Pitting Corrosion Resistance of Martensite of AISI 1045 Steel and the Beneficial Role of Interstitial Carbon

Mariko Kadovaki, Izumi Muto, Yu Sugawara, Takashi Doi, Kaori Kawano, and Nobuyoshi Hara

The pitting corrosion resistance of AISI 1045 carbon steel with as-quenched, tempered, and low-carbon martensitic microstructures was investigated in boric-borate buffer solutions with and without NaCl. Analysis by micro-scale polarization found that tempering and decarburizing treatments decreased the pitting corrosion resistance of as-quenched martensite. The high corrosion resistance of the as-quenched martensite was likely due to the large amount of interstitial carbon. The pitting corrosion resistances of as-quenched martensite, primary ferrite, and pearlite were compared using micro-scale polarization measurements. It was determined that the pitting corrosion resistances of the typical steel structures were ordered as follows: (high) as-quenched martensite > tempered martensite ≈ primary ferrite > pearlite (low). The pitting corrosion resistance of steel was shown to depend on its microstructure.

Background.—Quenched and tempered martensitic carbon steels are known for their high strength. The supersaturation of interstitial carbon and high dislocation density provide martensitic steels with their high strength. However, the toughness of as-quenched martensitic steels is relatively low. To optimize the balance between strength and toughness, the steels are subjected to tempering. Tempering involves heating the steels so that the non-equilibrium microstructure can return to near-equilibrium conditions. However, tempering also lowers the dislocation density due to the recovery and recrystallization processes. It has also been shown that the precipitation of carbides results in a decrease in the amount of interstitial carbon. While tempered martensitic carbon steels have excellent mechanical properties, the effect of tempering on the pitting corrosion behavior of carbon steels is unclear. While such steels can be successfully protected from corrosion by coating and/or painting, localized corrosion is readily initiated at cut edges and in coating defect areas in atmospheric environments. To prolong their service life and improve their reliability, it is necessary to elucidate the mechanism of pitting corrosion and assess the pitting corrosion resistance of as-quenched, and quenched and tempered martensitic steels.

Fundamental research on the corrosion mechanisms of carbon steels started during the 1950s. Stern found that the addition of carbon (0.11 mass% C) increased the corrosion rate of pure iron in 4% NaCl at pH 1 and 2. This increase in the corrosion rate was explained by the decrease in the hydrogen overvoltage due to the addition of carbon. It is known that iron carbides (Fe3C) act as cathodic sites. Foroulis and Uhling demonstrated that while the corrosion rate of carbon steels in 0.12 M HCl increased linearly with carbon content, the reduced carbon content combined with plastic deformation resulted in an increase in the corrosion rate. These results were explained by the lower hydrogen overvoltage introduced by cold-rolling, which is also associated with carbon atoms (Cottrell atmospheres). In addition, annealing serves to agglomerate iron carbides into larger particles, in effect reducing the total peripheral area of the carbides (cathode sites). Cleary and Greene studied the polarization behavior of several steels in dilute H2SO4 to determine the effects of the carbon content and microstructure on the electrochemical parameters. They concluded that the corrosion rates of carbon steels were closely related to the total area of iron carbides exposed to the steel surfaces. That is, the morphologies of iron carbides and carbon content have been recognized as important factors that determine the corrosion mechanisms of carbon steels.

In the case of martensitic carbon steels, Tomashov found that the corrosion rate of martensite in 1% H2SO4 was lower than that of the ferrite-pearlite structure because the carbide lamellae act as cathodic sites in the pearlite structure. Sarker et al. focused on the morphology of martensite. They investigated the galvanostatic corrosion behavior of carbon steels with ferrite-martensitic structures in a 3.5% NaCl solution and clarified that both the amount and the morphology of the martensite phase had an influence on the pitting corrosion behavior of steel. The specimen with an island-like martensitic structure exhibited high corrosion resistance. They concluded that the corrosion tendency was higher in cases with larger amounts of martensite. While the corrosion behavior of martensitic carbon steels has been addressed, questions remain regarding the corrosion resistance of martensitic carbon steels. The actual application of carbon steels almost always involves outdoor corrosion environments. As such, it is necessary to assess their localized corrosion resistance in chloride environments.

In the as-quenched condition, the martensite in carbon steels is supersaturated with carbon. Interstitial carbon is assumed to be of importance in the pitting corrosion resistance of martensitic steels. For the austenitic stainless steel, Martin et al. revealed that carburizing treatments improved the pitting corrosion resistance of stainless steels. They fabricated the carburized layer on type 316L austenitic stainless steel by conducting a “low-temperature colossal supersaturation (LTCCS)” treatment and investigated the corrosion behavior of the specimens in near-neutral chloride-containing solutions. They revealed that the pitting potential of the specimen with a carburized layer was higher than that of the specimen not subjected to a carburizing treatment. Heuer et al. reported that low temperature gas-phase carburization improves both the wear and the corrosion resistance of type 316L stainless steel in 0.6 M NaCl for pH values ranging from 8 to 13. Additionally, it was reported that interstitial carbon improved the corrosion resistance of steel not only in near-neutral solutions but also in acid solutions. By conducting low temperature plasma carburizing treatment, Sun demonstrated that in 1 M H2SO4, the corrosion potential of type 316L stainless steel increased and the corrosion current decreased. They also showed that the existence of interstitial carbon prevented both the initiation and propagation of pitting. Although there have been many studies about the relationship between the interstitial carbon and the corrosion behavior of austenitic steels with an fcc crystal structure, to our knowledge, there is little or no literature focusing on carbon steels with bcc and bct crystal structures.

