A Methodology for Fabrication of Highly Pitting Corrosion-Resistant Type 304 Stainless Steel by Plasma Carburizing and Post-Pickling Treatment

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Abstract

Low temperature plasma carburizing was performed to improve the pitting corrosion resistance of Type 304 stainless steel. The optimal composition of the plasma gas and post-treatment were then examined. Carburizing was carried out for 18 ks at 470 °C in H2-Ch4, Ar-H2-Ch4 or Ar-Ch4 plasma, and carburized layers ca. 9 μm in thickness with an average ca. 1.3 mass% carbon concentration were obtained. However, it was found that Cr23C6 precipitated in the carburized layer and intergranular corrosion occurred under anodic polarization in 0.1 M NaCl. The precipitation behavior of Cr23C6 differed according to the plasma gas composition: H2 gas was found to suppress the size of Cr23C6. No Cr23C6 was precipitated in the inner part of the carburized layer formed in the H2-Ch4 plasma, and no stable pit was initiated on the inner parts of the carburized layer under anodic polarization in 0.1 M NaCl. Pickling treatment using HF-HNO3 was applied to remove the Cr-depleted zones in the outer part of the plasma carburized layer. The Type 304 stainless steel after the plasma carburizing in the H2-Ch4 atmosphere and subsequent the HF-HNO3 pickling exhibited no pitting corrosion under anodic polarization even in 3 M NaCl at 25 °C.

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Stainless steels are successfully used in various industries due to their good corrosion resistance. However, pitting corrosion sometimes occurs in chloride-containing environments. The improvement of the pitting corrosion resistance of stainless steels remains an important task to increase the safety of structures and products which utilize stainless steels, and to reduce maintenance costs. While an increase in the chromium content and/or the addition of molybdenum has been shown to improve the pitting corrosion resistance of stainless steels, resource saving technological solutions are desired. To this end, surface carburizing treatments have been increasingly investigated in recent year. Martin et al. revealed that low temperature (below 500 °C) carburizing treatments improved the pitting corrosion resistance of Type 316 stainless steels. They demonstrated 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 corrosion resistance of a Mo-containing martensitic stainless steel in 0.6 M NaCl. Sun demonstrated that a low temperature carburized Type 316L stainless steel indicates low corrosion current in 1 M H2SO4. They also showed that the carburizing treatment prevented both the initiation and propagation of pitting.

In the surface carburized layers, carbon exists as an interstitial carbon, and the role of interstitial carbon in the inhibition of pit initiation has also been studied. In their investigation on a carburized Type 304 stainless steel, Chiba et al. demonstrated that no pit initiation occurs at MnS inclusions, which are known to act as initiation sites for pitting on stainless steels, due to the suppression of the dissolution rate of the stainless steel with interstitial carbon in a simulated environment resulting from the dissolution of MnS inclusions in chloride-containing solutions. Kadowaki et al. also found that the interstitial carbon suppresses the active dissolution rate of carbon steels in boric-borate buffer solutions at pH 8.0. In their comparison of the potentialdynamic anodic polarization behavior of as-quenched martensite (0.47 mass% C) and decarburized low-carbon martensite (less than 0.1 mass % C) specimens, it was found that the pitting corrosion resistance of the as-quenched martensite was higher than that of low-carbon phases because of higher resistance to dissolution. Furthermore, it was reported that the interstitial carbon changes the electrochemical state of the austenitic steels. Chiba et al. measured the work function and XPS (X-ray photoelectron spectroscopy) spectra of five Fe-33Mn-C steels with 0 to 1.1 mass% carbon content. They considered that the interstitial carbon provides partial chemical bonding to iron and manganese in the austenitic structure, and this suppresses the dissolution current density in a 0.05 M Na2B4O7-NaOH buffer solution at pH 10.0 with 0.1 M Na2SO4.

As mentioned above, carbon is an effective and useful alloying element for resource-saving type stainless steels with high pitting corrosion resistance. Among various carburizing techniques, plasma carburizing is one of the most promising and economical processes since it is fast, simple, and inexpensive. The application of plasma carburizing is expected to become increasingly commonplace in the near future. From a corrosion-resistant point of view, “low temperature” operations are required during plasma carburizing to prevent sensitization. While it is widely understood that sensitization readily occurs above 600 °C, the optimal gas compositions for plasma carburizing which suppress the sensitization remain unclear. The state of plasma is closely related to the gas composition, and this affects the surface temperature of the specimen during carburizing. In addition, when sensitization occurs, it is uncertain whether post-treatments are suitable for the removal of the Cr-depleted zones. The optimal gas composition for plasma carburizing and post-treatment method which obtains stainless steel surfaces with extremely high pitting corrosion resistance need to be determined.

