Microelectrochemical Aspects of Interstitial Carbon in Type 304 Stainless Steel: Improving Pitting Resistance at MnS Inclusion

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Type 304 stainless steel was subjected to low-temperature carburizing treatment to add excess interstitial carbon to its surface. The average carbon concentration in the carburized layer was ca. 2.6 mass%, and the lattice parameter was expanded by ca. 2.5% without any carbide precipitation. No pitting was initiated on the carburized stainless steel in 0.1 M NaCl. Microscopic polarization measurements of a small area with a MnS inclusion were performed in NaCl and Na2SO4 solutions to clarify the mechanism of the improved resistance against pitting corrosion. The anodic polarization in 0.1 M NaCl and 0.1 M Na2SO4 demonstrated that the carburizing treatment has little or no effect on the electrochemical dissolution behavior of the MnS inclusions. However, from the anodic polarization of the steel in the solution that simulates the vicinity of the dissolved MnS inclusions in chloride-containing environments, it was clarified that the carburizing treatment inhibits the active dissolution rate of the steel matrix to about one hundredth. It would appear that interstitial carbon inhibits the dissolution rate of the steel, resulting in a reduction in the dissolution depth of the trenches at the MnS/steel boundaries. It is likely that the carburization resulted in a suppression of both the acidification due to the hydrolysis reaction of Cr3+ and the potential decrease due to IR-drop in the trenches to the extent that the corrosivity inside the trenches is insufficient for the localized transition from the passive to active state. Therefore, pit initiation does not occur at the MnS inclusions on the carburized stainless steel in chloride-containing environments.

Stainless steels suffer from pitting corrosion in chloride-containing environments. Sulfide inclusions, such as MnS, are known to act as the initiation sites of pitting on stainless steels. MnS inclusions dissolve electrochemically in the passive region of stainless steels, causing the pit initiation on the steels in near-neutral chloride-containing environments. It has been proposed that the dissolution products of the MnS inclusions play an important role in pit initiation. The dissolution of MnS inclusions produces many types of sulfur-containing solutions. The synergistic effect of the elemental sulfur and chloride ions causes the dissolution of the stainless steel matrix at the MnS/steel boundaries, resulting in the formation of trenches; 3) the hydrolysis reaction of Cr3+ released from the steel matrix dissolution decreases the pH in the trenches, and at the same time, the electrode potential at the bottom of the trenches decreases due to the IR-drop. Finally, the transition from the passive to active state occurs locally at the bottom of the trenches. It would appear that inhibiting the dissolution of the steel side at the boundaries between the MnS inclusions and the steel matrix improves the pitting corrosion resistance of stainless steels in chloride-containing environments.

In previous work, we studied the pit initiation behavior at the MnS inclusions in stainless steels. The pit initiation mechanism was found to be as follows: 1) the dissolution of MnS inclusions in chloride-containing solutions leads to the deposition of elemental sulfur on and around the inclusions; 2) the synergistic effect of the elemental sulfur and chloride ions causes the dissolution of the stainless steel matrix at the MnS/steel boundaries, resulting in the formation of trenches; 3) the hydrolysis reaction of Cr3+ released from the steel matrix dissolution decreases the pH in the trenches, and at the same time, the electrode potential at the bottom of the trenches decreases due to the IR-drop. Finally, the transition from the passive to active state occurs locally at the bottom of the trenches. It would appear that inhibiting the dissolution of the steel side at the boundaries between the MnS inclusions and the steel matrix improves the pitting corrosion resistance of stainless steels in chloride-containing environments.

Experimental

Specimens and electrolytes.— The specimens used in this study were a commercial re-sulfurized Type 304 stainless steel bar with a diameter of 70 mm (mill-annealed) and a low-sulfur Type 304 stainless steel plate prepared by vacuum induction melting and hot-rolling (heat-treated at 1353 K for 0.5 h and quenched in water). The chemical compositions of the stainless steels are listed in Table I. In the case of the re-sulfurized stainless steel bar, the sulfur reacted with manganese during the solidification process to produce sulfide inclusions which were typically elongated and parallel to a hot-rolling direction. Generally, sulfide inclusions in stainless steels are composed of manganese, sulfur, and a small amount of chromium. In this paper, this type of inclusion is simply referred to as MnS. The steel bar and the plate were cut into ca. 15 × 25 mm coupons parallel to the rolling direction. In this paper, the specimens in this condition are referred to as “untreated”. Low-temperature carburizing was carried out at 743 K. The treatment procedure of the carburizing was the same as that
developed by Fujikawa et al.30 Prior to the carburizing, the specimens were machined to a maximum roughness of 1 μm. After the carburizing, the specimen surfaces were slightly dissolved in an acid solution or gently polished with 1 μm diamond paste to remove any carbon powder clinging to the specimens.