*Electrochemical Society Student Member.
**Electrochemical Society Member.
E-mail: mariko.kadovaki.so@dc.tohoku.ac.jp; mutoi@material.tohoku.ac.jp
**Micro-electrochemical measurements.**—Micro-electrochemical measurements are promising techniques for investigating the initiation process of pitting. Suter et al. developed a capillary-based micro-electrochemical measurement system and investigated the electrochemical behavior of a small area that contained only a single MnS inclusion in stainless steels.16,17 The development of this technique has led to significant advances in the understanding of pitting corrosion at non-metallic inclusions in stainless steels over the past twenty years.18–23 Chiba et al. developed a micro-electrochemical system for in situ high-resolution optical microscopy that can be used for the morphological analysis of pitting at the very beginning of the initiation process.24–26 The micro-electrochemical technique has also been used to investigate other alloy families such as aluminum alloys.27,28

It is well known that inclusions like MnS tend to become the initiation sites of pitting corrosion of stainless steels,29,30 and carbon steels.31 For macro-scale measurements, it is inevitable that the electrode areas contain non-metallic inclusions. However, for the case of micro-scale polarization, by adopting a small electrode area of approximately 100 μm × 100 μm, it is possible to choose an area without such inclusions. In previous research, a micro-electrochemical technique was applied to investigate the initiation site of pitting of AISI 1045 ferritic-pearlitic steel and clarified that the ferrite lamellae in pearlite acted as initiation sites for pitting.32

The objectives of this research are to assess the pitting corrosion resistance of AISI 1045 steel with different microstructures and to clarify the role of interstitial carbon in corrosion inhibition behavior. Micro-scale polarization measurements of a small area that contained only one structure (as-quenched martensite, tempered martensite, low-carbon martensite, primary ferrite, or pearlite) were performed to investigate the effect of microstructure on pitting corrosion resistance of carbon steel. The role of interstitial carbon in pitting corrosion on carbon steels was determined.

## Experimental

**Specimens.**—All of the specimens used in this study were machined from a commercial AISI 1045 carbon steel bar (20 mm in diameter). Table I shows the chemical composition of the steel. The steel was cut into approximately 20 mm × 15 mm × 5 mm coupons.

| C   | Si  | Mn  | P   | S   | Ni  | Cr  |
|-----|-----|-----|-----|-----|-----|-----|
| 0.47| 0.19| 0.85| 0.015| 0.015| 0.02 | 0.18 |
| Mo  | Cu  | Ti  | Nb  | Al  | N   | O   |
| 0.01| 0.01| <0.0001| <0.002| 0.024| 0.005| 0.002|

The only difference between the specimens discussed in the text was the heat-treatment. The specimens were heat-treated at 1523 K (1250°C) for 1.8 ks and then furnace-cooled to room temperature. The specimens prepared by this method are referred to as “annealed” specimens in this paper.

After heat-treatments, the surfaces of the specimens were mechanically ground using 1500-grit SiC paper and were finished by polishing with a 1 μm diamond paste. Ethanol was used as a lubricant during polishing. The specimens were then degreased with ethanol.

**Electrolytes.**—To understand the initiation behavior of atmospheric corrosion in marine environments, electrochemical measurements were performed in boric-borate buffer solutions with and without NaCl. The buffer solution was made by mixing 0.35 M H3BO3 and 0.075 M Na2B4O7. In the case of buffer solutions that contained NaCl, NaCl-added 0.35 M H3BO3 and NaCl-added 0.075 M Na2B4O7 solutions were used for mixing. The NaCl concentrations were set to 1, 100, and 500 mM. All of the solutions were prepared from deionized water and analytical grade chemicals.

| Electrolytes polarization measurements.**—Macro-scale anodic polarization curves were measured in the boric-borate buffer solutions with and without 1 mM NaCl under deaerated conditions at 298 K. With the exception of the electrode area (approximately 10 mm × 10 mm), the specimen surfaces were coated with an epoxy resin and subsequently with paraffin. Measurements were performed in a conventional three-electrode cell. The counter electrode was a Pt plate, and the reference electrode was Ag/AgCl (3.33 M KCl solution). All potentials cited in this paper are expressed with respect to the Ag/AgCl (3.33 M KCl) electrode (0.206 V vs. standard hydrogen electrode at 298 K). Before measurements were taken, a cathodic treatment (~1.2 V Ag/AgCl, 600 s) was conducted to remove any surface film that may have formed on the specimens. Potentiodynamic anodic polarization was started at −1.0 V (Ag/AgCl, immediately afterwards. The scan rate of the electrode potential was set at 3.8 × 10−4 V s−1 (23 mV min−1). After etching, the position of the micro-electrode area was marked by indentations made with a Vickers hardness tester. The specimen was then re-polished with a 1 μm diamond paste and coated with a sealant. The size of the micro-scale electrode area was approximately 100 μm × 100 μm.

The micro-scale anodic polarization curves were measured in the boric-borate buffer solutions (pH 8.0) with 100 mM and 500 mM NaCl under naturally aerated conditions at 298 K. For in situ real-time optical micro-scale observations of the electrode area, a system similar to that developed by Chiba et al. was used in this study.24 An acrylic plate with a small hole (mini-cell) was put into place to preserve the electrolyte on the specimen surface with a small working electrode area. A small Ag/AgCl reference electrode and a platinum wire (counter electrode) were set in the acrylic cell. The reference electrode was calibrated with the Ag/AgCl (3.33 M KCl) electrode before the experiments, and a battery-powered potentiostat18 was used for the micro-scale electrochemical measurements to reduce electrical noise. The potential scan rate was 3.8 × 10−4 V s−1 (23 mV min−1). The current and potential signals were measured using a data recorder at a time interval of 20 ms. During the micro-scale measurements, the electrode area was observed using an optical microscope with a water immersion objective lens with a magnification of 100. Both the lens and the electrode surface were immersed in the electrolyte. The theoretical lateral resolution was approximately 350 nm. The micro-scale polarization measurements for each microstructure were performed at least two times for reproducibility.

**Surface observations and analysis.**—An optical microscope, a confocal laser scanning microscope (CLSM), and a field emission scanning electron microscope (FE-SEM) were used to observe the
surfaces and the microstructure of the specimens. An accelerating voltage of 5 kV was used for the FE-SEM observations. Additionally, a field emission electron probe micro analyzer (FE-EPMA) was employed to determine the locations of the segregated regions of the substitutional alloying elements. An electron acceleration voltage of 10 kV was used. The beam diameter was approximately 100 nm. Prior to FE-EPMA analysis, the specimen surface was etched with 3 vol.% nital, and CLSM reflectance images were taken. Then, the observed area was marked with indentations made by a Vickers hardness tester. The specimen surface was then re-polished with a 1 μm diamond paste and analyzed by FE-EPMA.

