Improving Pitting Corrosion Resistance at Inclusions and Ductility of a Martensitic Medium-Carbon Steel: Effectiveness of Short-Time Tempering

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The optimal tempering conditions for a martensitic medium-carbon steel (0.47 mass% C) were investigated in terms of balancing ductility and pitting corrosion resistance. By tempering the as-quenched martensite, its Vickers hardness drastically decreased within 0.1 h, suggesting that ductility was sufficiently recovered by short-time tempering. Based on the results of micro-scale polarization in boric-borate buffer solutions with NaCl (pH 8.0), stable pits were initiated at non-metallic inclusions in the specimens tempered for at least 1 h; however, no stable pit was generated on the 0.1 h tempered and as-quenched specimens. Short-time tempering of martensite was suggested to be a feasible approach to striking an optimal balance between facilitating pitting corrosion resistance and achieving the desired mechanical properties of martensitic carbon steels.

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### Table I. Chemical composition of steel (mass%).

| Element | C  | Si | Mn | P  | S  | Ni | Cr | Mo | Cu | Ti | Nb | Al | N  | O  |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|         | 0.47 | 0.19 | 0.85 | 0.015 | 0.015 | 0.02 | 0.18 | 0.01 | 0.01 | <0.001 | <0.002 | 0.024 | 0.005 | 0.002 |

**Electrolytes.**—Potentiodynamic polarization was performed in boric-borate buffer solutions with NaCl. The solution pH values were adjusted to 8.0 by mixing NaCl-added 0.35 M H₃BO₃ and NaCl-added 0.075 M Na₂B₄O₇ solutions. The NaCl concentrations were set at 1 and 500 mM. All electrolytes were prepared from deionized water and analytical grade chemicals.

**Micro-scale polarization.**—Micro-scale potentiodynamic polarization was conducted to clarify the effect of the tempering treatment on the pitting corrosion resistance of the specimens. The procedure used to fabricate the micro-scale electrodes was described elsewhere. Micro-scale electrodes that contained only one non-metallic inclusion were fabricated to determine the localized corrosion resistance at non-metallic inclusions. The potentiodynamic anodic polarization was performed in boric-borate buffer solutions with 1 and 500 mM NaCl under naturally aerated conditions at 298 K. In this study, a system similar to that developed by Chiba et al. was used. The experimental procedures for micro-scale polarization were the same as those reported in the literature. The potential scan rate was 3.8 × 10⁻⁴ V s⁻¹ (23 mV min⁻¹). The electrode areas were measured by an optical microscope equipped with an image analysis system, and the current values were converted to current densities. All potentials cited in this paper are expressed with respect to the Ag/AgCl (3.33 M KCl) electrode (0.206 V vs. the standard hydrogen electrode at 298 K).

**Macro-scale polarization.**—Macro-scale potentiodynamic anodic polarization was performed in boric acid sodium borate buffer solutions with 1 mM NaCl under deaerated conditions at 298 K. The size of the electrode area was approximately 10 mm × 10 mm. Measurements were performed in a conventional three-electrode cell. Cathodic treatment (−1.2 V, 600 s) was carried out to remove air-formed film on the specimen, and anodic polarization began at −1.0 V. The scan rate of the electrode potential was set at 3.8 × 10⁻⁴ V s⁻¹, which was the same as that used in the micro-scale polarization. The electrode areas were scaled after polarization.

**Observations and analysis.**—Optical microscope and confocal laser scanning microscope (CLSM) observations on the electrode areas were conducted before and after polarization. A field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system was used to observe the electrode surfaces and the microstructure of the specimens. In the FE-SEM/EDS observations, an acceleration voltage of 20 kV was used. To reduce the charging effects, a thin conductive coating of Au was deposited on the specimen surface after polarization.

**Micro-vickers hardness test.**—The micro-Vickers hardness of the as-quenched and tempered martensitic structures was measured. The load applied to the specimens was 0.05 kg. The measurements were conducted five times for each specimen.