Because of its superior formability, weldability, and corrosion resistance, Type 304 stainless steel is the most commonly used austenitic stainless steel. However, while the plasma carburizing of Type 316L stainless steels has been extensively studied, few systematic studies on plasma carburizing for the improvement of pitting corrosion resistance of Type 304 stainless steels have been carried out. Type 304 is a typical metastable austenitic stainless steel which transforms from austenite to martensite under external stress at room temperature. The stability of austenite depends on its chemical composition and can be expressed in terms of the Md30, the temperature at which 50% of strain-induced martensite is obtained in a tension test for a true deformation of 0.3. Most of the applications of stainless steels require high formability. It is known that the formation of strain-induced martensite during plastic deformation is very important to attain high formability, yet some have demonstrated that the corrosion resistance decreases with increases in
the amount of strain-induced martensite.\textsuperscript{15,16} Because carbon acts as an austenite former, it would appear that the strain-induced martensite disappears during plasma carburizing. This affects the diffusion rate of carbon in the steels. The carburizing behavior in plasma depends on several factors, including the property of the substrate as well as the gas compositions. Sun et al. and Egawa et al. reported that the corrosion resistance of Type 304 stainless steels was improved by plasma carburizing.\textsuperscript{17,18} However, particularly in terms of the plasma gas composition, the application of plasma carburizing to improvement of the pitting corrosion resistance of Type 304 stainless steels have not been fully exploited.

In this study, we focused on the improvement of the pitting corrosion resistance of Type 304 stainless steel by plasma carburizing. Three types of Type 304 with different Md\textsubscript{30} were used. Plasma carburizing was performed in a H\textsubscript{2}-CH\textsubscript{4}, Ar-H\textsubscript{2}-CH\textsubscript{4} or Ar-CH\textsubscript{4} atmosphere at 470 °C for 18 ks to determine the effects of the chemical compositions of Type 304 and plasma gas compositions on sensitization and pitting corrosion resistance. Then, the suitability of pickling in a HF-HNO\textsubscript{3} solution was explored as a post-treatment method.

**Experimental**

**Steels and electrolytes.—** Three different Type 304 stainless steels were used as specimens. Table I shows the chemical compositions and Md\textsubscript{30} of the steels used in this study. The Md\textsubscript{30} was calculated using the following formula:\textsuperscript{19}

\[
\text{Md}_{30}[°C] = 551 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 29(Ni + Cu) - 18.5Mo - 68Nb
\]

where alloy compositions are expressed in mass\%. Steels A and B were low sulfur stainless steels. Steel A having the highest Md\textsubscript{30} was mainly used to investigate the effect of the stability of austenite on the crystal structure of the carburized layer by comparison with steel B having a lower Md\textsubscript{30} value comparable to commercial steel C. Because sulfide inclusions such as MnS are known to act as initiation sites for pitting,\textsuperscript{20–22} low-sulfur stainless steels (steels A and B) were used not only to elucidate the effect of the strain-induced martensite on carburizing but also to examine the intrinsic corrosion resistance of the carburized layer by excluding the influence of MnS. Steel B was also used to examine the effect of plasma gas composition on both the composition profile and the corrosion resistance of the carburized layer. Steel C was a commercial Type 304 stainless steel with 0.026 mass\% of sulfur and contained a substantial amount of MnS inclusions. This steel was used to examine the applicability of plasma carburizing to improve the pitting corrosion resistance of practical materials. The suitability of post-treatment in a HF-HNO\textsubscript{3} solution was investigated using the steel C. The plasma carburizing of the steel C was performed in the most appropriate plasma gas atmosphere determined using the steel B. The crystal structure, composition profile, and grain boundary sensitization of the carburized layer on the steel C were not analyzed, but they are assumed to be identical to those of the steel B.

The specimens were solution-treated at 1100 °C for 1.8 ks and quenched in water. After the heat-treatment, all the specimen surfaces were mechanically ground with SiC papers through a 1500 grit, mirror-polished with a 1 μm diamond paste, and cleaned ultrasonically with ethanol.

Electrochemical measurements were conducted in naturally aerated 0.1 and 3 M NaCl solutions at 25 °C. The solutions were prepared using deionized water and analytical grade sodium chloride.