Micro Vickers hardness test.—Micro Vickers hardness was used to determine the thickness of the decarburized layer on the decarburized specimen. The hardness was measured every 100 μm between the distances of 50 and 1850 μm measured from the outermost surface of the specimen. The load applied to the specimen was 50 g.

Results and Discussion

Characterization of the microstructures.—Metallographic inspection was performed to ascertain the characteristics of the microstructure of the as-Q and QT specimens. Figure 1 shows the SEM images of the as-Q and QT specimens etched with 3 vol.% nital. The microstructure of the as-Q specimen is shown in Figures 1a and 1b. As seen in Figure 1a, the microstructure of the as-Q specimens was a full martensitic structure. As seen from Figure 1b, the martensitic structure was a typical lath martensite. The elliptical hollows, indicated by the red arrow in Figure 1b, are characteristic of lath martensite. The lath width was approximately 1 μm. Retained austenite is sometimes observed in martensitic carbon steels.3,4 Some alloying elements, especially carbon, are known to decrease in the transformation temperature from austenite to martensite, and some austenite remains even at room temperature as a result. To evaluate the possibility of the existence of retained austenite in the as-Q specimens, the austenite to martensite transition temperature, M_s, can be used in the following formula:3,34

\[
M_s \left[K\right] = 772 - 308 \times \left[\%C\right] - 32.4 \times \left[\%Mn\right] - 27 \times \left[\%Cr\right] - 16.2 \times \left[\%Ni\right] - 10.8 \times \left[\%Si\right] - 10.8 \times \left[\%Mo\right]
\]

where alloy compositions are expressed in mass%. According to this formula, the M_s point of the steel used in study was approximately 592 K (320°C). Because this can be considered sufficiently high, it is improbable that austenite phases will be retained after water-quenching. This suggested that specimens with a full martensitic structure were successfully prepared by water-quenching.

In actual applications of martensitic steels, to improve the balance between strength and toughness, tempering is conducted after quenching. Tempering results in the non-equilibrium microstructure returning to near-equilibrium conditions by reheating. In the case of carbon steels, iron carbides are precipitated, and the amount of interstitial carbon decreases.1 In this study, a tempered martensitic structure was obtained by reheating the as-Q specimen at 923 K (650°C) for 20 h. Figure 1c shows the SEM images of the tempered martensitic structure etched with 3 vol.% nital, and Figure 1d is the image taken at high magnification. While there were negligible differences in the microstructures of the as-Q and QT specimens at a low magnification (see Figures 1a and 1c), small amounts of precipitate were observed only on the surface of the QT specimen at high magnification. This suggests that carbide precipitates form during tempering. The many white dots, which can be observed in Figure 1d, are the carbides formed as a result of tempering. These precipitates were round and had a diameter of less than 1 μm.

In our previous work, it was shown that the segregation of alloying elements such as sulfur resulted in pit initiation on carbon steel with ferrite and pearlite structures.3,4 To ascertain the distributions of alloying elements in the microstructures of as-Q and QT specimens, the FE-EPMA analysis was conducted. Figure 2 shows the CLSM reflectance image and the EPMA mappings of the as-Q specimen with a full martensitic structure. In Figure 2, no clear segregation of alloying elements can be observed in the martensitic structure. Since it has been reported that carbon tends to segregate in the retained austenite in the martensitic structure,3,5 no clear retained austenite was expected in our specimens. That is, because the carbon atoms existed

![Figure 1. SEM images of the specimens etched in 3% nital. Full martensitic structure of the as-Q (quenched) specimen at (a) low and (b) high magnification. Tempered martensitic structure of the QT (quenched and tempered) specimen at (c) low and (d) high magnification.](image-url)
Figure 2. (a) CLSM reflectance image and (b–f) EPMA mappings of the full martensitic structure of the as-Q specimen: (b) carbon, (c) sulfur, (d) manganese, (e) phosphorus, and (f) silicon.

in the interstitial sites in the martensite,\textsuperscript{1-5} no clear segregation of carbon was detected in the as-Q specimen. Also, because no clear segregation of sulfur, manganese, phosphorus, and silicon (see Figure 2c–2f) was detected by FE-EPMA, it can be assumed that these elements dissolved homogenously in the martensite. TEM (transmission electron microscopy) observations are required for further validation.

Figure 3 shows the CLSM reflectance image and the EPMA mappings of the QT specimen. The carbon-accumulation points indicated in Figure 3b were likely iron carbides, which precipitated during tempering. The dot-like accumulation of manganese can be faintly seen in Figure 3c. Figure 3d is the color-composite image of the carbon map (the green channel) and the manganese map (the red channel) in the area surrounded by the white lines shown in Figures 3b and 3c. In this figure, yellow indicates the coexistence of carbon and manganese at the same position due to the rule of the three primary colors. Pale yellowish (or dull olive) points are observed. The positions of manganese accumulation were consistent with those of carbon (carbides). It is known that carbide in steels readily forms in the presence of manganese. Calcagnotto et al. reported that manganese carbide is formed in 0.16C-0.17Mn-0.27Si steel (in mass%) during the transformation from austenite to martensite.\textsuperscript{36} The EPMA mapping of tempered martensite in our study indicated that manganese accumulated together with carbides. In contrast to carbon and manganese, as seen in Figures 3e–3g, no clear segregation of sulfur, phosphorus, or silicon was observed by FE-EPMA in the tempered martensitic structure. These elements appeared to have homogenously dissolved in the martensite.

Figure 3. (a) CLSM reflectance image and (b–g) EPMA mappings of a tempered martensitic structure of the QT specimen: (b) carbon, (c) manganese, (d) manganese and carbon, (e) sulfur, (f) phosphorus, and (g) silicon; (d) is a color-composite image of manganese and carbon in the area surrounded by white lines in images (b) and (c).