**X-ray diffraction analysis.**—X-ray diffraction analysis (XRD) using Cu-Kα radiation (Kα1: 1.54056 Å and Kα2: 1.54439 Å) with a Ni filter was conducted. XRD data were collected over a 2θ range from 40° to 100° with a step width of 0.02°. The scan speed was 1° min⁻¹. The Kα2 peaks were stripped (stripping ratio Kα2/Kα1 = 0.5) from the scans using computer software.

**Results and Discussion**

**Microstructure characterization.**—Metallographic inspection was carried out to characterize the microstructures of the as-quenched and tempered martensitic specimens. Fig. 1 shows SEM images of the specimens. As shown in Fig. 1a, the microstructure of the as-quenched specimen was a typical lath martensite. The grains were nearly elliptically shaped, which is a characteristic feature of lath martensite.
shows the XRD patterns of the as-quenched and tempered martensitic specimens. As seen, all peaks were assigned to the bct structure.25 According to the JCPDS (Joint Committee on Powder Diffraction Studies) card,26 the peak of austenite, with the (111) fcc structure, is expected to appear at 2θ = 42.795°. However, in Fig. 2, no corresponding peak appears, which indicates that the austenite phase was likely not retained, and the full martensitic structure was obtained by water quenching.

Tempering is required after quenching to improve the balance between strength and ductility.1 For carbon steels, Fe3C is formed during tempering, and the concentration of interstitial carbon decreases.5 In this work, tempered martensitic structures were prepared by reheating the as-quenched specimen at 873 K for 0.1, 1, 10, 15, and 20 h. Figs. 1b–1f shows SEM images of the microstructure of tempered specimens. As shown in Fig. 1b, many small white particles and strip-like precipitations were observed in the 0.1 h tempered specimen, showing evidence of the carbides formed by tempering. As shown in Fig. 1c, the shape of the carbides in the 1 h tempered specimen was round with a diameter of less than 0.3 μm. In the 10 h tempered martensite (Fig. 1d), the sizes of the carbides were approximately 0.5 μm. A comparison of Figs. 1a to 1f reveals that the sizes of the carbides increased with tempering time up to 10 h. After 10 h, negligible differences were observed in the size and number of the carbides in the tempered martensite.

The carbides grew during the tempering treatments, meaning that the interstitial carbon decreased with tempering time. Therefore, it was concluded that the interstitial carbon concentration was ordered as follows: as-quenched > 0.1 h > 1 h > 10 h > 15 h > 20 h tempered martensite. Our previous research demonstrated that interstitial carbon is an important factor that affects the pitting corrosion resistance of carbon steels in chloride solutions.6 It was revealed that a high amount of interstitial carbon supplies martensitic carbon steel with high pitting corrosion resistance.6 Therefore, in this study, it is expected that the pitting resistance of the as-quenched martensite is high compared with tempered martensite and that the tempering time will affect the pitting corrosion resistance of these steels.

Change in hardness with tempering.—The adjustment of the balance between strength and ductility is a major concern for high strength steels. Tempering reduces the strength but increases the ductility of martensite. It is known that the relationship between the Vickers hardness and the amount of interstitial carbon29–33 from 0.004 to 0.47 mass%, the interstitial carbon content estimated in this research. After 10 h of tempering, the hardness was dramatically decreased to 300. From 0.1 to 20 h of tempering, the hardness gradually decreased to 200. As indicated in Fig. 3, the hardness of the specimens drastically decreased within 0.1 h, suggesting that ductility was sufficiently recovered by short-time tempering at 873 K.

During tempering, the martensite decomposes into carbide (cementite) and ferrite, and the carbon atoms diffuse to form the carbides. This process facilitates a decrease in hardness. The decrease in hardness is attributed to the following: 1) the decrease in the interstitial carbon content and 2) recovery and recrystallization of martensite, which result in a reduction in the internal stress, changes in the dislocation density, and the grain-size effect. Ohmura et al. applied nanoindentation techniques to compare the matrix strength of as-quenched and tempered martensite of Fe-0.4C (mass%).27,28 A comparison of the nano- and macro-scale hardness values suggested that rather than the dislocation density and the grain size effect, it is the strength of the martensite that contributes to the Vickers hardness after tempering above 723 K.