**Plasma carburizing.—** The plasma carburizing of the specimens was performed in a conventional plasma carburizing unit. The steel specimen (30 mm × 30 mm × 2 mm) after the solution heat-treatment and subsequent polishing was fixed to an alumina holder placed in the center of the chamber (a stainless steel spherical vacuum chamber 150 mm in diameter). The specimen was connected to a DC power supply with a connecting cable, and the specimen acted as a cathode of the DC discharge. The specimen was heated as a result of bombardment of ions and fast neutral species. The treatment temperature was adjusted to 470 °C by controlling the supply current. The temperature was measured by means of a sheath thermocouple (Type K) inserted into a 1 mm diameter hole drilled in the holder, and the surface of the specimen was attached to the tip of the thermocouple. The sheath of the thermocouple was used as the connecting cable with the specimen and the DC power supply.

Prior to carburizing, the chamber was evacuated to a pressure lower than 5 × 10\textsuperscript{-4} Pa. Then, plasma gases were introduced into the chamber: the pressure of the chamber was kept at 750 Pa during plasma carburizing. The gas compositions in the plasma carburizing are shown in Table II. Plasma carburizing was conducted for 18 ks from the time the temperature reached 470 °C. After the carburizing, the specimens were cooled in the chamber.

**Macro-scale polarization.—** Potentiodynamic anodic polarization measurements were carried out using a conventional three-electrode cell. The counter electrode was a Pt plate, and the reference electrode was an Ag/AgCl (3.33 M KCl) electrode. In this paper, all the potential values refer to the Ag/AgCl (3.33 M KCl) electrode (0.206 V vs. standard hydrogen electrode at 25 °C). The potential scan rate was 3.8 × 10\textsuperscript{-4} V s\textsuperscript{-1}. The electrode areas were ca. 10 mm × 10 mm. The electrode area was formed by masking with an epoxy resin and then paraffin. The electrode areas were scaled to convert the measured current values to the current densities after polarization measurements were taken. To check the reproducibility, the polarization measurements were repeated independently at least two times using different specimens.

**Micro-scale polarization.—** Micro-scale potentiodynamic anodic polarization measurements were carried out using a micro-electrochemical system similar to that developed by Chiba et al.\textsuperscript{23} A small acrylic cell was put on the specimen surface to preserve the solution. A Pt wire was used as the counter electrode. A small Ag/AgCl reference electrode was inserted into the cell. Prior to the experiments, the reference electrode was calibrated with the Ag/AgCl (3.33 M KCl) electrode. A battery powered potentiostat was employed to reduce electrical noise.\textsuperscript{24} The potential scan rate was 3.8 × 10\textsuperscript{-4} V s\textsuperscript{-1}. Electrode areas were ca. 100 μm × 100 μm. In order to convert the measured currents to the current densities, the electrode areas were correctly measured by an optical microscope equipped with an image analyzing system.

**HF-HNO\textsubscript{3} pickling.—** In order to remove the Cr-depleted zones on the carburized stainless steels, the specimens were immersed in...
Observation and analysis.—The specimen surfaces were observed by an optical microscope and a confocal laser scanning microscope (CLSM). In the metallographic inspection, the specimen was embedded in an epoxy resin, and the cross-section of the specimen was mechanically ground with SiC papers through a 1500 grit and mirror-polished with a 1 μm diamond paste. The cross section of the specimen was etched in 10 mass% oxalic acid at the current density of 1 × 10⁴ A m⁻² at 25 °C.

The grain boundaries of the carburized steels were examined using a scanning transmission electron microscope (STEM) at an accelerating voltage of 200 kV. The sample for the STEM observation was prepared by focused ion beam (FIB) cross-sectioning. The samples were obtained by milling the specimen surface with a gallium ion beam, and were lifted out using a manipulator.

To obtain the elemental depth profile of the carburized steels, analysis was conducted by radio frequency glow discharge optical emission spectroscopy (rf-GD-OES) equipped with a Marcus-type rf-GD source geometry and a hollow anode 4 mm in diameter. In order to determine the phases and lattice parameters of the carburized layers and the untreated specimens, an X-ray diffraction (XRD) 0–20 scan was conducted using Cu-Kα radiation (Kα1: 1.5405 Å and Kα2: 1.5443 Å) with a Ni filter. Kα2 peaks were stripped (stripping ratio Kα2/Kα1 = 0.51) from the scans using computer software. The GD-OES and XRD analyses were repeated independently at least two times using different specimens.

Results and Discussion

Characterization of carburized layer.—In order to characterize the plasma-carburized layer, the cross-sections of the specimens were observed by optical microscope. Figure 1 shows the CLMS reflectance image of the cross section of the carburized steel B. This specimen was carburized in an H₂-CH₄ atmosphere, and the cross-section was etched in a 10 mass% oxalic acid. The thickness of the surface layer was 8.8 μm. In the steel matrix, the grain boundaries were partly etched. On the other hand, no etching was observed in the surface layer. It is hard to distinguish the grain boundaries in the surface layer compared with the steel matrix. From the comparison of the etching behavior of the surface layer and the steel matrix shown in Fig. 1, the corrosion resistance of the surface layer seems to have been higher than that of the steel matrix. In addition, no dark phases, which are associated with the precipitation of chromium carbides, were observed in the surface. The etched morphology of the cross-sections of the carburized steels A and C were almost the same as that of the steel B, given in Fig. 1.