Before the polarization measurements, the specimens were mechanically ground with SiC paper through a 1500 grid, finishing with 1 μm diamond paste, and finally cleaned ultrasonically with ethanol. The non-metallic inclusions are clearly visible in the as-polished condition without etching since they are darker than the steel matrix.

Electrochemical measurements were performed in 0.1 M NaCl and 0.1 M Na2SO4 solutions. The pH of both the 0.1 M NaCl and the 0.1 M Na2SO4 solutions was 5.8. To ascertain the depassivation behavior of the steels in sulfur-containing environments, 3 M NaCl-1 mM Na2S2O3 and 3 M NaCl-1 mM Na2S2O3-0.1 M Na2CO3 were also used. The pH of these solutions was adjusted to 3.0 with HCl to produce sulfur suspensions by disproportionation and/or reduction reactions with thiosulfate ions.21 All the solutions were prepared from deionized water and analytical grade chemicals. All the measurements were conducted at 298 K under naturally aerated conditions.

**Characterization of carburized layer and inclusion.**—Vickers hardness was measured on the cross-section of the carburized re-sulfurized Type 304 stainless steel using a micro-Vickers hardness tester with a 10 g load and a loading time of 10 s. After the micro-Vickers hardness measurements, the cross-section was etched with 10 mass% oxalic acid to define the interface between the carburized layer and the stainless steel matrix. A radio frequency glow discharge optical emission spectroscopy (rf-GD-OES) was used to analyze the elemental depth profile of the carburized stainless steel. The instrument employs a Marcus-type rf-GD source geometry and a hollow anode 4 mm in diameter. An X-ray diffraction analysis (XRD), using Cu-Kα radiation (wavelength: λ = 1.5418 Å) with a Ni filter, was carried out to identify the lattice parameters of the untreated and the carburized re-sulfurized Type 304 stainless steels. A JEOL JSM-7100F field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system was employed to analyze the chemical compositions of MnS inclusions at an accelerating voltage of 20 kV.

**Microscopic polarization measurements under in situ observation.**—Anodic polarization curves were taken for the re-sulfurized and the low-sulfur Type 304 stainless steels (untreated and carburized conditions). With the exception of the electrode area (ca. 10 mm × 10 mm), the surface of the specimen was coated with an epoxy resin and subsequently with paraffin. The measurements were performed in a conventional three electrode cell; the counter electrode was a platinum plate and the reference electrode was an Ag/AgCl (3.33 M KCl) electrode. The working electrode potential was scanned at a constant rate of 3.8 × 10⁻⁴ V s⁻¹ (23 mV min⁻¹). The sizes of the electrode areas were scaled accurately to convert the measured current value to current density after the measurements.

**Results and Discussion**

**Characterization of carburized layer and MnS inclusion.**—Figure 2 exhibits the optical microscope image of the cross-section of the re-sulfurized Type 304 stainless steel treated in the low-temperature...
Carburizing process. The cross-section of the specimen was etched with 10 mass% oxalic acid. In the surface layer, it was hard to distinguish the grain boundaries. The thickness of the surface layer was estimated to be around 20 μm. The measurements of Vickers hardness were carried out before the etching. At point 1 and 2, the hardness was 425 Hv and 210 Hv, respectively. Since the hardness of the surface layer was higher than that of the steel matrix, it was assumed to be a carburized layer. Moreover, a comparison of the etching behaviors suggests it is likely that the corrosion resistance of the carburized layer is higher than the base (the untreated steel matrix).