The amount of interstitial carbon is known to be related to the strength and hardness of martensite. The relationship between the Vickers hardness and the amount of interstitial carbon in martensite tends to be linear29–33 and it is generally thought that the concentration of the interstitial carbon can be roughly estimated from the Vickers hardness. In the tempering treatments, the carbides showed almost no growth after 10 h (Figs. 1d to 1f), which suggests that interstitial carbon was almost completely consumed to form carbides after long-time tempering. The interstitial carbon content after 20 h of tempering was postulated to be 0.004 mass%, which is the solubility limit of carbon at 873 K.31 The carbon content of the as-quenched martensite was 0.47 mass% (see Table I). Assuming that a linear relationship indeed exists between the Vickers hardness and the amount of interstitial carbon from 0.004 to 0.47 mass%, the interstitial carbon content of the 0.1 h tempered martensite was estimated to be approximately 0.1 mass%. According to the literature, the carbon content of the as-quenched martensite, which has a Vickers hardness of 300, is approximately 0.1 mass%.31 This value correlates well with the interstitial carbon content estimated in this research. After 10 h of tempering, it was estimated that no significant change occurred in the interstitial carbon content. This result is reasonable considering the many reports that the amount of interstitial carbon decreases exponentially with tempering time.535 In the above estimation procedure, precipitation hardening by the carbides was ignored for simplicity.

Inclusion characterization.—The composition and morphology of the non-metallic inclusions were examined by FE-SEM/EDS. Based on the inclusion morphology and composition, the inclusions were classified into two types: “large elongated” and “small round”. Fig. 4a shows an SEM image and the corresponding EDS maps of a large elongated type of inclusion. Manganese and sulfur were observed in the inclusion, and no oxygen was detected. EDS point analysis was performed at Point 1 shown in Fig. 4a, and the relative composition is listed in Table II. As shown in this table, the relative concentrations of manganese and sulfur were almost the same at Point 1, indicating that this type of inclusion was a typical MnS inclusion. This type of
inclusion is referred to as elongated MnS. The length of the elongated MnS inclusions ranged from 10 to 50 μm.

Fig. 4b presents an SEM image and the corresponding EDS maps of a small round-type inclusion. This type of inclusion consisted of bright and dark areas in the SEM images. In the SEM image shown in Fig. 4b, the left side of the inclusion appears bright, and the right side is dark. Aluminum, oxygen, and a small amount of magnesium were present in the bright area. In contrast, calcium, sulfur, and a small amount of manganese were detected in the dark area. The EDS point analysis was performed at Points 2 and 3 shown in Fig. 4b, and the relative compositions are listed in Table II. At Point 2, the concentrations of magnesium, aluminum, and oxygen were 3, 27, and 55 at.%, respectively, and the concentrations of calcium and sulfur were both 1 at.%. Based on these results, the bright area in the round-type inclusion was likely a mixture of Al₂O₃, MgO, and CaS (referred to as Al₂O₃-MgO-CaS). At Point 3, the concentrations of magnesium, aluminum, sulfur, calcium, and manganese were 1, 11, 16, 11, and 5 at.%, respectively. Thus, the dark area was determined to be a mixture of MgO, Al₂O₃, CaS, and MnS (referred to as MgO-Al₂O₃-CaS-MnS). In this paper, this type of inclusion is referred to as a mixed oxide/sulfide inclusion. The diameter of the mixed oxide/sulfide inclusions was less than 5 μm. The inclusions of this type were thought to be generated from the slag used in the melting and refining processes of the steel.

