Interstitial nitrogen and carbon have been reported to successfully improve the corrosion resistance of iron-based metals. Because the solid solubility limits of nitrogen and carbon in austenite phase is higher than those in the ferrite and martensite phases, interstitial elements are typically used in austenitic stainless steels. Low temperature plasma nitriding treatments have been known to result in the formation of a precipitation free nitrogen super saturated solid solution layer on austenitic stainless steels. These are characterized by a crystal structure similar to that of face centered cubic (fcc) austenite with interstitial nitrogen, and are known to exhibit high localized corrosion resistance. Many researchers have demonstrated that plasma nitriding treatments below 723 K form a precipitation free nitrogen solid solution layer which results in the improvement of pitting and crevice corrosion resistance, whereas plasma nitriding treatments above 723 K form nitride precipitates, such as chromium nitride (CrN), in a nitrogen solid solution layer and decrease corrosion resistance. Other nitriding treatments without nitride precipitates, such heat-treatment in a nitrogen atmosphere and a nitrogen gas pressurized electro-slag remelting process, also improve the pitting corrosion resistance of austenitic stainless steels. Baba et al. detected ammonia (NH₃) as a dissolution product of interstitial nitrogen in austenitic stainless steels by absorptionmetry, and proposed that the hydroxide ions (OH⁻) generated as a by-product of the NH₃ production reaction improved the localized corrosion resistance of austenitic stainless steels with interstitial nitrogen. In an experiment on a low temperature plasma nitrided Type 316L stainless steel, Flis-Kabulska et al. found an increase in the near-surface pH using an antimony microelectrode during voltammetric measurements. Alkalization is likely to be one of mechanisms contributing to the improved localized corrosion resistance of austenitic stainless steels with interstitial nitrogen. Low temperature (below 773 K) carburizing treatments, which result in an interstitial carbon content of more than 10 at% with no precipitation of carbides, have been reported to improve the corrosion resistance of austenitic stainless steels. Interstitial carbon suppresses the passive current density in near-neutral chloride-containing environments. Since carbonate ions (CO₃²⁻), believed to be a dissolution product of interstitial carbon, did not inhibit the dissolution of the stainless steel in the simulated environment, the improvement of the pitting resistance was attributed to the expansion of the lattice parameter of the austenitic stainless steel in the presence of interstitial carbon. Lattice parameter expansion has also been reported in the presence of interstitial nitrogen. While interstitial nitrogen and carbon have been revealed to effectively improve the corrosion resistance of austenitic stainless steels, the effect of interstitial elements on the corrosion resistance of iron-based metals with a ferrite phase without additional elements, such as chromium, nickel, and molybdenum, has not been reported. Since it is possible that the interstitial nitrogen has an effect on both the aqueous environment, by alkalizing, for example, as well as the solid solution metal itself, by expanding the lattice parameter, interstitial nitrogen was employed to improve corrosion resistance of carbon steel in this work.

Conventional plasma nitriding treatments have been applied to ferrous metals, such as carbon steels, to produce iron nitrides with the intention of improving the hardness and the tribological properties of the metals. Plasma nitriding treatments, typically carried out at temperatures above 773 K, result in the formation of both an outer nitrogen compound layer and an inner nitrogen solid solution layer with iron nitride precipitates (at the nitrogen diffusion zone) in the case of ferrous metals with a ferrite phase. The outer nitrogen compound layer is known to be mainly iron nitride in Nital solutions and did not maintain the original microstructures of matrix. On the other hand, the original microstructure of the matrix remains in the internal nitrogen diffusion zone, which also contains iron nitride precipitate dispersed as random needles in the ferrite grains. This needle-like iron nitride precipitate appears on the Nital etched cross-sections and can be observed with optical microscopes and scanning electron microscopes (SEM). Mouri et al. and Bouanis et al. demonstrated the improvement of plasma nitrided carbon steels is due to the formation of a nitrogen compound layer on the surfaces; however, the effect of interstitial nitrogen on the corrosion resistance of carbon steels is not well understood. In order to evaluate the effect of interstitial nitrogen on corrosion resistance, it is necessary to form a precipitation free nitrogen solid solution layer on the inner side of a mechanically removable nitrogen compound layer. Because no nitride precipitate occurs in austenitic stainless steels when low temperature plasma nitriding treatment is carried out at temperatures below 723 K, it may well be that a precipitation free nitrogen solid solution layer is formed on carbon steels when the temperature is lower than that of conventional treatments.

