of thiosulfate ions.
17   Therefore, the depth of the dissolved MnS inclusions was deduced²³ assuming that the
18   MnS inclusions dissolved electrochemically according to the following reaction^{13,31}:

1 The mass of the dissolved MnS inclusion, m (g), can be expressed by the following
2 equation:

$$m \text{ (g)} = \frac{Q \cdot M}{n \cdot e \cdot N_A} , \quad (2)$$

3 where Q is the electric charge attributed to the MnS inclusion dissolution, M is the
4 molar mass of MnS ($M = 87 \text{ g mol}^{-1}$), n is the number of electrons involved in the MnS
5 dissolution reaction ($n = 4$ in eq. 1), e is the charge of electron ($e = 1.16 \times 10^{-19} \text{ C}$) and
6 N_A is the Avogadro's number ($N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$). The average dissolved depth
7 (μm) of the MnS inclusion is estimated by the following equation:

$$\delta \text{ (}\mu\text{m)} = \frac{m}{S \cdot \rho} , \quad (3)$$

8 where S is the MnS inclusion area, and ρ is the density of MnS ($\rho = 4 \times 10^{-3} \text{ ng } \mu\text{m}^{-3}$)³¹.

9 The calculated values are listed in Table III. The average dissolved depth of the
10 inclusions during the polarization in 0.1 M Na₂SO₄ was 0.65, 0.29, and 0.26 μm for the
11 specimens exposed for 1, 30, and 90 days, respectively. In 0.1 M NaCl solution, the
12 dissolved depth was 1.7, 0.41, and 1.0 μm for the specimens exposed for 1, 30, and 90
13 days, respectively. The calculated average dissolved depth of the inclusions was larger
14 than the estimated thickness of the oxide film formed on the inclusions; however, it
15 should be noted that the MnS inclusions dissolved mainly at the edges while the center

1 dissolved only slightly as shown in the SEM images in Figs. 7 and 8. The oxide film
2 formed on the MnS inclusions was assumed to suppress the dissolution of the center
3 portion of the inclusions. Although the oxide film inhibits the dissolution of the MnS
4 inclusions, the protective ability of the oxide film is imperfect, which results in the
5 oxidation (discoloration) of the inclusion surface during the anodic polarization. The
6 electric charges measured in 0.1 M NaCl were larger than those in 0.1 M Na₂SO₄,
7 implying that chloride ions accelerated the dissolution of the inclusions; however, it is
8 clear that the atmospheric exposure in air at 298 K and 50% RH suppresses the MnS
9 inclusion dissolution even in chloride-containing solutions.

10 As shown in Fig. 6, a stable pit was initiated at the MnS inclusion on the specimen
11 exposed for 1 day in 3 M NaCl; however, no stable pit was initiated at the MnS
12 inclusions on the specimens exposed for 30 and 90 days. The thickness of the oxide film
13 on the inclusion exposed for 30 and 90 days was double that of the film exposed for 1
14 day, and the amount of the dissolved MnS inclusion decreased to about half that of the
15 specimen exposed for 1 day. Judging from these results, it is assumed that the decrease
16 of the dissolution of the MnS inclusions resulted from the growth of the oxide film on
17 the inclusions, which improved the resistance of the investigated stainless steel to
18 pitting initiated at the MnS inclusions. It was demonstrated that a precursor of the pit

1 initiation at the MnS inclusions is the dissolution of the steel side at the MnS/steel
2 boundaries forming the trenches where the pit initiation occurs as a local active
3 dissolution of the steel matrix. Elemental sulfur, which is one of the dissolution products
4 of the MnS inclusions, and chloride ions cause the dissolution of the steel matrix,
5 forming the trenches at the boundaries. The suppression of the MnS inclusion
6 dissolution is likely to have impacts on the trench formation at the MnS/steel boundaries
7 in terms of reducing the deposition of elemental sulfur. As can be seen in Fig. 4, the S
8 concentrations in the surface films on the inclusions exposed for 30 and 90 days were
9 lower compared with that on the inclusion exposed for 1 day. This seems to contribute
10 to the decrease in the amount of dissolution of the inclusions after 30 and 90 days of
11 exposure.