**Effect of tempering on the pitting resistance of martensitic structures.**—The pitting corrosion resistance of the martensitic structures was measured using micro-scale anodic polarization. The specimens examined were the as-quenched and tempered martensitic versions, and the tempering times were 1, 10, 15, and 20 h. Fig. 5 presents the micro-scale anodic polarization behavior in boric-borate buffer solution with 500 mM NaCl (pH 8.0). Fig. 6 shows optical microscopy images of the electrode areas before and after polarization. For the micro-scale polarization results presented in Fig. 5, small areas without any inclusions were selected as the working electrode areas (see Figs. 6a, 6c, 6e, 6g, and 6i) such that the intrinsic pitting corrosion resistance of the as-quenched and tempered martensitic structures could be determined. No cathodic treatment was performed, and polarization began in the passive region at −0.1 V to inhibit the active dissolution of steel matrix. The cathodic currents were initially measured. The open circuit potentials (OCPs) of the as-quenched specimen, 1 h tempered specimen, 15 h tempered specimen, and 10 h tempered specimen were −0.07 V, −0.09 V, 0.00 V, and 0.21 V, respectively. The OCP for the 10 h tempered specimen was about 0.2 V more positive as compared with other specimens, while the reason is unclear. For the 15 h tempered martensite, a sharp increase in the current density was observed at 0.05 V due to pitting. In contrast, no pitting was generated during anodic polarization of the other specimens (as-quenched, 1 h tempered, and 10 h tempered). The surfaces of these specimens appeared to be well passivated even in the chloride-containing...
crevice corrosion at the boundary of the masking and electrode areas. As indicated in Figs. 6b, 6d and 6f, in the case of the as-quenched specimen and the specimens tempered for at most 10 h, the surfaces of the specimens were faintly discolored, but no initiation of pitting was generated. The pitting corrosion resistance of the martensite tempered for at most 10 h was found to be greater than that of the martensite tempered for at least 15 h. In other words, the short-time tempered martensitic specimens exhibit higher pitting corrosion resistance, and the pitting potentials are similar to that of the as-quenched martensite. As indicated in Fig. 3, the ductility of the as-quenched martensite is likely sufficiently recovered by 0.1 h of tempering. It is proposed that short-time tempering is a feasible approach to obtaining an optimal balance between pitting corrosion resistance and ductility of martensitic steels. In this work, the micro-scale polarization condition was conducted at least two times. It was confirmed that the pitting potentials were almost the same, and the same corrosion behavior was seen. Our previous research reported that the pitting corrosion resistance of as-quenched martensite was higher than that of low-carbon martensite prepared by decarburization because the active dissolution rate of the steel matrix decreases due to the interstitial carbon. It has been shown that the active dissolution of type 304 austenitic stainless steel was suppressed by interstitial carbon in chloride solutions. Therefore, the high pitting corrosion resistance of the as-quenched martensite, 1 h tempered martensite, and 10 h tempered martensite can be attributed to the interstitial carbon in the martensitic structures. The amount of interstitial carbon decreases during tempering because of the precipitation of carbides (see Fig. 1). As a result, the pitting corrosion resistance of the 15 h and 20 h tempered steels is thought to decrease.

As displayed in Fig. 1, the carbides precipitated and grew with increasing tempering time; however, the carbides cannot possibly act as the pit initiation sites because dissolution of the carbides is more difficult than dissolution of the steel matrix. In the SEM images shown in Fig. 1, the bright particles are the carbides (cementite), and the steel matrix appears darker. The etching rate of the steel matrix was likely higher than that of the carbides. It appears that the corrosion resistance of the steel matrix was lower than that of the carbides. Kadowaki et al. conducted in situ observations during micro-scale polarization of the pearlite structure (ferrite and cementite lamellae) in a boric-borate buffer solution containing 100 mM NaCl and found that the cementite (iron carbide) acts as a barrier against the growth of the pits initiated in the ferrite lamellae. In addition to the above explanation, although there were many small carbides in the specimens tempered for at most 10 h, no pit was initiated on these specimens. No correlation was observed between the precipitation morphology of the carbides and the pitting corrosion resistance. This result also indicates that the carbides do not act as the initiation sites of pitting. The lower pitting corrosion resistance of the 15 h and 20 h tempered specimens is concluded to be attributed to the decrease in the interstitial carbon content.