In this study, plasma nitriding treatment at 603 K was applied in order to form a precipitation free nitrogen solid solution layer on a
carbon steel. The characterization of the plasma nitrided carbon steel was carried out with electron probe microanalyzers (EPMA), radio frequency glow discharge optical emission spectroscopy (rf-GD-OES), X-ray diffraction analysis (XRD), and a scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (SEM/EDS). Anodic polarization measurements were taken to ascertain the effect of interstitial nitrogen on the corrosion resistance of carbon steel. The passivation behavior of the precipitation free nitrogen solid solution layer was analyzed in terms of both the dissolution products of interstitial nitrogen into solutions and the changes in the work function of carbon steel with interstitial nitrogen.

### Experimental

**Specimens and electrolytes.**—A commercial carbon steel with a thickness of 4.5 mm was used in this study. The chemical composition of the steel is shown in Table I. The carbon steel was cut into ca. 15 × 25 mm coupons parallel to the rolling direction. The steel was annealed at 1173 K for 0.5 h in a vacuum. In this paper, the specimens in this context are referred to as “untreated”. Plasma nitriding treatment was carried out at 603 K for 12 h in a 50 vol% N2–50 vol% H2 gas mixture at 250 Pa pressure (TOKAI ION CO., LTD). Prior to the plasma nitriding, the carbon steel was ground with SiC paper P-220. Plasma nitriding treatments result in the formation of an outer nitrogen compound layer and an inner nitrogen solid solution layer on carbon steels. Both the nitrogen compound and the nitrogen solid solution layers formed on the carbon steel through the plasma nitriding treatment were examined in this study.

Before the polarization measurements, the untreated carbon steel was ground with SiC paper up to P-1200, and then polished with 6 μm and 1 μm diamond pastes. The plasma nitrided carbon steel was polished with 6 μm and 1 μm diamond pastes to remove the nitrogen compound layer and to expose the nitrogen solid solution layer. The unpolished plasma nitrided carbon steel was used as the nitrogen compound layer. All the specimens were cleaned ultrasonically with ethanol.

Anodic polarization curves were measured in 0.1 M Na2SO4 solution over a pH range of 4–12. The pHs of the solution were adjusted with 0.1 M NaNO3 were also used. All the solutions were prepared from deionized water. EPMA analyses were carried out at 15 kV electron accelerating voltage and 10 μA beam current. The nitrogen concentration depth profiles of the plasma nitrided and the untreated carbon steels were obtained by HORIBA GD-Profiler2 radio frequency glow discharge optical emission spectroscopy (rf-GD-OES). The instrument employs a Marcus-type rf-GD source geometry and has a hollow anode 4 mm in diameter. Rigaku MiniFlex 600 X-ray diffraction analysis (XRD), using Cu-Kα radiation (wavelength: λ = 1.5418 Å) with a Ni filter, was performed to determine the composition of the nitrogen compound layer and to identify the lattice parameters of the nitrogen solid solution layer and the untreated carbon steel. The scanning speed and the step size were 2 degree per minute and 0.02 degree, respectively. The chemical compositions of the inclusions in the untreated carbon steel and the nitrogen solid solution layer were analyzed using FEI Quanta 250 FEG field emission scanning electron microscope (FE-SEM) equipped with an AMETEX EDAX Octane Elite energy-dispersive X-ray spectroscopy (EDS) system at an electron accelerating voltage of 20 kV (ZAF correction). Secondary electron images were taken at an electron accelerating voltage of 5 kV. The surface morphology of the nitrogen compound layer, which was the unpolished plasma nitrided carbon steel surface, was observed by an optical microscope and the FE-SEM.