Figure 3 shows the GD-OES depth profiles of the relative concentration of carbon, iron, chromium, and nickel. The relative concentration of carbon decreased gradually from the surface to inside the steel. The carburized layer was determined to be ca. 16 μm in thickness. The interface between the carburized layer and the untreated region was defined as the medium point between the maximum and minimum carbon concentration. The average carbon concentration in the carburized layer was ca. 2.6 mass% (12 at%), which was higher than the solubility limit of austenitic stainless steels.31

Figure 4 displays the XRD patterns of the carburized and the untreated specimens. As shown in this figure, all peaks were assigned to the austenitic phase (γ) of stainless steels,32 indicating no carbide precipitation occurred. The diffraction peaks shifted to lower angles after the carburizing. The diffraction peaks of the (111) face-centered cubic structure of the carburized and the untreated specimens were detected at 2θ = 42.449° and 43.551°, respectively. From these results, the lattice parameter of the austenitic phase was calculated to have changed from 3.599 Å to 3.688 Å. The interstitial carbon expanded the lattice parameter by ca. 2.5%.

In order to confirm the compositional changes of MnS inclusions with the carburizing treatment, EDS spectra were taken on the inclusions. Figure 5 shows the SEM images and EDS spectra of the MnS inclusions in the untreated stainless steel and the carburized layer of the treated specimen. The relative compositions of manganese, sulfur, iron, chromium, nickel, and oxygen are listed in Table II. The atomic ratio of Mn and S of the both inclusions was almost identical at 1:1, indicating that the carburizing treatment does not result in a dramatic change in the MnS inclusion composition.

Pitting corrosion resistance of carburized stainless steel.— In order to compare the pitting corrosion resistance of the carburized and the untreated re-sulfurized Type 304 stainless steels, Figure 6 displays the macroscopic anodic polarization curves measured in 0.1 M NaCl. In the case of the untreated stainless steel, sharp increases in the current density, which indicate the initiation of stable pitting, were observed at ca. 0.4 V. In the case of the carburized stainless steel, on the other hand, the surface of the stainless steel was completely passivated, and no sharp increase occurred, indicating no pit initiation. For stainless steels, MnS inclusions are known to act as the initiation sites of pitting in chloride-containing environments.2–7 It was expected that the higher pitting corrosion resistance of the carburized stainless steel is closely related to the electrochemical property of the MnS inclusions and the steel matrix around the inclusions.

Effect of carburizing on MnS inclusion dissolution.— In order to compare the anodic dissolution behaviors of the MnS inclusions in the untreated and the carburized stainless steels, the anodic polarization of a micro-scale electrode area containing a MnS inclusion was carried out in 0.1 M Na2SO4. The untreated and the carburized re-sulfurized Type 304 stainless steels were used for the anodic polarization. Figure 7 shows the microscopic anodic polarization curve of a small area with a MnS inclusion in the untreated specimen and the
Figure 5. (a) SEM image of MnS inclusion in untreated stainless steel and (b) EDS spectrum at Point 3. (c) SEM image of MnS inclusion in carburized layer and (b) EDS spectrum at Point 4.

The MnS inclusion was in the center of the 6.8 × 10⁻⁸ m² electrode area. The polarization was started at −0.2 V. Cathodic current was measured initially, and anodic current was measured above 0.07 V. The anodic current increased gradually with the electrode potential. The further increase in the anodic current attributed to the surface dissolution of the MnS inclusion brought about a broad peak around 0.4 V. The anodic current decreased above 0.48 V and returned to the passive current density of the stainless steel matrix. The anodic polarization was then stopped at around 0.6 V. Figures 7b–7e exhibit the optical microscope and SEM images of the inclusion. The inclusion which was light gray in the air before the polarization (Fig. 7b) became light brown during the polarization (Fig. 7c), implying that the surface of the inclusion dissolved during the polarization. Additionally, many gas bubbles were generated on the inclusion and at the MnS/steel boundary during the polarization (Fig. 7c). Almost the entire MnS inclusion disappeared on the electrode surface after rinsing with deionized water (Figs. 7d and 7e). The surface of the MnS inclusion dissolved during the anodic polarization, and then a large part of the inclusion fell off the specimen surface when the electrode surface was rinsed with deionized water after the polarization. In 0.1 M Na₂SO₄, only the MnS inclusions dissolve, and no trench is formed at the MnS/steel boundary.