**Effect of tempering time on the active dissolution rate of martensite.**—From the above results, a high amount of interstitial carbon appeared to improve the pitting corrosion resistance. As mentioned above, it was revealed that interstitial carbon inhibits the active dissolution of the steel matrix. To investigate the quantitative effect of the tempering time on the active dissolution rate, macro-scale anodic polarization measurements were conducted in deaerated boric-borate buffer solution with 1 mM NaCl at pH 8.0. The specimens used in these measurements were the as-quenched and tempered martensite (0.1, 10, and 20 h). As observed in Fig. 7a, the OCPs of all specimens were approximately −0.7 V. In the micro-scale polarization results presented in Fig. 5, the OCPs of these specimens ranged from −0.1 to 0.2 V. This difference was due to air-formed films. For the micro-scale polarization, cathodic treatment was performed at −1.2 V for 600 s prior to the potentiodynamic polarization. Therefore, surface oxide films were removed before polarization. In contrast,
density is seemed to be related to pitting corrosion resistance. In the rate provide better corrosion resistance, and hence the peak current passivation rates of steel matrix. Low dissolution rate and high passivation density in the active region is determined by the dissolution and passivation corrosion morphologies. This finding is confirmed that the interstitial carbon suppresses the dissolution current of the martensitic structures, and this is likely the predominant reason for the higher pitting corrosion resistance of the martensite tempered for at most 10 h. The interstitial carbon is also thought to be related to the growth rate of passive films, changes in surface reactivity, and the electronic structure of steels. More comprehensive research is required to clarify how interstitial carbon is related to the inhibition of pitting corrosion in carbon steels.

**Pitting corrosion resistance at MnS inclusions.**—From the above results, short-time tempering was proposed as a successful treatment for achieving better pitting corrosion resistance of martensite steels. In the case of commercial steels, it is inevitable that they contain non-metallic inclusions. Because non-metallic inclusions readily act as pit initiation sites on steels in chloride and decrease their pitting potential, to strike a balance between the mechanical properties and the pitting corrosion resistance, it is necessary to investigate the effect of the tempering time on the pitting corrosion resistance at inclusions. In this work, micro-scale polarization curves for small electrodes including only one MnS inclusion were measured. Fig. 8 displays optical microscopy images of the working electrodes and CLSM reflectance images of the MnS inclusions. These images were captured before polarization for the as-quenched and tempered martensitic specimens. The tempering times were 0.1, 1, 10, and 15 h. The MnS inclusions in the as-quenched, 0.1 h tempered, 1 h tempered, 10 h tempered, and 15 h tempered martensitic specimens were referred to as inclusions A, B, C, D, and E, respectively. The sizes of the inclusions in all electrodes were approximately 15 μm in length.

Fig. 9 shows the micro-scale anodic polarization behavior in the boric-borate buffer solution with 1 mM NaCl at pH 8.0 and optical microscopy images of the electrode areas after polarization. Because pitting corrosion was readily initiated at the MnS inclusions, the chloride concentration in this solution was one five-hundredth of that used in the polarization shown in Fig. 5. Polarization began in the passive region at −0.1 V. For the 15 h tempered martensite, a stable pit was initiated at inclusion E immediately after immersion. No polarization curve was recorded in this case. The pitting potential of the 15 h tempered martensite was expected to be less than −0.1 V. In the case of the 10 h tempered martensite, a sharp increase in current density was observed at −0.04 V because of pit initiation at inclusion D. In addition, pitting corrosion was initiated on the 1 h tempered martensite at 0.42 V. As shown in Figs. 9d to 9f, pitting corrosion of these specimens was confirmed to be generated at inclusions C, D, and E. It was found that the pitting corrosion resistance at the MnS inclusions decreased with tempering time. Interestingly, for the 0.1 h tempered and as-quenched specimens, no pitting was initiated even though the electrode areas included the MnS inclusions. Under anodic polarization (Fig. 9a), for the 0.1 h tempered and as-quenched specimens, the passive current densities were stable, the values were approximately 2 × 10⁻² A m⁻² in the potential range from −0.1 to 1 V, and no current spike was generated in the passive region. Above 1 V, the oxygen evolution reaction was measured. After polarization, as indicated in Figs. 9b and 9c, the surfaces of these specimens were faintly discolored, but no pitting appeared. From the above results, the pitting resistances of the 0.1 h tempered and as-quenched martensite were clearly superior to those of martensite tempered for longer periods of time (1, 10, and 15 h). In the solution with 1 mM NaCl, the initiation of pitting at the MnS inclusion was completely suppressed on martensite tempered for at most 0.1 h.