Macro-scale polarization behavior of martensitic steel.—Macro-scale polarization measurements were conducted to investigate the pitting corrosion resistance of the as-Q and QT specimens. Figure 4 shows the anodic polarization curves for the as-Q and QT specimens in the deaerated boric-borate buffer solutions (pH 8.0) with and without 1 mM NaCl at 298 K. As seen from Figure 4a, in the solution without NaCl, a region of active dissolution appeared on both the as-Q and QT specimens at approximately $-0.6$ V\textsubscript{Ag/AgCl}. The critical current densities for passivation of the as-Q and QT specimens are summarized in Table II. The peak current density in the active dissolution range was defined as the critical current density for passivation. Even at a near-neutral pH of 8.0, the peak current density of the QT specimen was higher than that of the as-Q specimen. Above $-0.5$ V\textsubscript{Ag/AgCl}, the current density decreased with the electrode potential, and the transition from the active to the passive state was observed for both the as-Q and QT specimens. The passive ranges were from approximately $-0.2$ to $1$ V\textsubscript{Ag/AgCl}, and the current densities decreased to a steady value of approximately $2 \times 10^{-2}$ A m$^{-2}$. Because the
Figure 4. Macro-scale anodic polarization curves of the as-Q (as-quenched martensite) and QT (tempered martensite) specimens in deaerated boric-borate buffer (pH 8.0) (a) without and (b) with 1 mM NaCl at 298K.

passive current densities of the as-Q and QT specimens were the same, it can be concluded that the protective ability of the passive film on the as-Q specimen is comparable to that on the QT specimen.

Also in the chloride-containing solution, active dissolution ranges were observed for the as-Q and QT specimens of approximately −0.6 V<sub>Ag/AgCl</sub>, and active-passive transitions were also generated. The critical current densities for passivation of the as-Q and QT specimens in the chloride-containing solution are summarized in Table II. Also in the same case of the chloride-free solution, the peak current density of the QT specimen was higher than that of the as-Q specimen. From −0.6 to 0 V<sub>Ag/AgCl</sub>, the current densities decreased with the electrode potential, but increases in the current densities were measured above approximately 0.1 V<sub>Ag/AgCl</sub>. The breakdown of the passive films is likely due to the presence of chloride ions. It was confirmed that the chloride ions caused the pitting corrosion of the as-Q and QT specimens above 0.1 V<sub>Ag/AgCl</sub>. The pitting potential of the as-Q and QT specimens in the chloride-containing solution are summarized in Table II. The pitting potential was defined as the potential at which the current density progressively began to increase in the passive region. The pitting potential of both specimens were almost the same. However, many current spikes due to metastable pit initiation were clearly generated on the QT specimen. Above 0.7 V<sub>Ag/AgCl</sub>, the dissolution current density of the QT specimen was larger than that of the as-Q specimen, indicating that the corrosion rate on the steels depends on their microstructure. In this study, the rate of pitting dissolution was faster on the QT specimen than that on the as-Q specimen. In the case of the solutions, one with and one without chloride, as shown in Figures 4a and 4b, the large increases in current densities above 1 V were due to oxygen evolution. While the current peaks between approximately −0.2 and 0 V<sub>Ag/AgCl</sub> are likely due to the oxidation reaction from Fe<sup>2+</sup> to Fe<sup>3+</sup>, this fact was not clearly determined. After the polarization, the corrosion morphology was inspected using an optical microscope, it was clarified that the current increase after 0.1 V<sub>Ag/AgCl</sub> was not due to crevice corrosion.

Figure 5. Micro-scale anodic polarization curves of the small areas consisting of as-quenched martensite or tempered martensite in boric-borate buffer (pH 8.0) with 500 mM NaCl.

| Table II. Critical current density for passivation and pitting potential of the as-Q and QT specimens. |
|---------------------------------------------------------------|
| Critical current density [A m<sup>−2</sup>] (in chloride-free solution) | 0.38 | 1.22 |
| Critical current density [A m<sup>−2</sup>] (in 1 mM chloride-containing solution) | 0.46 | 1.79 |
| Pitting potential [V vs. Ag/AgCl] (in 1 mM chloride-containing solution) | 0.18 | 0.17 |

Assessment of pitting corrosion resistance of martensite.—To assess the pitting corrosion resistance of martensitic structures and to clarify the effect of tempering, micro-scale polarization curves for a small electrode area on the as-quenched or tempered martensite without inclusions were measured. The solution used for these experiments was the boric-borate buffer with 500 mM NaCl. Figure 5 shows the micro-scale anodic polarization curves in the boric-borate buffer solution (pH 8.0) with 500 mM NaCl. The optical microscopy images of the electrode areas before and after polarization are shown in Figure 6. Figure 7 shows the optical microscopy images of the electrode area (taken from the video recording) during the initiation processes of pit “A1” shown in Figure 6. In the macro-scale polarization (see Figure 4), the open circuit potentials (OCPs) of both the as-Q and QT specimens were approximately −0.75 V<sub>Ag/AgCl</sub>. However, for the micro-scale polarization curves, shown in Figure 5, the OCPs of both
specimens were approximately $-0.08 \text{ V}_{\text{Ag/AgCl}}$. This is likely due to the surface films on the specimens. In the case of micro-scale polarization, no cathodic treatment was performed prior to potentiodynamic polarization, and the solution was naturally aerated. Polarization was started at $-0.1 \text{ V}_{\text{Ag/AgCl}}$ to eliminate the influence of active dissolution on pitting corrosion initiation.

As shown in Figure 5, a sharp increase in current density was observed at $0.179 \text{ V}_{\text{Ag/AgCl}}$ for the tempered martensite. A comparison of Figures 6a and 6b confirms that one large stable pit (indicated by the red arrow) and many small pits surrounding it were generated on the tempered martensite after polarization, whereas no pitting was initiated on the as-quenched martensite. From the in situ observation (Figure 7), it was confirmed that the pit was initiated in the electrode surface, not at the electrode/coating interface. In the case of the as-quenched martensite, the current density gradually increased with the electrode potential, and no sharp increase was observed in the passive region. Rather, an increase in the current density was observed due to the oxygen evolution reaction at potentials above $1 \text{ V}_{\text{Ag/AgCl}}$. After polarization, while no pit initiation was observed on the as-quenched martensite, as indicated in Figures 6c and 6d, the surface of the specimen was faintly discolored. In this study, no pit initiation was found on the as-quenched martensite even in the chloride-containing solutions. The pitting resistance of the as-quenched martensite is undoubtedly superior to that of the tempered martensite.