Table II. Relative composition (atomic %) of Point 3 and Point 4 shown in Fig. 5.

| Point No. | Mn | S  | Fe | Cr | Ni | O   |
|-----------|----|----|----|----|----|-----|
| 3         | 46 | 46 | 2  | 6  | <1 | <1  |
| 4         | 31 | 31 | 23 | 12 | 3  | <1  |

Figure 6. (Color online) Macroscopic polarization curves of untreated and carburized re-sulfurized Type 304 stainless steels measured in 0.1 M NaCl at 298 K. Electrode areas were ca. 1 × 10⁻⁴ m².

Figure 8 shows the microscopic anodic polarization curve of a small area with a MnS inclusion in the carburized stainless steel in 0.1 M Na₂SO₄ and the surface appearances of the inclusion before and after the polarization. The cross-section parallel to the rolling direction of the carburized stainless steel embedded in an epoxy resin was used for the polarization. The thickness of the carburized layer was estimated to be around 16 μm by the GD-OES depth profile, and hence the micro-scale electrode area was prepared to include a MnS inclusion in the carburized layer. The electrode area was 2.1 × 10⁻⁸ m² in size. The size of MnS inclusions which can be observed using an optical microscope in the carburized and the untreated re-sulfurized Type 304 stainless steels was 1–8 μm in width and 1–150 μm in length. The MnS inclusions included in the electrode area in the carburized layer were relatively thinner and longer than that in the untreated specimen. The polarization was started at −0.2 V. Also in this case, the dissolution of the MnS inclusion brought about broad current peak in the potential range from 0.3 V to 0.46 V. The dissolution of the MnS inclusion in the carburized layer was found to occur almost in the same potential range as that in the untreated stainless steel. In this measurement (Fig. 8a), the electrode area was about one-third the size of that in the experiment represented in Fig. 7a, implying that the area ratio of MnS/steel in Fig. 8a was approximately three times larger than that in Fig. 7a. Since the dissolution current density of MnS inclusions is thought to be higher than that of stainless steel, the current density in Fig. 8a was about three times higher than that in Fig. 7a. Figures 8b–8e exhibit the optical microscope and
Figure 7. (Color online) (a) Microscopic polarization curve of untreated re-sulfurized Type 304 stainless steel measured in 0.1 M Na₂SO₄ at 298 K (electrode area: ca. 6.8 × 10⁻⁸ m²). Optical microscope images of MnS inclusion in the electrode area (b) in air before and (c) in the solution with a water immersion objective lens after the polarization. (d) Optical microscope image of MnS inclusion in the electrode area in the air after rinsing with deionized water. (e) SEM image of MnS inclusion in the electrode area after the polarization.

SEM images of the inclusion before and after the polarization. As was the case for the untreated stainless steel in 0.1 M Na₂SO₄ (Fig. 7), the inclusion which was light gray in the air before the polarization (Fig. 8b) became brown during the polarization (Fig. 8c), implying that the surface of the inclusion dissolved during the polarization. Additionally, many gas bubbles were generated on the inclusion and at the MnS/steel boundary during the polarization (Fig. 8c). A part of the MnS inclusion disappeared from the electrode surface after rinsing with deionized water (Figs. 8d and 8e). The surface of the MnS inclusion dissolved during the anodic polarization, and then a part of the inclusion fell off the specimen surface when the electrode surface was rinsed with deionized water after the polarization. From the results shown in Figs. 7 and 8, it was concluded that the carburizing has little or no effect on the anodic dissolution behavior of the MnS inclusions.

Effect of carburizing on pit initiation at MnS inclusion.—The anodic polarization curve of a micro-scale electrode area of the untreated re-sulfurized Type 304 stainless steel with a MnS inclusion was measured in 0.1 M NaCl. Figure 9 shows the microscopic anodic
Figure 9. (Color online) (a) Microscopic polarization curve of untreated re-
sulfurized Type 304 stainless steel measured in 0.1 M NaCl at 298 K (electrode
area: ca. 6.0 × 10^{-8} m^2). Optical microscope images of MnS inclusion in the
electrode area in air (b) before and (c) after the polarization. (d) SEM image
of MnS inclusion in the electrode area after the polarization.