After polarization, the morphology of the MnS inclusions on the as-quenched and 0.1 h tempered martensitic specimens (inclusions A and B in Figs. 9b and 8d) was observed via FE-SEM. Fig. 10 shows SEM images and the corresponding EDS maps of inclusion A on the as-quenched specimen. Figs. 10c and 10d display the EDS maps of manganese and sulfur in the area corresponding to Fig. 10a. Because
Figure 8. Optical microscopy images of electrode surfaces including one MnS inclusion and CLSM reflectance images of the inclusions on (a, b) as-quenched, (c, d) 0.1 h tempered, (e, f) 1 h tempered, (g, h) 10 h tempered, and (i, j) 15 h tempered martensitic specimens.

Figure 9. (a) Micro-scale anodic polarization curves of small areas including one MnS inclusion in boric-borate buffer (pH 8.0) with 1 mM NaCl, and optical microscopy images of the electrode areas of (b) as-quenched, (c) 0.1 h tempered, (d) 1 h tempered, (e) 10 h tempered, and (f) 15 h tempered martensitic specimens after polarization.

The existence of both manganese and sulfur was confirmed at the position indicated by the yellow arrow in Fig. 10, this inclusion was clearly MnS. Fig. 10b shows an enlarged view of the area enclosed by the yellow lines in Fig. 10a. As observed in Fig. 10b, the MnS inclusion certainly dissolved at the position indicated by the white arrow, and the bare steel surface was exposed to the chloride-containing solution. Even so, no pitting was initiated. Fig. 11 shows SEM images and the corresponding EDS maps of inclusion B on the 0.1 h tempered specimen after polarization. Both manganese and sulfur were also detected, indicating that this inclusion was MnS. As in the case of the as-quenched specimen (see Fig. 10b), for inclusion B, the area indicated by the white arrow in Fig. 11b dissolves. However, no pit was initiated during polarization. In the boric-borate buffer solution with 1 mM NaCl at pH 8.0, the pitting corrosion resistance of the 0.1 h tempered martensite was comparable to that of the as-quenched martensite. As presented in Fig. 7, the short-time tempered and as-quenched martensite showed relatively low current densities in the active dissolution region, which is probably the reason for the inhibition of stable pit initiation at MnS inclusions. The pH on the exposed bare steel surface was likely decreased by the hydrolysis reaction of ions released from the MnS inclusion, but no further decreases in pH suggested to be generated in the case of the 0.1 h tempered and as-quenched martensite. It can be concluded that this occurred because active dissolution was sufficiently suppressed by the interstitial carbon in the short-time tempered martensite.

Pitting corrosion resistance at mixed oxide/sulfide inclusions.—To assess the pitting corrosion resistance at mixed oxide/sulfide inclusions, micro-scale polarization was also performed for a small
Figure 10. SEM images of inclusion A shown in Fig. 8b after polarization at (a) low and (b) high magnification, where (b) is the image of the area surrounded by yellow lines in image (a). EDS maps of (c) manganese and (d) sulfur in the area corresponding to image (a).

Figure 11. SEM images of inclusion B shown in Fig. 8d after polarization at (a) low and (b) high magnification, where (b) is the image of the area surrounded by yellow lines in image (a). EDS maps of (c) manganese and (d) sulfur in the area corresponding to image (a).

electrode area including a mixed oxide/sulfide inclusion. Fig. 12 displays optical microscopy images of electrodes with mixed oxide/sulfide inclusions and CLSM reflectance images of the inclusions. The specimens analyzed were the as-quenched and tempered martensite (0.1, 1, and 10 h). All images were captured before polarization. The inclusions in the as-quenched, 0.1 h tempered, 1 h tempered, and 10 h tempered martensitic specimens were referred to inclusions F, G, H, and I, respectively. The size of the inclusions in all electrodes was approximately 3 μm in diameter. Fig. 13 shows the micro-scale anodic polarization behavior in the boric-borate buffer solution (pH 8.0) with 1 mM NaCl and optical microscopy images of the electrode areas after polarization. Polarization also began in the passive region at −0.1 V. In the case of the 10 h tempered martensite, a stable pit was initiated at inclusion I immediately after immersion. The polarization curve was not recorded in this case. The pitting potential of this specimen was expected to be less than −0.1 V. For the 1 h tempered martensite, a sharp increase in current density was observed at −0.06 V. As observed in Figs. 13d and 13e, it is clear that pitting corrosion on these specimens was generated at inclusions H and I.