The lower active dissolution rate of the as-Q specimen compared to that of the QT specimen, as can be seen in Figure 4, is likely related to the difference in the pitting corrosion resistance. The local breakdown of the passive film is induced by chloride ions resulting in the initiation of active dissolution, which causes hydrolysis reactions of metal ions to occur locally on the bare steel surface. If the active dissolution rate is low, there is a greater likelihood that severe acidification (below passivation pH) will be rectified and that repassivation will occur. Although the boric-borate solution used has a pH buffering action, local acidification is thought to be possible under the condition that the local dissolution rate is significantly high. It is expected that a low active dissolution rate results in higher pitting corrosion resistance.

No pitting was generated on the as-Q specimen (as-quenched martensite) in the micro-scale polarization, as shown in Figure 5. However, in the macro-scale anodic polarization in the solution with $1 \text{ mM NaCl}$ (Figure 4b), an increase in current density due to pitting was observed even on the as-Q specimen. This difference is likely due to the effect of non-metallic inclusions in the electrode areas. When carrying out macro-scale polarization on the commercial AISI 1045 carbon steel bar (sulfur concentration was 0.015 mass%), it is inevitable that the electrode areas contain non-metallic inclusions, such as manganese sulfide (MnS). On the other hand, in the case of the micro-scale polarization, because the electrode areas are extremely small (approximately $100 \mu m \times 100 \mu m$), it is possible to choose areas without inclusions. It is also known that the presence of MnS inclusions readily results in the pitting corrosion of carbon steels.20,30,31 Chiba et al. demonstrated that the trench, which formed at the boundary of MnS and the steel matrix, was the initiation site of pitting in stainless steels.29 In this study, a small area without inclusions was selected as the electrode area during the micro-scale polarization, and the pitting corrosion resistance of the microstructures themselves could be evaluated.

Initial pit morphology on tempered martensite.—To investigate the reason for the difference in the pitting corrosion resistance of the as-Q and QT specimens, the morphological changes in the pit that formed on the tempered martensite marked by pit “A1” in Figure 6b were analyzed. Figure 7 shows the optical microscopy images from the electrode area (taken from the video recording) during the initiation processes of pit “A1” shown in Figure 6. The electrode area was observed with the water immersion objective lens during potentiodynamic anodic polarization ($23 \text{ mV min}^{-1}$). Figure 7a shows the electrode surface just before pit initiation: this point was defined as time 0 (s). After initiation, pit growth was monitored by recording the change in the pit size (2 $\mu m$) with increasing time. The pit was 1$\mu m$ in diameter at approximately 100 s. The pit was clearly observed during the polarization process, and increasing activity was monitored in the passive region.
as 0 s for the following analysis. The electrode potential at 0 s was 0.179 V_{Ag/AgCl}. At 0.09 s, a small round pit marked “A1” was initiated. As shown in Figure 7c (0.19 s), the pit was initially quite round; it then became hexagonal from 0.19 to 0.39 s and grew in size with the growth proceeding in all directions. Judging from the results of the in situ observations, it was concluded that the pit in the tempered martensite grew isotropically.

In our previous research, it was found that the pit initiated in the pearlite phase, which consists of ferrite and cementite (Fe₃C) lamellae, proceeded anisotropically.32 This was due to the barrier provided by cementite against pit growth in the early stage of pitting corrosion. In contrast, the pit on the tempered martensite grew isotropically. Figure 8 summarizes the morphological changes in the outlines of the mouth of pit “A1”. As can be seen in this figure, the pit on the tempered martensite changed in shape from round to hexagonal during the very early stage of pitting. As shown in Figure 1d, round carbide inclusions (Fe₃C) were observed in the tempered martensite. However, as seen from Figure 8, unlike the cementite lamellae in the pearlite, the carbides in the tempered martensite did not act as a barrier against pit growth. This may well have been because the carbides in the tempered martensite were too small to protect against pit propagation.

In our in situ observations based on optical microscopy, it is impossible to clarify the role of the small carbides in pit initiation on the tempered martensite since the carbides are too small to be observed by optical microscopy. Even so, it is reasonable to assume that the carbides do not act as initiation sites for pitting. Yumoto et al. synthesized stoichiometric Fe₃C films with Fe:C=75:25 (at.%), and it was demonstrated that the dissolution rate of the cementite was one-half of that of metallic iron (ferrite) in 1% NaCl.37 Tsuchiya et al. examined the anodic polarization behavior of carbon steel (0.12% C) and its constituent phases in a borate buffer solution of pH 8.45 and showed that the anodic dissolution rate of Fe₃C at the passivation potential of the steel is one order of magnitude lower than that of ferrite.38

**Pitting corrosion behavior of low-carbon martensite in the decarburized layer.**—As mentioned above, the pitting corrosion resistance of the as-quenched martensite was much higher than that of the tempered martensite (see Figure 5). This difference in pitting corrosion resistance does not result from the difference in the type of crystal structure. The crystal structure of the as-quenched martensite is bct structure, which is similar to that of the tempered martensite. The tempered martensite has a bcc structure. The axial ratio in the bct structure is similar to that of the bcc structure, with a compression relative to bcc of c/a = 1.4 and 1.0 in as-quenched and tempered martensite, respectively. As such, it is reasonable to assume that the type of crystal structure has no effect on the pitting corrosion resistance of the as-quenched and the tempered martensite from an electrochemical point of view.

While the segregation of alloying elements sometimes affects pitting corrosion resistance, there was no clear segregation of sulfur, silicon, or phosphorus in either the as-Q or QT specimens, as can be seen in Figures 2 and 3. The significant difference between these specimens was the amount of interstitial carbon and the existence of iron carbides in the martensite phases. Tempering results in a decrease in the amount of interstitial carbon due to the precipitation of the iron carbides.

To distinguish the effects of the interstitial carbon and the iron carbides on pitting corrosion resistance, the corrosion behavior of low-carbon martensite was investigated. To obtain low-carbon martensite, decarburized specimens were prepared. The steel was heated at 1523 K (1250 °C) for 10 h in a gas mixture of 21 vol.% O₂ and 79 vol.% N₂ and then water-quenched. A decarburized surface layer was formed by the oxidation of the carbon in the steel matrix. To determine the thickness of the decarburized layer, the hardness profile of the cross-section of the specimen was measured. Figure 9 shows the change in the micro Vickers hardness with distance from the outermost surface of the decarburized specimen. It is clear that the inner part was harder than the outer surface. Over the distance from 50 to 550 μm, the hardness was approximately 170. This was attributed to the decarburization of the specimen surfaces. The thickness of the decarburized layer was estimated to be 550 μm. Judging from the hardness,4 the carbon content of the decarburized martensite was estimated to be less than 0.1 mass%. In this paper, the martensite in the decarburized layer is referred to as “low-carbon martensite.”