polarization curve and the surface appearances of the MnS inclusion
before and after the polarization. The MnS inclusion was in the cen-
ter portion of the electrode area, which was 6.0 × 10^{-8} m^2 in size.
Figure 10 indicates the changes in surface appearance of the inclusion
during the polarization shown in Fig. 9a. As shown in Figs. 10c–10h,
gas bubbles which were generated above ≈0.1 V were observed at the
MnS/steel boundary. A comparison of Figs. 10a, 10c, and 10d clearly
indicates that the surface dissolution of the MnS inclusion occurred
above 0.3 V. Chiba et al. have revealed that the dissolution of MnS
inclusions results in the deposition of elemental sulfur at the bound-
aries between the MnS inclusions and the stainless steel matrix.21

As shown in Fig. 9a, in the potential range of the dissolution of the
MnS inclusion, current spikes due to the initiation of metastable pits
were measured at 0.43 and 0.45 V, and a sharp increase in current
density indicating a stable pit initiation was measured at 0.46 V. The
potential control was interrupted immediately after the stable pit ini-
tiation. Figures 9b and 9c display the optical microscope images of
the MnS inclusion before and after the polarization. From the in situ
observation of the electrode surface during the polarization (Figs. 10f
and 10g), it was confirmed that the metastable pits marked “A” and
“B” were initiated at 0.43 V and 0.45 V, respectively, and then the
stable pit marked “C” in Fig. 10h was initiated at 0.46 V. All these pits
were initiated at the MnS/steel boundary. Figure 9d shows the SEM
image of the inclusion after the polarization. As seen in this figure,
the MnS/steel boundary preferentially dissolved deeply, and a trench
was formed at the site marked “D”. Chiba et al. have demonstrated
that the formation of trenches at the MnS/steel boundaries occurs in
chloride-containing environments.21 The synergistic effect of elemen-
tal sulfur, which is one of the dissolution products of MnS inclusions,
and chloride ions causes the dissolution of the steel side at the bound-
ary, forming the trench. The trench formation proceeds in the depth
direction by the steel matrix dissolution. The hydrolysis reaction of
Cr^{3+} released from the steel causes a decrease in the pH of the solution
in the trench. At the same time, the electrode potential at the bottom

Figure 10. (Color online) Changes in optical microscope images of the un-
treated stainless steel electrode surface in 0.1 NaCl at 298 K with a water
immersion objective lens during the polarization shown in Fig. 9a.
of the trenches decreases due to the IR-drop. Therefore, the transition from the passive to active state occurs locally at the bottom of the trench. The pit initiation at the MnS inclusions in chloride-containing environments is thought to be the local active dissolution that occurs in these trenches.

For the carburized specimen, the anodic polarization curve of a micro-scale electrode area with a MnS inclusion in the carburized layer was measured in 0.1 M NaCl. The cross-section parallel to the rolling direction embedded in the epoxy resin was also used in this measurement. Figure 11 shows the microscopic anodic polarization curve and the surface appearances of the MnS inclusion before and after the polarization. The size of the electrode area was $1.5 \times 10^{-8}$ m$^2$. In this measurement (Fig. 11a), the electrode area was about one-fourth the size of that in the experiment represented in Fig. 9a. In the potential range from 0.3 V to 0.43 V, a small broad peak appeared, and small current spikes were measured which were very small compared with those indicating the initiation of the metastable pit on the untreated specimen in 0.1 M NaCl (Fig. 9a). Figure 12 indicates the changes in surface appearance of the inclusion during the polarization shown in Fig. 11a. As was the case with the untreated stainless steel in 0.1 M NaCl (Fig. 10), gas bubbles were generated at the MnS/steel boundary during the polarization (Figs. 12c–12f). Above 0.3 V, the surface color of the MnS inclusion became slightly darker due to the surface dissolution of the inclusion (Figs. 12c–12f); however, neither metastable nor stable pits were initiated at the MnS inclusion in the carburized layer (Figs. 11b, 12f, and 11c). The SEM observation after the polarization (Fig. 11d) indicated that the surface of the MnS inclusion dissolved, which implied that elemental sulfur was produced as a dissolution product of the MnS inclusion.