The GD-OES analysis was conducted on the steel B to ascertain the existence of the carbon in the surface layer and to measure the concentration of interstitial carbon. Figure 2a compares the GD-OES depth profiles of carbon concentrations of the steel B carburized in the Ar-H₂-CH₄, Ar-CH₄, and H₂-CH₄ atmospheres. In the GD-OES analysis, iron, chromium, nickel, carbon, and oxygen were measured, and the relative concentrations were calculated. The carbon concentration was more than 3.0 mass% at the surface and substantially decreased to ca. 2 mass% after starting glow-discharging. After that, it decreased gradually from the surface to inside the steel. At deeper than ca. 17 μm, the carbon concentration reached to a steady state value of less than 0.1 mass%, which corresponds to the carbon concentration of the steel B (see Table I). It seems that the high concentration of carbon at the surface originated from adventitious carbon. The carbon concentration of the carburized steel B (H₂-CH₄ plasma) was slightly higher than that carburized in the Ar-H₂-CH₄ and Ar-CH₄ atmospheres. The GD-OES measurements for each gas composition were repeated independently at least two times using different specimens. While the carbon concentrations at the surfaces were slightly different due to the different degree of surface contamination, the concentration profiles were similar at depths of ca. 1.0 μm and greater for each condition.

In the GD-OES analysis, the interface between the carburized layer and the steel matrix was generally defined as the medium point between the maximum and minimum carbon concentrations. In the case of the H₂-CH₄ plasma, the thickness of the carburized layer was determined to be ca. 9.0 μm. This value is consistent with
observation on the cross-section shown in Fig. 1. The average carbon concentrations in the carburized layer were estimated from the GD-OES profiles in the depth from 1.5 to 9.0 μm. The average carbon concentration in the carburized layer formed in H₂-CH₄ plasma was estimated to be 1.4 mass%, which was higher than the solubility limit of austenitic stainless steels at 1100°C. In the case of the Ar-H₂-CH₄ plasma, the thickness of the carburized layer was 8.5 μm, and the average carbon concentration was 1.3 mass%. In the case of the Ar-CH₄ plasma, the thickness was 9.0 μm, and the average carbon concentration was 1.2 mass%. The small variations observed indicate that the thickness and the average carbon concentration of the carburized layer were independent of the gas composition. That is, regardless of the gas composition, a supersaturation of carbon was obtained by plasma carburizing. If the average carbon concentration of the carburized layer depends on the gas composition, the beneficial role of excited species of hydrogen in the carburizing process is likely to be expected.

Figure 2b shows the GD-OES depth profiles of the relative concentrations of carbon, chromium, and nickel of the carburized steel B (H₂-CH₄ plasma). The concentration of chromium in the carburized layer was approximately 20 mass%, which was slightly higher than that in the steel matrix. No significant enrichment of chromium was observed in the carburized layer. The concentration of nickel in the carburized layer was slightly lower than that of the steel matrix. The concentrations of chromium and nickel are comparable to those of the steel matrix. The surface layer was likely to be composed of austenite with supersaturated carbon. The chromium and nickel depth profiles of the carburized steel B were not dependent on the plasma gas composition.

In order to confirm the crystal structure of the carburized layers, an XRD analysis was performed. Figures 3b and 3c show the XRD patterns of the carburized steels A and B (Ar-H₂-CH₄ plasma). As a reference, the as-polished steel A was used. In addition, Figs. 3d and 3e exhibit the XRD patterns of the steel B carburized in Ar-CH₄ atmosphere. As seen in Fig. 3a, three peaks were observed at 2θ = 43.74°, 44.62°, and 50.83° for the as-polished steel A. On the basis of JCPDS (Joint Committee on Powder Diffraction Standards) references patterns, the peaks at 2θ = 43.74°, 50.83° were assigned to the (111) and (200) planes of austenite, respectively. And, the peak at 2θ = 44.62° was attributed to the (110) plane of martensite. It was considered that the strain-induced martensite was formed by surface grounding and polishing on the steel A.