12

13 3.5. Trench at MnS/steel boundary

14 In order to compare the dissolution morphology at the MnS/steel boundaries
15 introduced by the inclusion dissolution in chloride-containing environments, the
16 potentiodynamic anodic polarization from -0.2 V to 0.35 V was carried out in 3 M NaCl.
17 The specimen was the re-sulfurized Type 304 stainless steel exposed to air at 298 K and
18 50% RH for 90 days. The size of the electrode area was $4.5 \times 10^{-8} \text{ m}^2$. Figure 10 shows

1 the microscopic anodic polarization curve and the optical microscope and SEM images
2 of the MnS inclusion before and after the polarization. The potential control was
3 interrupted at 0.35 V where the stable pit was initiated at the inclusion on the specimen
4 exposed for 1 day in 3 M NaCl (Fig. 6a). In Figs. 6a and 10a, increases in the current
5 densities due to the dissolution of the MnS inclusions were observed above
6 approximately 0.2 V in both the anodic polarization curves of the specimens exposed
7 for 1 and 90 days, but no pit was initiated at the MnS inclusion on the specimen
8 exposed for 90 days. The color of the MnS inclusion on the specimen exposed for 90
9 days changed from light gray to brown (Figs. 10b and 10c). The same behavior was
10 observed for the specimen exposed for 1 day (Figs. 6d and 6g). Figure 11 displays the
11 enlarged SEM images of the MnS inclusions after the polarization. As shown in Fig. 11a
12 (1 day exposure), the surface of the inclusion apparently dissolved, and a trench was
13 formed along the MnS/steel boundary. In contrast, for the specimen exposed for 90 days
14 (Fig. 11b), the surface of the MnS inclusion remained flat, and a trench partially formed
15 at the right side of the inclusion. It seems reasonable to conclude that exposure for 90
16 days decreased the amount of dissolution of the MnS inclusion and inhibited the trench
17 formation at the MnS/steel boundary, resulting in the improvement of pitting corrosion
18 resistance at the MnS inclusions in the stainless steels. As seen in Figs. 4b and 4c, the

1 surface oxide films on the inclusions contained around 20 at% of S even after 30 and 90
2 days of exposure; therefore, it is recognized that this film, the oxide enrichment layer on
3 the MnS inclusion surfaces, suppressed the inclusion dissolution rate but did not
4 completely prevent the onset of the dissolution.

5 From the results and the analysis thus far, it is possible that the mechanism for the
6 improving the pitting corrosion resistance of the investigated stainless steel by the
7 exposure to air at 298 K and 50% RH over 30 days is as follows. The exposure leads to
8 the growth of the oxide layer on the MnS inclusions (Figs. 4 and 5), suppressing the
9 dissolution of the MnS inclusions (Figs. 7, 8, and 9). Chiba et al. detected elemental
10 sulfur on and around the dissolving MnS inclusions. They demonstrated that the
11 synergistic effect of the elemental sulfur and chloride ions in environments caused the
12 dissolution of the stainless steel matrix, resulting in the formation of the trench at the
13 MnS/steel boundaries ⁴⁰. The elemental sulfur is likely to be produced by
14 disproportionation reaction ^{52,53} and/or reduction reaction ⁵⁴ of thiosulfate ions which
15 are the dissolution products of MnS inclusions ⁵¹. The suppression of the MnS
16 dissolution by the growth of the oxide layer on the inclusions is supposed to decrease
17 the deposition of the elemental sulfur and inhibits the formation of the trench at the
18 boundaries (Figs. 10 and 11). Additionally, they proposed that the pit initiation at the

1 MnS inclusions is assumed to be the local transition from the passive to active state
2 occurred at the bottom of the trenches ⁴⁰. The localized transition from the passive to
3 active state results from the decrease of pH in the trenches due to the hydrolysis reaction
4 of Cr^{3+} released from the dissolution of the stainless steel and the decrease of the
5 electrode potential at the bottom of the trenches. Therefore, the trench formation is a
6 trigger for the pit initiation at the MnS inclusions. The atmospheric exposure for over 30
7 days (atmospheric aging) results in the inhibition of the trench formation at the
8 boundaries. This explains why the MnS inclusions become less active due to
9 atmospheric exposure (Fig. 6). From this point of view, the application of surface
10 modifications of the inclusions has clear potential in designing an improved technique
11 for the pitting corrosion resistance of stainless steels.