Although a trench like dissolution morphology was observed at the MnS/steel boundary on the carburized specimen, the trench was clearly shallower than that formed at the MnS/steel boundary on the untreated stainless steel shown in Fig. 9d marked “D”. It is expected that the low-temperature carburizing treatment improves the corrosion resistance of the stainless steel matrix in environments containing elemental sulfur generated by the dissolution of MnS inclusions. From the above results, it is clear that the low-temperature carburizing treatment does not improve the dissolution resistance of the MnS inclusions. The reason for no pit initiation at the MnS inclusion would be attributed to the change in the electrochemical property of the stainless steel matrix. The carburizing treatment which introduces interstitial carbon in the stainless steel matrix is considered to improve the corrosion resistance of the stainless steel matrix.

The 1:1 atomic ratio of Mn and S in the MnS inclusions is not changed by the carburizing treatment (Fig. 5 and Table II), and the broad current peak attributed to the dissolution of the MnS inclusion on the anodic polarization curve of the carburized specimen (Fig. 8a) is generated in almost the same potential range as that for the untreated stainless steel (Fig. 7a). Judging from these results, the dissolution behavior of the MnS inclusions in the carburized layer is the same as that in the untreated stainless steel. This means that it can be
Figure 13. (Color online) Macroscopic polarization curves of (a) untreated and (b) carburized low-sulfur Type 304 stainless steels measured in 3 M NaCl-1 mM Na2S2O3 at pH 3.0. (c) Macroscopic polarization curve of untreated low-sulfur Type 304 stainless steel in 3 M NaCl-1 mM Na2S2O3-0.1 M Na2CO3 at pH 3.0. Electrode areas were ca. 1 × 10⁻⁴ m².

Figure 14. Enlarged SEM images of the trenches formed at the MnS/steel boundaries after the polarization marked by the broken lines in (a) Fig. 9 (the untreated stainless steel) and (b) Fig. 11 (the carburized stainless steel).

assumed that elemental sulfur is produced as a dissolution product at the MnS/steel boundary during the MnS inclusion dissolution even in the case of the carburized specimens.

Effect of carburizing on active dissolution rate of steel matrix.— As mentioned above, we believe that the dissolution of the steel matrix forming the trenches at the MnS/steel boundaries caused by the coexistence of elemental sulfur and chloride ions is a key point for pit initiation at the MnS inclusions. To compare the active dissolution rate of the untreated and the carburized stainless steel matrix in a sulfur suspension with chloride ions, macroscopic anodic polarization curves were measured. For the macroscopic polarization of the carburized stainless steel, the carburized surface was used as the electrode surface. The low-sulfur Type 304 stainless steel was used. The sulfur suspension was produced by the acidification of the thiosulfate-containing solutions. It has been reported that thiosulfate ions (S2O3²⁻) are one of the MnS dissolution products. It is known that the solution pH around the inclusions gradually decreases due to the dissolution of the MnS inclusions, and finally reaches approximately around 3. It is assumed that elemental sulfur is produced as a dissolution product at the MnS/steel boundary during the MnS inclusion dissolution even in the case of the carburized specimens.

Figure 13 shows the macroscopic anodic polarization curves in the sulfur suspension with chloride ions. The corrosion potential of the untreated steel in 3 M NaCl-1 mM Na2S2O3 at pH 3.0 was in the active state, and the active dissolution rate of the stainless steel matrix at −0.3 V was about 500 A/m². After the polarization, the surface of the specimen was black, implying the formation of an iron sulfide layer. The corrosion potential of the carburized steel was located in the active state; however the dissolution current density was clearly suppressed. The dissolution rate of the carburized stainless steel at −0.3 V was reduced to about 5 A/m², which is one hundredth of the untreated stainless steel. Moreover, the color of the specimen surface remained silver, suggesting that iron sulfide was not produced as a dissolution product. One possible mechanism for the improved resistance to pitting corrosion as a result of the carburizing treatment in chloride-containing solutions is as follows: 1) MnS inclusions dissolve during anodic polarization, which causes the deposition of elemental sulfur at the MnS/steel boundaries; 2) The stainless steel matrix at the boundaries slightly dissolves, but no deep trenches are formed due to the reduced dissolution rate of the steel matrix in the coexistence of elemental sulfur and chloride ions after the carburization; 3) Finally, the decrease in the generation of elemental sulfur and the dilution of the solutions in the shallow trenches result in the repassivation of the steel trench walls at the boundaries. Figure 14 displays enlarged views of the areas enclosed by the broken lines in Figs. 9d and 11d. The dissolution of the steel matrix formed a wide, deep trench at the MnS/steel boundary on the untreated stainless steel (Fig. 14a). In contrast, on the carburized stainless steel, a narrow, shallow trench was observed (Fig. 14b). In the case of the carburized specimens, it is likely that the decrease in the pH caused by the hydrolysis reaction of Cr3⁺ and the decrease of electrode potential due to IR-drop in the shallow trenches are insufficient for the localized transition from the passive to active state. The formation of the shallow trench at the boundary indicates that elemental sulfur is generated around the inclusion, implying that the acidification of the solution results from the dissolution of the inclusion; however, the reduced active dissolution rate of the steel matrix prevents the pH from decreasing in the trench. Therefore, the MnS inclusions in the carburized stainless steel do not act as initiation sites of pitting in chloride-containing environments.