The CLSM reflectance image of the microstructure of the low-carbon martensite etched with 3 vol.% nital is shown in Figure 10a. The generation of a typical bct martensite structure was confirmed. Then, to ascertain the existence of the distributions and/or segregation of alloying elements in the microstructure of the low-carbon martensite, FE-EPMA analysis was conducted. The results of the EPMA mapping of the area shown in Figure 10a are shown in Figures 10b–10f. From these images, no clear local accumulation or segregation of alloying elements was detected by FE-EPMA. Additionally, no carbide was precipitated. These results are similar to those of the martensitic structure of the as-Q specimen (see Figure 2).

To clarify the effect of the interstitial carbon on the pitting corrosion resistance of the martensitic structure, the micro-scale polarization of low-carbon martensite was performed in the boric-borate buffer (pH 8.0) with 500 mM NaCl. Figure 11a shows the optical microscopy image of the decarburized layer etched with 3 vol.% nital. In the decarburized layer, a small area was indented to mark the position for the electrode area. Then, the specimen surface was re-polished and coated. Figure 11b shows the optical microscopy image of the electrode area before immersion. The image was taken in air. The electrode area is indicated in Figure 11a by the broken white lines. As the electrolyte, the boric-borate buffer (pH 8.0) with 500 mM NaCl was introduced on the surface of the electrode area, a stable pit was initiated before polarization was started. The immersion potential and polarization curve were not recorded in this case. Figure 11c shows the optical microscopy image of the electrode area after immersion. This image was also taken in air. After immersion, one large pit was
initiated on the electrode surface near the edge of the coating. After the polarization, the corrosion morphology was inspected using an optical microscope, and it was clarified that this case was not the crevice corrosion. As indicated in Figure 5, the OCPs of the as-quenched and tempered martensite were approximately $-0.08 \text{ V}_{\text{Ag/AgCl}}$. It was suggested that the pitting potential of the low-carbon martensite was lower than $-0.08 \text{ V}_{\text{Ag/AgCl}}$ in the boric-borate buffer (pH 8.0) with 500 mM NaCl.

It was clear that the carbides played no role in the pitting corrosion resistance of the low-carbon martensite because no clear precipitation in the microstructure was observed by FE-EPMA (Figure 10). Therefore, the lower pitting corrosion resistance of the low-carbon martensite should be attributed to the decrease in interstitial carbon. That is, the as-quenched martensite exhibited a higher pitting corrosion resistance of steel with a martensitic structure. This result correlates well with the work of Martin et al., who demonstrated that the pitting corrosion resistance of austenitic stainless steels is improved by carburizing treatments.12 Chiba et al. reported that the interstitial carbon in type 304 stainless steel suppresses the active dissolution rate of the metal matrix and inhibits pit initiation at MnS inclusions in NaCl solutions.26 Moreover, Sun revealed that an expanded lattice parameter accelerates passive film growth as well as changes in the surface reactivity and work-function in austenitic stainless steel.15 The authors believe that the interstitial carbon in the martensitic structure inhibited pit initiation. Further studies are needed for an atomic-level understanding of the corrosion prevention mechanism of interstitial carbon.

Comparison of pitting corrosion resistance of martensite, primary ferrite, and pearlite.— Comparison of the pitting corrosion resistance of the typical phases of carbon steels, the primary ferrite, pearlite, and martensite phases, is attractive from an engineering and scientific point of view.

According to the Fe-Fe$_3$C binary phase diagram,39 the primary ferrite phases are formed at approximately $1100 \text{ K} \ (830 \text{ °C})$ (A$_3$ point) during slow cooling from the austenite region, and then at approximately $1000 \text{ K} \ (730 \text{ °C})$ (A$_1$ point), austenite phases transform to the pearlite structure, which has a lamellar structure of ferrite and cementite (Fe$_3$C) phases. The diffusion of carbon occurs during the transformations. For water-quenching from the austenite region, the transformation of austenite to martensite occurs without any diffusion of carbon. In general, the interstitial carbon concentration is ordered as follows: martensite (as-quenched) $>$ primary ferrite $\approx$ ferrite lamella (pearlite). Our results confirmed that interstitial carbon is the important factor in the pitting corrosion resistance of carbon steels. The pitting corrosion resistance of as-quenched martensite was expected to be higher than that of primary ferrite and pearlite structures.

To obtain the typical primary ferrite and pearlite structure, the specimen was furnace-cooled to room temperature after heating at 1523 K for 1.8 ks. Figure 12 shows the SEM images of the annealed specimen with the primary ferritic-pearlitic structure after etching with 3 vol.% nital. The bright areas in Figure 12a represent pearlite, and the dark areas represent primary ferrite. Figure 12b shows the FE-SEM image of the primary ferrite phase and the lamellar structure of the pearlite. The surface of the pearlite was quite rough due to the lamellar structure of the ferrite and cementite phases. It appears that these phases have different etching rates in 3 vol.% nital. In the
Figure 12. SEM images of the annealed specimen with primary ferrite-pearlite structure etched in 3% nital at (a) low and (b) high magnification.

Figure 13. CLSM reflectance image and EPMA mappings of primary ferrite-pearlite structure of the annealed specimen. (a) CLSM image and EPMA mappings of (b) carbon, (c) sulfur, (d) sulfur and carbon, (e) manganese, (f) phosphorus, and (g) silicon; (d) is a color-composite image of sulfur and carbon in the area surrounded by white lines in images (b) and (c).