The XRD pattern of the carburized steel A shown in Fig. 3b exhibits two clear peaks at 2θ = 42.73° and 49.45°. In addition to these, the peaks at 20 = 42.73° and 49.45° were assigned to the (111) and (200) planes of austenite, respectively. The small peak at 20 = 44.78° and 44.70° were unknown. Due to plasma carburizing, the martensite peak disappeared, and the carburized layer of the steel A was shown to be mainly composed of the austenite. It was suggested that the phase transformation from the martensite to austenite proceeded during the plasma carburizing at 470°C. The phase stability of martensite decreases with increasing carbon concentration according to the formula of M₁₇₃₀ (Equation 1).

In Fig. 3b, the peaks of the austenite clearly shifted to lower angles. From the (111) peaks, the lattice parameters of the austenite of the as-polished and carburized steel A were obtained to be 3.582 and 3.662 Å, respectively. It is clear that the expansion of the lattice was accomplished by the carburizing due to the supersaturation of interstitial carbon.

As shown in Fig. 3c, the carburized steel B also exhibited two clear peaks at 2θ = 42.77° and 49.45°, and a small shoulder was observed at 2θ = 44.08°. The peaks at 2θ = 42.77° and 49.45° were assigned to the (111) and (200) planes of austenite, respectively. On the basis of the JCPDS references patterns, the small shoulder at 2θ = 44.08° corresponded to the (511) plane of Cr₃C₆. The carburized layer of steel B also consisted of austenite. The small peak for the austenite in the surface layer of the steel B were shifted to lower angles due to the interstitial carbon. From the (111) peaks of the carburized steel B, the obtained lattice parameter was 3.659 Å, which was almost the same as that of the carburized steel A. This result suggests that the carbon concentration of the carburized layer in the steel B was almost the same as that in the steel A. The small shoulder attributed to the Cr₃C₆ precipitation implies that the surface of the carburized steel B could be sensitized by the plasma carburizing. While the reason for the absence of a peak of Cr₃C₆ for the carburized steel A is unclear, it may be due to the difference in the amount of Cr₃C₆ between steels A and B.

By comparing Figs. 3c, 3d, and 3e, the XRD patterns of the carburized steel B were similar regardless of the gas composition, except for the peak of Cr₃C₆. The peak of Cr₃C₆ disappeared by the plasma carburizing in the Ar-CH₄ and H₂-CH₄ atmospheres. While the exact reason why the peak of Cr₃C₆ disappeared remains unclear, it is suggested that the plasma gas composition changes plasma bombardment effects on the specimen surface and affects the sensitization behavior in the surface region. The shift of the (111) peak for the specimen carburized in the H₂-CH₄ plasma is slightly larger than for the specimen carburized in the Ar-H₂-CH₄ and Ar-CH₄ plasma atmospheres, suggesting that the plasma gas composition affects the carbon concentration in the carburized layers, which coincides with the results of the GD-OES analysis (Fig. 2).

Anodic polarization behavior of carburized steels.—In order to clarify the pitting corrosion resistance of the carburized steels, the potentiodynamic anodic polarization curves were measured. Figure 4a shows the macro-scale anodic polarization curves of the carburized steels A and B in naturally aerated 0.1 M NaCl at 25°C. As a reference, the pitting potential of the as-polished steel A was measured. For the as-polished steel A, polarization started at ~0.20 V, and the cathodic current was observed below approximately ~0.06 V. Above ~0.06 V, a passive current was observed. Several current spikes (sharp increase and decrease in current) were generated above 0.4 V, and a large
Figure 4. (a) Anodic polarization curves of as-polished steel A and carburized steels A and B in 0.1 M NaCl at 25°C. Plasma carburizing was conducted in the Ar-H₂-CH₄ atmosphere. (b) Optical micrograph of the carburized steel B after the polarization.

Figure 5. (a) STEM bright field image of a grain boundary of the surface of carburized steel B (Ar-H₂-CH₄ plasma). (b) Electron diffraction pattern at Point A.

Effect of plasma gas composition on anodic polarization behavior.—The results for the different gas compositions presented thus far suggest that the suppression of the precipitation of Cr₂₃C₆ was responsible for the improvement of the pitting corrosion resistance of stainless steels treated with the plasma carburizing. To inhibit the precipitation of Cr₂₃C₆ during the plasma carburizing, the optimization of the gas composition in the plasma carburizing was carried out using the steel B.