Interstitial carbon is supposed to dissolve into carbonate ions (CO3²⁻) in aqueous solutions. In order to ascertain the effect of the carburized treatment on the active dissolution rate of the stainless steel matrix in a sulfur suspension with chloride ions, the polarization curve of the untreated low-sulfur Type 304 stainless steel in a carbonate-containing solution (3 M NaCl-1 mM Na2S2O3-0.1 M Na2CO3 at pH 3.0) is presented in Fig. 13. As shown in this figure, there was no difference between the active dissolution rate of the stainless steel matrix in the solutions with and without carbonate ions. This is evidence that the reason for the improved pitting corrosion resistance at
The low-temperature carburizing treatment was conducted with Type 304 stainless steel with MnS inclusions, and a carburized layer with ca. 16 μm in thickness was formed. The average concentration of carbon in the carburized layer was ca. 2.6 mass%. Analysis by XRD clearly indicated no precipitation of carbides and a 2.5% expansion of the lattice parameter.

2. The low-temperature carburizing treatment did not affect the chemical composition or electrochemical property of the MnS inclusions. The inclusions in the carburized layer dissolves in the same potential range as those in the untreated stainless steel in 0.1 M Na2SO4 and 0.1 M NaCl solutions; however, no pit was initiated at the inclusions in the carburized layer in 0.1 M NaCl solution.

3. In the sulfur suspension with chloride ions, which simulates the environments that results from the dissolution of MnS inclusions in chloride-containing solutions, the low-temperature carburizing treatment suppresses the active dissolution rate of the steel matrix by a factor of approximately one hundredth, making it difficult for the dissolution of the stainless steel matrix at the MnS/steel boundaries of the carburized specimens to take place. As a result, the trenches at the boundaries remain shallow. The corrosion in the trenches is thought to be insufficient for the localized transition from the passive to active state to occur. Therefore, MnS inclusions in the carburized stainless steel do not act as initiation sites of the pitting in chloride-containing environments.

Conclusions

1. The low-temperature carburizing treatment was conducted with Type 304 stainless steel with MnS inclusions, and a carburized layer with ca. 16 μm in thickness was formed. The average concentration of carbon in the carburized layer was ca. 2.6 mass%. Analysis by XRD clearly indicated no precipitation of carbides and a 2.5% expansion of the lattice parameter.

2. The low-temperature carburizing treatment did not affect the chemical composition or electrochemical property of the MnS inclusions. The inclusions in the carburized layer dissolved in the same potential range as those in the untreated stainless steel in 0.1 M Na2SO4 and 0.1 M NaCl solutions; however, no pit was initiated at the inclusions in the carburized layer in 0.1 M NaCl solution.

3. In the sulfur suspension with chloride ions, which simulates the environments that results from the dissolution of MnS inclusions in chloride-containing solutions, the low-temperature carburizing treatment suppresses the active dissolution rate of the steel matrix by a factor of approximately one hundredth, making it difficult for the dissolution of the stainless steel matrix at the MnS/steel boundaries of the carburized specimens to take place. As a result, the trenches at the boundaries remain shallow. The corrosion in the trenches is thought to be insufficient for the localized transition from the passive to active state to occur. Therefore, MnS inclusions in the carburized stainless steel do not act as initiation sites of the pitting in chloride-containing environments.