The CLSM reflectance image and the EPMA mappings of the annealed specimen, which consisted of the primary ferrite and pearlite structures, are shown in Figure 13. The image in Figure 13b confirms the existence of carbon in the cementite lamellae of the pearlite structure. Additionally, as shown in Figures 13c and 13d, the local accumulation of sulfur was detected in the pearlite (indicated by the yellow arrow). Figure 13d is the color-composite image of carbon (green channel) and sulfur (red channel) in the area surrounded by white lines in Figures 13b and 13c. This figure indicates that the sulfur-concentrated points are located in the ferrite lamellae but not in the cementite. The sulfur-concentrated point does not correspond to the carbon-concentrated areas (cementite lamellae). At this sulfur-concentrated point, no accumulation of manganese was detected by FE-EPMA, as is clear from Figure 13e, suggesting that sulfur accumulation was caused by segregation during the transformation from austenite to pearlite and not by the formation of MnS. According to the literature, phosphorus and silicon are known to segregate at the grain boundary of carbon steels. However, no clear segregation of phosphorus and silicon was detected by FE-EPMA in either the primary ferrite or pearlite (see Figures 13f and 13g). These elements appear to have dissolved homogeneously into the ferrite phase.

Micro-scale polarization curves for a small electrode area that included only one structure, either pearlite, the primary ferrite, or the as-quenched martensite, were compared for the boric-borate buffer solutions. The micro-scale anodic polarization curves from a small area consisting of primary ferrite and another area consisting of as-quenched martensite in the boric-borate buffer solution (pH 8.0) with 500 mM NaCl are shown in Figure 14. In Figure 14, the polarization curve of the as-quenched martensite shown in Figure 5 is presented again. To prevent the active dissolution on the specimen surface during anodic polarization, this polarization was also carried out without any cathodic treatment, and the potentiodynamic polarization was started at −0.1 V. Figure 15 shows the optical microscopy images of the same electrode area consisting of primary ferrite before and after polarization as that shown in Figure 14. Both images were taken in air. In Figure 14, a sharp increase in current density was observed on the primary ferrite at 0.192 VAg/AgCl. After polarization, small pits were initiated on the specimen surface, whereas no pit initiation was generated on the as-quenched martensite, indicating that the pitting corrosion resistance of primary ferrite was lower than that of as-quenched martensite. After the polarization, the corrosion morphology was inspected using an optical microscope, it was clarified that the current increase in the
primary ferrite was not due to crevice corrosion. The difference in pitting corrosion resistance can be attributed to the difference in the amount of the interstitial carbon in the ferrite and martensite phases. It is well known that the solubility limit of carbon in ferrite is relatively low (approximately 0.01 mass% at 850 K). The pitting corrosion resistance of primary ferrite being lower than that of martensite can be explained by the lower amount of interstitial carbon in the primary ferrite. The pitting potential of primary ferrite was 0.192 V Ag/AgCl, as shown in Figure 14. As shown in Figure 5, a stable pit was initiated on the tempered martensite at 0.179 V Ag/AgCl. The pitting corrosion resistance of the primary ferrite is comparable to that of tempered martensite. Because there was no notable difference in the pitting corrosion resistance between these two specimens, it can be concluded that the interstitial carbon concentration of primary ferrite was comparable to that of tempered martensite. In this study, the specimens were tempered at 923 K for 20 h. It is reasonable to assume that the supersaturated carbon was completely precipitated as carbides during tempering. This explains the similarity in the pitting corrosion resistance of primary ferrite and tempered martensite.

Figure 15. Optical microscopy images of the electrode surface consisting of primary ferrite (b) before and (c) after polarization shown in Figure 14.

Figure 14. Micro-scale anodic polarization curves of the small areas consisting of primary ferrite or martensite in boric-borate buffer (pH 8.0) with 500 mM NaCl.

Figure 16. Micro-scale anodic polarization curves of the small areas consisting of primary ferrite, pearlite, and martensite in boric-borate buffer (pH 8.0) with 100 mM NaCl.

Figure 16 shows the micro-scale anodic polarization curves of electrode areas consisting of primary ferrite, pearlite, and as-quenched martensite in solution with 100 mM NaCl. The polarization curve of the pearlite was measured in our previous research. The large increase in current recorded at 0 V Ag/AgCl on the pearlite structure was due to the pit initiation by chloride ions. We have clarified that the pitting corrosion resistance of the pearlite is lower than that of primary ferrite and that the points where sulfur is segregated in the pearlite are likely to act as initiation sites for pitting. As indicated in Figure 13, a sulfur accumulation point was observed in the pearlite in this study. In the case of primary ferrite and martensite in the boric-borate buffer (pH 8.0) with 100 mM NaCl, no pit was initiated according to the data in Figure 16. There were negligible differences between the polarization curves of the primary ferrite and the as-quenched martensite. It was concluded that the pitting corrosion resistance of primary ferrite and martensite was higher than that of pearlite in the chloride solution at pH 8.0. As shown in Figures 13 and 2, no clear segregation of alloying elements (sulfur, manganese, phosphorus, and silicon) was observed by FE-EPMA in the primary ferrite or the as-quenched martensite. That is, the higher pitting corrosion resistance of the primary ferrite and the as-quenched martensite than that of pearlite can be attributed to the lack of segregated alloying elements.

In conclusion, the pitting corrosion resistance of the typical steel structures was ordered as follows: (high) as-quenched martensite > tempered martensite ≈ primary ferrite > pearlite (low). The pitting corrosion resistance depends on the microstructure of the steel. The segregation of sulfur significantly decreases the pitting corrosion resistance of carbon steel. In contrast, a large amount of interstitial carbon provides superior pitting corrosion resistance. Further studies are needed to clarify the detailed mechanisms of the interstitial carbon on the prevention of pitting corrosion in carbon steels.

Conclusions

1. Under the micro-scale polarization in the boric-borate buffer with 500 mM NaCl (pH 8.0), pitting corrosion was initiated at 0.179 V Ag/AgCl on tempered martensite, but no pit initiation was observed on as-quenched martensite. The pitting corrosion
resistance of the as-quenched martensite was superior to that of tempered martensite.

2. The in situ observation of tempered martensite revealed that the pits at the initial stage were hexagonally shaped, and there were no barriers against pit growth even though small carbide inclusions were located in the lath of the tempered martensite.