Figure 6 exhibits the macro-scale anodic polarization curves of the carburized steel B in naturally aerated 0.1 M NaCl at 25°C. Plasma carburizing was conducted in an Ar-H₂-CH₄, Ar-CH₄, or H₂-CH₄ atmosphere. In Fig. 6, the polarization curve of the steel B carburized in the Ar-H₂-CH₄ shown in Fig. 4 is presented again. In each case, potentiodynamic polarization started at −0.2 V. For the specimen precipitate, and all the spots were assigned to diffraction pattern of Cr₂₃C₆. Apparently, the precipitation of Cr₂₃C₆ at the grain boundaries occurred during the plasma carburizing. It is considered that the precipitation of Cr₂₃C₆ formed Cr-depleted zones in the grain boundaries, which caused the intergranular corrosion. The existence of Cr₂₃C₆ agrees with the XRD analysis given in Fig. 3c. While no Cr₂₃C₆ was detected in the XRD pattern shown in Fig. 3a, the large increase in current for the carburized steel A was thought to have originated from the dissolution of sensitized grain boundaries. After polarization, intergranular corrosion was also confirmed on the electrode surface. In the case of the steel A, the martensite disappeared as a result of the plasma carburizing, however the sensitization of the surface layer happened in the same manner as the steel B.

The specimen temperature during plasma carburizing was measured by a thermocouple and was kept at 470°C. This temperature is sufficiently below the precipitation temperature of Cr₂₃C₆. According to the time-temperature-sensitization (TTS) diagram for Type 304 stainless steels, 29 the nose temperature is located between 600 to 800°C. A long-time heat-treatment (above 1000 h) is required for sensitization at 470°C. However, the treatment duration was 18 ks (5 h) in this study. Since the precipitates were observed, the actual surface temperature of the specimens during the carburizing seems to have increased in excess of 600°C due to plasma bombardment.
carburized in Ar-CH₄, the corrosion potential was −0.01 V. The anodic current increased with potential, and no passivation was observed. Due to carburization in H₂-CH₄, a weak tendency toward passivation appeared in the potential region from −0.05 to 0.15 V; however, the current increased considerably above 0.15 V. While no large enhancement of the corrosion resistance was accomplished, the change of the gas composition brought about the change of the anodic polarization behavior of the carburized steels. This suggests that by controlling the gas composition during plasma processing, it is possible to suppress the sensitization of the carburized layer and also to optimize the corrosion resistance.

In order to confirm the precipitation of Cr₂₃C₆ at the grain boundaries of the steel B carburized in the H₂-CH₄, a STEM observation at a grain boundary was performed. Because of the likelihood of a temperature gradient at the surface of the specimen during carburizing, STEM observations were made at the outer and inner part of the carburized layer. Figure 7a shows the STEM bright field images of a grain boundary. Figure 7a reveals that the size of Cr₂₃C₆ in the carburized steel B (H₂-CH₄ plasma) was smaller than that treated in the Ar-H₂-CH₄. The STEM observation at the outer part of the carburized layer showed a precipitate (black) was observed at the lower-left side of the grain boundary, and several precipitates (white-gray) existed at the upper-right side of the grain boundary. The precipitate in the upper-right area was different from that at the lower-left of the image. The boundary between the upper-right and lower-left areas in the image corresponds to a grain boundary. A precipitate (black) was observed at the lower-left side of the grain boundary, and several precipitates (white-gray) existed at the upper-right side of the grain boundary. The precipitate in the lower-left grain was ca. 150 nm in size, and the precipitates in the upper-right grain were ca. 50 nm. The precipitates were considered to be Cr₂₃C₆. A comparison between Figs. 5a and 7a reveals that the size of Cr₂₃C₆ in the carburized steel B (H₂-CH₄ plasma) was smaller than that treated in the Ar-H₂-CH₄. Apparently, the gas composition affects the surface temperature of the specimen during carburizing. In their characterization of metallic sputtering in DC glow discharges of a H₂-Ar atmosphere, Tabarés and Tafalla reported that a strong decrease in the sputtering signal was observed upon the addition of H₂ to pure Ar plasma. It is therefore believed that less plasma bombardment occurred in H₂-CH₄ than in Ar-H₂-CH₄ or Ar-CH₄.

We selected the plasma processing temperature based on the report by Sun. According to this report, no precipitation of Cr₂₃C₆ is expected in the carburizing condition at 470°C for 18 ks. However, the precipitation of Cr₂₃C₆ was observed as shown in Figs. 5 and 7a. The difference between this study and Sun’s report is thought to be due to the plasma gas composition since it influences the surface temperature. The treatment temperature is thought to influence the precipitation of Cr₂₃C₆ and the carbon concentration in carburized layer. Formosa et al. pointed out that slip bands and grain boundaries seem to be preferential sites for the precipitation of M₇C₃ under low temperature carburizing. Although the results of this work indicate that the gas composition can affect carbide precipitation, the exact mechanism remains unclear and further studies are needed.