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References

1. G. S. Frankel, J. Electrochem. Soc., 145, 2186 (1998).
2. A. Sznitkowski, Z. Szklarska-Smilowksa, M. Rybczyk, and A. Szummer, Corros. Sci., 9, 123 (1969).
3. Z. Szklarska-Smilowksa, Pitting corrosion of metals, p.69, NACE, Houston, Tex (1986).
4. H. Bohn, T. Suter, and A. Schreyer, Electrochem. Acta, 40, 1361 (1995).
5. T. Suter and H. Bohn, Electrochem. Acta, 42, 3275 (1997).
6. J. Stewart and D. E. Williams, Corros. Sci., 33, 457 (1992).
7. P. Schmuki, H. Hildebrand, A. Friedrich, and S. Virtanen, Corros. Sci., 47, 1239 (2005).
8. T. Suter, E. G. Webb, H. Bohn, and R. C. Alkire, J. Electrochem. Soc., 148, B174 (2001).
9. E. G. Webb, T. Suter, and R. C. Alkire, J. Electrochem. Soc., 148, B186 (2001).
10. E. G. Webb and R. C. Alkire, J. Electrochem. Soc., 149, B272 (2002).
11. H. Krawiec, V. Vignal, and R. Oltra, Electrochem. Commun., 6, 655 (2004).
12. I. Muto, Y. Izumiyama, and N. Hara, J. Electrochem. Soc., 154, C439 (2007).
13. I. Muto, D. Ito, and N. Hara, J. Electrochem. Soc., 156, C55 (2009).
14. J. F. Park, S. Matsch, and H. Bohn, J. Electrochem. Soc., 149, B34 (2002).
15. S. E. Lott and R. C. Alkire, J. Electrochem. Soc., 136, 973 (1989).
16. E. G. Webb and R. C. Alkire, J. Electrochem. Soc., 149, B280 (2002).
17. H. Krawiec, V. Vignal, O. Heintz, R. Oltra, and J. Olive, J. Electrochem. Soc., 152, B213 (2005).
18. R. Ke and R. Alkire, J. Electrochem. Soc., 142, 4056 (1995).
19. J. E. Castle and R. Ke, Corros. Sci., 30, 409 (1990).
20. C. S. Brossia and D. G. Kelly, Corros. Sci., 40, 1851 (1998).
21. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 160, C511 (2013).
22. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, Mater. Trans., 55, 857 (2014).
23. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 159, C341 (2012).
24. F. J. Martin, E. J. Lemieux, T. M. Newbauer, R. A. Bayles, P. M. Natishan, H. Kahn, G. M. Michal, F. Ernst, and A. H. Heuer, Electrochem. Solid-State Lett., 10, C76 (2007).
25. A. H. Heuer, H. Kahn, L. J. O’Donnell, F. Ernst, G. M. Michal, R. J. Rayne, F. J. Martin, and P. M. Natishan, Electrochem. Solid-State Lett., 13, C37 (2010).
26. Y. Sun, Surf. Coat. Technol., 204, 2789 (2010).
27. J. Su, Corros. Sci., 52, 2661 (2010).
28. F. J. Martin, P. M. Natishan, E. J. Lemieux, T. M. Newbauer, R. J. Rayne, R. A. Bayles, H. Kahn, G. M. Michal, F. Ernst, and A. H. Heuer, Metall. Mater. Trans. A, 40A, 1805 (2009).
29. A. H. Heuer, H. Kahn, F. Ernst, G. M. Michal, D. B. Hovis, R. J. Rayne, F. J. Martin, and P. M. Natishan, Acta Mater., 60, 716 (2012).
30. H. Fujikawa and T. Watanabe, Solid State Phenom., 118, 161 (2006).
31. M. Mayuzumi, J. Otha, and K. Kako, Corrosion, 56, 70 (2000).
32. JCPDS Card No. 33
33. M. Mavrikakis, B. Hammer, and J. K. Norskov, Phys. Rev. Lett., 81, 2819 (1998).
34. H. L. Skriver and N. M. Rosengaard, Phys. Rev. B, 46, 7157 (1992).
35. G. Kresse and J. Hafner, Surf. Sci., 459, 287 (2000).