12

13

14 **4. Conclusions**

15 1. The MnS inclusion in the re-sulfurized Type 304 stainless steel exposed to air for 1
16 day at 298 K and 50% RH acted as the initiation site of stable pitting during the
17 anodic polarization measurement in 3 M NaCl. The surface of the inclusion slightly
18 dissolved, and a trench was formed along the MnS/steel boundary.

- 1   2. The exposure for 30 and 90 days improved the resistance of the investigated
2   re-sulfurized Type 304 stainless steel to stable pitting at the MnS inclusions in 3 M
3   NaCl. In the case of the specimens exposed for 90 days, the surface of the inclusion
4   remained flat, and the trench formation at the boundary was effectively inhibited
5   during the anodic polarization measurement in 3 M NaCl.
- 6   3. The AES depth profiles demonstrated that the thickness of the oxide film formed on
7   the MnS inclusions increased with the exposure period. The amount of dissolution
8   of the inclusion during the anodic polarization was suppressed by the atmospheric
9   exposure.
- 10   4. The proposed mechanism for the improving the pitting corrosion resistance of the
11   investigated stainless steel by the exposure over 30 days is as follows: 1) the
12   exposure leads to the growth of the oxide film on the MnS inclusions, preventing the
13   inclusions from dissolving; 2) the suppression of the MnS dissolution is thought to
14   decrease the deposition of elemental sulfur on and around the inclusions; 3) the
15   decrease in the deposition of the elemental sulfur inhibits the formation of the trench
16   at the boundaries; 4) the inhibition of the trench formation at the boundaries makes
17   the MnS inclusions less active as the initiation sites for pitting.
- 18

1

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- 3
- 4
- 5

1   **Caption list**

2

3   **Table I**

4   Chemical composition (mass%) of re-sulfurized Type 304 stainless steel.

5

6   **Table II**

7   Relative composition (at%) of Point 1, 2, and 3 shown in Fig. 2.

8

9   **Table III**

10   Dissolution amount of MnS inclusion calculated from the broad current peak in Figs.

11   7a-c and 8a-c.

12

13   **Figure 1**

14   Optical microscope image of micro-scale electrode area.

15

16   **Figure 2**

17   SEM images of MnS inclusions exposed to air at 298 K and 50% RH for (a) 1 day, (b)

18   30 days, and (c) 90 days, and EDS spectra at (d) Point 1, (e) Point 2, and (f) Point 3.

1

2   **Figure 3**

3   AES spectra of (a-c) stainless steel matrix and (d-f) MnS inclusion; exposure periods
4   were (a, d) 1 day, (b, e) 30 days, and (c, f) 90 days.

5

6   **Figure 4**

7   AES depth profiles of (a-c) MnS inclusion and (d-f) stainless steel matrix; exposure
8   periods were (a, d) 1 day, (b, e) 30 days, and (c-f) 90 days.

9

10   **Figure 5**

11   Changes in thicknesses of oxide film on MnS inclusion and stainless steel matrix as a
12   function of exposure period in air at 298 K and 50% RH.

13

14   **Figure 6**

15   Microscopic polarization curves of re-sulfurized Type 304 stainless steel exposed to air
16   at 298 K and 50% RH for (a) 1 day, (b) 30 days, and (c) 90 days measured in 3 M NaCl
17   (electrode areas: (a) *ca.* $5.1 \times 10^{-8} \text{ m}^2$, (b) *ca.* $5.6 \times 10^{-8} \text{ m}^2$, (c) *ca.* $5.3 \times 10^{-8} \text{ m}^2$).

18   Optical microscope images of MnS inclusions in the electrode areas (d-f) before and

(g-i) after the polarization; exposure periods were (d, g) 1 day, (e, h) 30 days, and (f, i) 90 days. SEM images of MnS inclusions in the electrode areas after the polarization; exposure periods were (j) 1 day, (k) 30 days, and (l) 90 days.