For the 0.1 h tempered martensite, an increase in the current density was observed at 0.07 V. However, the current decreased immediately, indicating that the surface of the specimen was spontaneously repassivated. This current spike (rapid increase and decrease in current density) appears to be due to the initiation of a meta-stable pit with the dissolution of inclusion G. Above 0.07 V, the current density reached a steady value of $2 \times 10^{-2}$ A m$^{-2}$, and no other current peak was observed in the potential range below 1 V. The oxygen evolution reaction was measured above 1 V. A comparison between Figs. 12c and 13c confirms that discoloration occurred on inclusion G and the surrounding area. However, unlike the 1 h and 10 h tempered martensite, pit growth was inhibited in the 0.1 h tempered martensite. In the case of the as-quenched specimen, no pit was initiated (see Fig. 13b). The current density was stable from −0.1 to 1 V, and no current spike was observed in the passive region. Above 1 V, the increase in the current density was due to the oxygen evolution reaction. After polarization, the surface of the specimen was faintly discolored, as shown in Fig. 13b, but no pit was initiated. From the above results, in the case of the 0.1 h tempered and as-quenched martensite, the initiation of stable pitting at the mixed oxide/sulfide inclusion was suppressed even in the solution with 1 mM NaCl.

After polarization, the morphologies of the inclusions on the as-quenched martensitic specimen (inclusion F in Fig. 12b) and the 0.1 h tempered martensite specimen (inclusion G in Fig. 12d) were observed via FE-SEM. Fig. 14 shows SEM images and the corresponding EDS maps of inclusion F after polarization. Figs. 14c to 14h display the EDS maps corresponding to Fig. 14a. Aluminum, magnesium, and oxygen were detected in the upper portion of inclusion F. From these results, the upper portion of this inclusion appeared to be Al$_2$O$_3$-MgO-CaS, and CaS was likely dissolved during polarization. As shown in Fig. 14a, the lower area of the inclusion disappeared, and the bare steel surface was exposed. Fig. 15 shows the EDS spectra of Point 4 (corresponding to the lower portion of the inclusion) and Point 5 (the steel matrix) shown in Fig. 14b. At Point 4, a sulfur peak was detected. Therefore, the lower portion of this inclusion was likely MgO-Al$_2$O$_3$-CaS-MnS before polarization, and this area was likely dissolved during polarization. Fig. 14b shows an enlarged view of
the area enclosed by the yellow lines in Fig. 14a. A comparison of Figs. 14b and 12b reveals the dissolution of a small area of the steel matrix adjacent to the inclusion as well as the inclusion itself. However, this steel dissolution did not result in the initiation of stable pitting. Reformatskaya et al. reported that the dissolution of a CaS inclusion accelerated the dissolution reaction of the steel matrix. However, for the as-quenched martensite, stable pit initiation was inhibited. The reason again is that the current density in the active region of the as-quenched martensite was sufficiently low. In this case, no current spike was observed in the polarization curve (Fig. 13a), which is most likely attributed to the notably small dissolution amount of the steel matrix. Another possibility is that dissolution of the inclusions and the exposed bare steel surface proceeded immediately after immersion (before polarization).

Fig. 16 shows SEM images and the corresponding EDS maps of inclusion G (0.1 h tempered) after polarization. As observed in Fig. 16, a portion of inclusion G dissolved during polarization. The current spike at 0.07 V in Fig. 13a appears to be due to this dissolution.

However, as with the as-quenched martensite, this dissolution did not result in the initiation of stable pitting because of the suppression of dissolution current density in the active region by the interstitial carbon in the 0.1 h tempered martensite. Because aluminum, magnesium, and oxygen were detected, the remaining portion of this inclusion was likely Al2O3-MgO. The MnS and CaS also dissolved in this case.