Figure 7b shows the STEM bright field images around a grain boundary in the inner part of the carburized layer of the carburized steel B. The inner part of the carburized layer was fabricated by polishing to ca. 5 μm from the surface. The boundary dividing into the upper and lower areas was clearly observed at the center of the image. The contrast in the upper area was different from that in the lower one. Because the contrast likely represents a difference in the crystal orientation, it can be assumed that the observed boundary was a grain boundary. This image indicates that no precipitate was observed at the grain boundary. Therefore, the pitting corrosion resistance of the inner part of the carburized layer is expected to be higher than that of the outer part.

**Pitting corrosion resistance of outer and inner parts of carburized layer.—**It is well-known that the initiation sites of pitting corrosion on practical stainless steels are sulfide inclusions, such as MnS. Using steel C, it can be possible to elucidate the effect of carburizing on the pitting corrosion resistance clearly since the sulfur concentration of steel C is higher than that of steels A and B.

Figure 8 shows the macro-scale anodic polarization curves of the carburized steel C in naturally aerated 0.1 M NaCl at 25°C. Plasma carburizing was conducted in the H₂-CH₄ atmosphere. For comparison, the polarization curve of the steel B carburized in the H₂-CH₄ shown in Fig. 6 is presented again. In each case, potentiodynamic polarization started at −0.2 V. For the carburized steel C, the corrosion potential was 0 V, and the anodic current increased with potential and there was no passivation. Because the chromium content and Md₃₀ of steel C are similar to those of steel B, the carburized layer of the steel C was expected to be equivalent of that of the steel B. This difference in the polarization behavior of carburized steels B and C is thought to be the result of the sulfur content.
Using steel C, the pitting corrosion resistance of the inner and outer parts of the carburized layer was examined by the micro-scale polarization curves. In order to check the reproducibility, the polarization measurements of the inner and outer parts of the carburized layer were repeated independently at least two times using different specimens.

Figure 9a shows the micro-scale anodic polarization curves of the outer and inner parts of the carburized layer on the carburized steel C in naturally aerated 0.1 M NaCl at 25 °C. A taper polishing technique was used to obtain the electrode areas. The tilt angle was around 3°. The electrode areas were ca. 100 μm x 100 μm. For the outer part of the carburized layer, the polarization started at −0.27 V, and cathodic current was observed below −0.07 V. After that, the anodic current gradually increased with potential, and a large increase in current was generated at 0.7 V. For the inner part of the carburized layer, potentiodynamic polarization began at −0.27 V, and cathodic current was observed from −0.27 to −0.04 V. Then, the anodic current gradually increased with potential, and several current spikes were observed in the potential range from 1.3 to 1.45 V. Finally, the current increased at 1.5 V.

Figures 9b and 9c show the CLMS reflectance images of the outer part of the carburized layer before and after the polarization, respectively. In the lower-right area of the electrode, two pits (black spots) were generated (Fig. 9c), and the entire surface of the electrode area corroded. This indicates that the large increase in current at 0.7 V was due to pit formation. The electrode surface (ca. 100 μm x 100 μm) included the grain boundaries: and the pits appeared to have initiated at the grain boundaries. Figures 9d and 9e show the CLMS reflectance images of the inner part of the carburized layer before and after the polarization, respectively. While corrosion had slightly generated on the entire surface of the electrode after the polarization, no large pit appeared. This image implies that the sharp increase in current at 1.5 V was mainly caused by oxygen evolution rather than pit formation.

From the result given in Fig. 9, it was found that the inner part of the carburized layer has high pitting resistance. This is because no Cr₂₃C₆ was precipitated at the grain boundaries (Fig. 7b), which implies no formation of Cr-depleted zones. In addition, because the inner part of the carburized layer was fabricated by polishing to ca. 5 μm in thickness, it is considered that the thickness of the Cr-depleted zones was estimated to be less than 5 μm, and in other words the carburized layer within 5 μm in depth from the surface was sensitized by the plasma carburizing.

The micro-scale polarization curve for the inner part of the carburized layer (Fig. 9) is similar to the macro-scale polarization curve for the surface of the carburized layer in the previous study reported by Chiba et al.,8 in which re-sulfurized Type 304 was used and no trace of surface sensitization was observed. Although the surface sensitization mechanism remains unclear, the present results suggest that if surface sensitization doesn’t occur, plasma carburization is very effective in improving the pitting corrosion resistance of stainless steels containing MnS inclusions.

**Improvement of pitting corrosion resistance by HF-HNO₃ pickling.**—The inner region of the carburized layer has a higher pitting corrosion resistance than the outer region. The removal of the Cr-depleted zones in the outer part would result in a marked improvement in the pitting corrosion resistance of the carburized steels. HF-HNO₃ pickling was applied for the post-treatment after the plasma carburizing, and its effectiveness in removing the Cr-depleted zones in the outer part was determined.