Figure 7

Microscopic polarization curves of re-sulfurized Type 304 stainless steel exposed to air at 298 K and 50% RH for (a) 1 day, (b) 30 days, and (c) 90 days measured in 0.1 M Na₂SO₄ (electrode areas: (a) *ca.* $4.8 \times 10^{-8} \text{ m}^2$, (b) *ca.* $3.6 \times 10^{-8} \text{ m}^2$, (c) *ca.* $4.8 \times 10^{-8} \text{ m}^2$). Optical microscope images of MnS inclusions in the electrode areas (d-f) before and (g-i) after the polarization; exposure periods were (d, g) 1 day, (e, h) 30 days, and (f, i) 90 days. SEM images of MnS inclusions in the electrode areas after the polarization; exposure periods were (j) 1 day, (k) 30 days, and (l) 90 days.

Figure 8

Microscopic polarization curves of re-sulfurized Type 304 stainless steel exposed to air at 298 K and 50% RH for (a) 1 day, (b) 30 days, and (c) 90 days measured in 0.1 M NaCl (electrode areas: (a) *ca.* $6.1 \times 10^{-8} \text{ m}^2$, (b) *ca.* $2.7 \times 10^{-8} \text{ m}^2$, (c) *ca.* $6.1 \times 10^{-8} \text{ m}^2$). Optical microscope images of MnS inclusions in the electrode areas (d-f) before and

(g-i) after the polarization; exposure periods were (d, g) 1 day, (e, h) 30 days, and (f, i) 90 days. SEM images of MnS inclusions in the electrode areas after the polarization; exposure periods were (j) 1 day, (k) 30 days, and (l) 90 days. Optical microscope images of initiation sites of metastable pits at small (diameter $< 1 \mu\text{m}$) MnS inclusions (m-o) before and (p-r) after the polarization.

Figure 9

Changes in electric charges per unit MnS inclusion area measured in the anodic polarization curves shown in Figs. 7a-c (0.1 M Na_2SO_4) and Figs. 8a-c (0.1 M NaCl) as a function of exposure period in air at 298 K and 50% RH.

Figure 10

(a) Microscopic polarization curve of re-sulfurized Type 304 stainless steel exposed to air at 298 K and 50% RH for 90 days measured in 3 M NaCl (electrode area: *ca.* $4.5 \times 10^{-8} \text{ m}^2$). Optical microscope images of MnS inclusion in the electrode area (b) before and (c) after the polarization. (d) SEM image of MnS inclusion in the electrode area after the polarization.

1

2   **Figure 11**

3   Enlarged SEM images of MnS inclusions in the electrode areas marked by broken lines

4   in (a) Fig. 6j and (b) Fig. 10d.

5

6

1 **Table I**

C	Si	Mn	P	S	Ni	Cr	Mo	Cu	Ti	Al	O	N	Fe
0.051	0.39	1.51	0.039	0.0215	8.27	18.28	0.21	0.35	0.002	0.002	0.0023	0.0799	Bal.

2

3

4 **Table II**

Point No.	Exposure period	Mn	S	Fe	Cr	Ni	O
1	1 day	48	42	4	5	<1	<1
2	30 days	48	44	3	5	<1	<1
3	90 days	38	38	14	8	1	<1

5

6

1

2 **Table III**

	0.1 M Na ₂ SO ₄			0.1 M NaCl		
	1 day	30 days	90 days	1 day	30 days	90 days
Electrode area (m ²)	4.8×10^{-8}	3.6×10^{-8}	4.8×10^{-8}	6.1×10^{-8}	2.7×10^{-8}	6.1×10^{-8}
Electric charge of MnS dissolution (μC)	0.59	0.49	0.25	2.2	0.44	0.98
MnS inclusion area (μm ²)	71	131	73	97	83	75
Electric charge of MnS dissolution per unit area (Cm ⁻²)	8280	3730	3330	22300	5280	13100
Mass of dissolved MnS inclusion (ng)	0.18	0.15	0.076	0.67	0.14	0.31
Average dissolution depth of MnS inclusion (μm)	0.65	0.29	0.26	1.7	0.41	1.0

3

Figure 1

Fig. 1

Figure 2

Fig. 2

Figure 3

Fig. 43

Figure 4

Fig. 54

Figure 5

Fig. 65

Figure 6

Fig. 36

Figure 7

Fig. 7

Figure 8

Fig. 8

Figure 9

Fig. 9

Figure 10

Fig. 10

Figure 11

(a) 1 day

(b) 90 days

Fig. 11