Possibility of an optimal balance between corrosion resistance and mechanical properties.—In this study, long-time tempering decreased the pitting corrosion resistance of martensitic carbon steel. In the cases with and without non-metallic inclusions, the pitting corrosion potentials decreased with tempering time. Fig. 17 summarizes the relationship among the tempering time, Vickers hardness, and pitting corrosion potentials. The pitting potentials of the small areas with and without inclusions were determined from the micro-scale polarization curves shown in Figs. 5, 9a, and 13a. For both the mixed oxide/sulfide inclusions and the MnS inclusions, the micro-scale polarization for a small area with the inclusion was conducted at least two times, and it was confirmed that the pitting potentials were almost the same. As shown in this figure (Fig. 17), the Vickers hardness was decreased significantly by 0.1 h of tempering. The Vickers hardness is related to the strength and ductility, and tempering reduces the strength but increases the ductility of martensite. The change in the Vickers hardness shown in Fig. 17 suggests that the ductility of the martensite recovered sufficiently due to short-time tempering within 0.1 h at 873 K. Fortunately, the pitting corrosion resistance of the 0.1 h tempered martensite is the same as that of the as-quenched martensite even though the electrode area contains inclusions. As seen in Figs. 10b, 11b, 14b, and 16b, in
Figure 14. SEM images of inclusion F shown in Fig. 12b after polarization at (a) low and (b) high magnification, where (b) is the image of the area surrounded by yellow lines in image (a). EDS maps of (c) manganese, (d) sulfur, (e) calcium, (f) magnesium, (g) aluminum, and (h) oxygen in the area corresponding to image (a).

Figure 15. EDS spectra at Points 4 and 5 in Fig. 14b.

Figure 16. SEM images of inclusion G shown in Fig. 12d after polarization at (a) low and (b) high magnification, where (b) is the image of the area surrounded by yellow lines in image (a). EDS maps of (c) manganese, (d) sulfur, (e) calcium, (f) magnesium, (g) aluminum, and (h) oxygen in the area corresponding to image (a).

Figure 17. Vickers hardness and pitting potentials of martensitic specimens with various tempering times at 873 K. The pitting potentials of the areas without inclusions, with MnS, and with mixed oxide/sulfide were determined from the micro-scale polarization curves shown in Figs. 5, 9a, and 13a, respectively.
the case of the 0.1 h tempered and as-quenched specimens, stable pit initiation was inhibited even if the inclusion dissolved and the bare steel surface was exposed to the chloride solution. This appears to be because the high amount of interstitial carbon suppresses the active dissolution of the steel matrix (see Fig. 7). As explained by the Vickers hardness data (Fig. 3), the interstitial carbon content of the 0.1 h tempered martensite was roughly estimated to be 0.1 mass%. In other words, approximately 0.1 mass% C is needed to prevent pit initiation at the non-metallic inclusions. Judging from these results, short-time tempering of martensite is a feasible approach to striking an optimal balance between facilitating pitting corrosion resistance and achieving the desired mechanical properties of martensitic carbon steels.

Conclusions

1. In boric-borate buffer with 500 mM NaCl (pH 8.0), no pitting was initiated on the small areas of the as-quenched, 1 h tempered, and 10 h tempered martensitic AISI 1045 carbon steel without inclusions. However, stable pits occurred on the 15 h and 20 h tempered martensite. Ductility (Vickers hardness data (Fig.3), the interstitial carbon content of the 0.1 h tempered martensite was roughly estimated to be 0.1 mass%. In other words, approximately 0.1 mass% C is needed to prevent pit initiation at the non-metallic inclusions. Judging from these results, short-time tempering of martensite is a feasible approach to striking an optimal balance between facilitating pitting corrosion resistance and achieving the desired mechanical properties of martensitic carbon steels.

2. In the potentiodynamic micro-scale polarization of a small electrode area with one MnS or mixed oxide/sulfide inclusion measured in the boric-borate buffer with 1 mM NaCl (pH 8.0), no stable pit was generated on the 0.1 h tempered and as-quenched specimens. In contrast, stable pits were initiated at the inclusions in the specimens tempered for at least 1 h. It was confirmed that short-time tempering produces higher pitting corrosion resistance at non-metallic inclusions (MnS and mixed oxide/sulfide).

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