Mixtures of HF and HNO₃ are used in descaling processes of stainless steels after annealing of cold-rolled strips.32–34 During annealing, a Cr-depleted layer is generated between the Cr-enriched oxide-scale...
and the steel matrix. While the Cr-depleted layer readily dissolves in the HF-HNO₃ solutions, and the undercutting of the oxide-scale occurs, the formation of a Cr₂O₃-rich passive film prevents the steel matrix from dissolving. The active dissolution rate of Fe-Cr-Ni alloys in the HF-HNO₃ solution increases as the chromium and nickel contents in the steels decrease. Therefore, it was expected that HF-HNO₃ solutions effectively remove the Cr-depleted (Fe-rich) zones at the grain boundaries in the outer part of the carburized layer.

Figure 10 shows the optical microscope images of the as-polished and carburized steel C after the HF-HNO₃ treatment. The grain boundaries faintly appeared on the as-polished specimen, and many small black spots were seen in Fig. 10a. In the case of the carburized steel C, as seen in Fig. 10b, the grain boundaries were etched, and the dissolution inside the grain was observed on the carburized specimen after the HF-HNO₃ pickling. It appears that the precipitation of Cr²3C₆ occurred and that the Cr-depleted zone was formed on the surface of the carburized steel C. The strong etching of the grain boundaries suggests that the Cr-depleted zones were formed in most grain boundaries on the surface and the effective removal of the Cr-depleted zones occurred in the carburized layer. A comparison between Fig. 10a and 10b suggests that the HF-HNO₃ pickling provided the effective dissolution of the Cr-depleted zones and the passivation of the steel matrix.

In order to confirm a marked improvement in the pitting corrosion resistance of the specimens by the HF-HNO₃ pickling, the macro-scale anodic polarization curves were measured in naturally aerated 3 M NaCl. Figure 11 shows the potentiodynamic anodic polarization curves of the specimens after the HF-HNO₃ pickling. For the as-polished specimen (after the HF-HNO₃ pickling), a large increase in current was observed at 0.31 V due to the formation of a stable pit. This implies that a small number of sulfide inclusions, such as MnS, remained at the surface even after the HF-HNO₃ pickling, and those act as the initiation sites of pitting. In contrast, in the case of the carburized specimen after the HF-HNO₃ pickling, passivation behavior was observed, and the anodic current gradually increased with potential up to 1 V. After that, the further increase in current was observed due to oxygen evolution. Neither meta-stable nor stable pit formation was observed even in 3 M NaCl. This result shows the carburized layer after the HF-HNO₃ pickling has extremely high pitting corrosion resistance even though the initiation sites of pitting, such as MnS, seems to remain at the surface of the carburized layer. This suggests that the HF-HNO₃ pickling removed the Cr-depleted zone effectively and the interstitial carbon introduced by the plasma carburizing highly suppressed the active dissolution of the steel matrix. In this study, it was found that the pitting corrosion resistance of practical Type 304 stainless steels dramatically was improved by the plasma carburizing in an H₂-CH₄ atmosphere and subsequent the HF-HNO₃ pickling.

### Conclusions

1. The plasma carburizing of Type 304 stainless steels was performed for 18 ks at 470°C in H₂-CH₄, Ar-H₂-CH₄ or Ar-CH₄ atmosphere. In all cases, the thicknesses of the carburized layer were ca. 9 μm, the average carbon concentrations were ca. 1.3 mass%. The carburized layers consisted of austenite with supersaturated carbon.

2. Intergranular corrosion was observed after anodic polarization of the carburized layer in 0.1 M NaCl. The STEM observations reveal that Cr₂3C₆ was precipitated at the grain boundaries of the carburized layer treated in the Ar-H₂-CH₄.

3. The size of Cr₂3C₆ in the steel carburized in the H₂-CH₄ atmosphere was smaller than those of the steel treated in the Ar-H₂-CH₄ or Ar-CH₄ and no Cr₂3C₆ was formed in the inner part of the carburized layer formed in the H₂-CH₄ plasma.

4. In micro-scale anodic polarization (electrode area: ca. 100 μm × 100 μm), no stable pit was generated at the inner part of the carburized layer formed in the H₂-CH₄ plasma.

5. Type 304 stainless steel after the plasma carburizing in the H₂-CH₄ atmosphere and subsequent the HF-HNO₃ pickling exhibited no pit formation under the anodic polarization even in 3 M NaCl. It was found that the HF-HNO₃ pickling removed the Cr-depleted zones formed by the plasma carburizing.

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