3. Under the micro-scale polarization in the boric-borate buffer with 500 mM NaCl (pH 8.0), pits were readily initiated on the low-carbon martensite at the open circuit potential (approximately −0.08 V_{Ag/AgCl}). The low pitting corrosion resistance of low-carbon martensite could be attributed to the low concentration of interstitial carbon. Interstitial carbon provided high pitting corrosion resistance to martensitic carbon steels.

4. In the boric-borate buffer with 500 mM NaCl (pH 8.0), pits were initiated in the primary ferrite at 0.192 V_{Ag/AgCl}. Additionally, in the boric-borate buffer with 100 mM NaCl (pH 8.0), pits were initiated in the pearlite, but none were initiated in either the primary ferrite or martensite. This indicates that the pitting corrosion resistance of the typical steel structures is ordered as follows: (high) as-quenched martensite > tempered martensite ≈ primary ferrite > pearlite (low).

Acknowledgments

This research was supported by the New Energy and Industrial Technology Development Organization (NEDO) and JSPS KAKENHI grant Numbers JP15K14175 and JP17H01331. This research was also supported by the Program for Leading Graduate Schools, “Interdepartmental Doctoral Degree Program for Multi-dimensional Materials Science Leaders”, by the Ministry of Education, Culture, Sports, Science and Technology.

References

1. W. G. Moffatt, G. W. Pearshall, and J. Wulff, The Structure and Properties of Materials, Volume I, Structure, p. 194, John Wiley & Sons, New York, NY (1964).
2. J. K. Tien and G. S. Ansell, Alloy and Microstructural Design, p. 5, Academic Press, New York, NY (1976).
3. A. K. Jena and M. C. Chaturvedi, Phase Transformations in Materials, p. 45, Prentice Hall, Englewood Cliffs, NJ (1992).
4. B. Lištěc, H. M. Tensi, and W. Luty, Theory and Technology of Quenching, p. 5, Springer-Verlag, Berlin, Heidelberg (1992).
5. H. Berns and W. Theisen, Ferrous Materials: Steel and Cast Iron, p. 38, Springer, New York, NY (2008).
6. M. Stern, J. Electrochem. Soc., 102, 663 (1955).
7. H. J. Cleary and N. D. Greene, Corros. Sci., 9, 3 (1969).
8. Z. A. Forouhi and H. H. Uhlig, J. Electrochem. Soc., 111, 522 (1964).
9. A. H. Cottrell and B. A. Bidwell, Proc. Phys. Soc. A, 62, 49 (1948).
10. N. D. Tomashov, Theory of Corrosion and Protection of Metals, p. 515, Macmillan, New York, NY (1966).
11. P. P. Sarkar, P. Kumar, Manas Kumar Manna, and P. C. Chakraborti, Mater. Lett., 59, 1215 (2005).
12. 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).
13. A. H. Heuer, H. Kahn, L. J. O’Donnell, F. Ernst, G. M. Michal, R. J. Rayne, F. J. Martin, and P. M. Natishan, Acta Mater., 60, 716 (2012).
14. Y. Sun, Surf. Coat. Technol., 204, 2789 (2010).
15. T. Suter and H. Böhní, Electrochim. Acta, 32, 3275 (1997).
16. T. Suter, E. G. Webb, H. Böhní, and R. C. Alkire, J. Electrochem. Soc., 148, B174 (2001).
17. I. Muto, Y. Inumiyama, and N. Hara, J. Electrochem. Soc., 154, C439 (2007).
18. M. C. Inman and H. R. Tipler, Electrochim. Acta, 44, 4315 (1999).
19. A. H. Cottrell and B. A. Bidwell, Proc. Phys. Soc. A, 62, 49 (1948).
20. J. Shinozaki, I. Muto, T. Omura, M. Numata, and N. Hara, J. Electrochem. Soc., 158, C302 (2011).
21. E. G. Webb and R. C. Alkire, J. Electrochem. Soc., 149, B272 (2002).
22. E. G. Webb and R. C. Alkire, J. Electrochem. Soc., 149, B280 (2002).
23. E. G. Webb and R. C. Alkire, J. Electrochem. Soc., 149, B286 (2002).
24. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 159, C341 (2012).
25. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 160, C511 (2013).
26. A. Chiba, S. Shibukawa, I. Muto, T. Doi, K. Kawano, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 162, C270 (2015).
27. N. Birbilis and R. G. Buchheit, J. Electrochem. Soc., 152, B140 (2005).
28. J. Li, B. Hurley, and R. Buchheit, J. Electrochem. Soc., 162, C563 (2015).
29. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, Mater. Trans., 55, 857 (2014).
30. B. Lim, R. Hu, C. Ye, Y. Li, and C. Lin, Electrochim. Acta, 55, 6542 (2010).
31. Z. Szklarska-Smialowska, Corrosion, 28, 388 (1972).
32. M. Kadokawa, I. Muto, Y. Sugawara, T. Doi, K. Kawano, and N. Hara, J. Electrochem. Soc., 164, C261 (2017).
33. P. Payson and C. H. Savage, Trans. A. S. M., 33, 261 (1944).
34. C. Y. Kung and J. J. Rayment, Metall. Trans. A, 13A, 328 (1982).
35. A. J. Clarke, J. G. Speer, M. K. Miller, R. E. Hackenberg, D. V. Edmonds, D. K. Matlock, F. C. Rizzo, K. D. Clarke, and E. De Moor, Acta Mater., 56, 16 (2008).
36. M. Calcagnotto, D. Ponge, and D. Raabe, Acta Mater., 56, 182 (2008).
37. H. Yamamoto, Y. Nagamine, J. Nagahama, and M. Shimotomai, Vacuum, 65, 527 (2002).
38. A. Tsuchiya, N. Hara, K. Sugimoto, A. Honda, and H. Ishikawa, Zairyo-to-Kankyō, 45, 217 (1996).
39. J. Tribe, J. Electrochem. Soc., 3, 55 (1972).
40. M. C. Imman and H. R. Tipler, Acta Metall., 6, 73 (1958).
41. Y. J. Li, P. Choi, S. Goto, C. Borchers, D. Rabeae, and R. Kirchheim, Acta Mater., 60, 4005 (2012).
42. K. Oikawa, H. Mitsu, H. Ohtani, and K. Ishida, ISIJ Int., 40, 182 (2000).