**Anodic polarization measurements.**—The anodic polarization curves of the untreated carbon steel, the nitrogen solid solution layer, and the nitrogen compound layer were measured using an IVIUM pocketSTAT potentiostat. With the exception of the electrode area (ca. 10 mm × 10 mm), the surface of the specimen was coated with epoxy resin (AR-R30, Nichiban) and subsequently with paraffin. The measurements were performed in a conventional three electrode cell; the counter electrode was a platinum plate and the reference electrode was an Ag/AgCl (3.33 M KCl) electrode. All potentials cited in this paper refer to the Ag/AgCl (3.33 M KCl) electrode (0.206 V vs. standard hydrogen electrode at 298 K). The working electrode potential was scanned at a constant rate of 0.4 mV s⁻¹. The sizes of the electrode areas were scaled accurately to convert the measured current value to current density after the measurements.

**Work function measurements.**—The work functions of the untreated carbon steel, the nitrogen solid solution layer, and the nitrogen compound layer were determined using RIKEN KEIKI AC-2 photoemission yield spectroscopy in air (PYS). The photoemission yields were measured as a function of the incident photon energy (PYS spectrum). The work function was considered to be commensurate with the photoelectric threshold energy. The proportional relationship between the photoemission yield and the incident photon energy is known to be as follows:

\[
Y^{1/n} \propto (hv - x),
\]

where \(Y\) is the photoemission yield, \(n\) is a parameter dependent on the specimen type (metals: \(n = 2\), semiconductors: \(n = 1–3\), organic materials: \(n = 3\)), \(hv\) is the incident photon energy, and \(x\) is the photoelectric threshold energy (work function). The PYS spectra were measured with a 50 nW UV source power, and the values of \(Y^{1/n}\) were plotted as intensity using \(n = 2\) in this work.

### Results and Discussion

**Characterization of nitrogen solid solution and nitrogen compound layers.**—Figure 1 exhibits the optical microscope image of the cross-section of the plasma nitried carbon steel etched with 3% Nitral solution. A thin and slightly etched nitrogen compound layer was formed on the plasma nitried carbon steel surface. The maximum thickness of the nitrogen compound layer was ca. 7 μm. The ferrite and pearlite region under the nitrogen compound layer was assumed

| C   | Si  | Mn  | P   | S   | Ni  | Cr  | Mo  | Cu  | Ti  | Nb  | Al  | O   | N   | Fe  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.16| 0.02| 0.85| 0.014| 0.006| 0.02| 0.02| <0.01| 0.02| 0.011| 0.015| 0.032| 0.002| 0.003| Bal |

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(From "Journal of The Electrochemical Society, 164 (2) C17-C26 (2017)" by [Author(s)].)
to be a nitrogen solid solution layer. No needle-like nitride precipitate was observed in the estimated nitrogen solid solution layer.

The EPMA analyses were carried out to ascertain the nitrogen distribution in the plasma nitrided carbon steel. The backscattered electron images and nitrogen mappings of the cross-section of the plasma nitrided carbon steel are shown in Fig. 2. The nitrogen enriched layer on the plasma nitrided carbon steel surface spread to the ferrite and pearlite region, as shown in Figs. 2a and 2b. The maximum thickness of the nitrogen enriched layer was ca. 7 μm, and corresponded to the slightly etched nitrogen compound layer (Fig. 1). There was no nitride precipitate observed in the ferrite and pearlite region under the nitrogen compound layer. Figures 2c and 2d show the nitrogen distribution in the ferrite and pearlite region. The nitrogen concentration in the region decreased gradually with depth inside the steel, indicating a nitrogen solid solution layer was formed under the nitrogen compound layer through the plasma nitriding process. From the results of the etching (Fig. 1) and the EPMA nitrogen mappings (Fig. 2), it is clear that both the nitrogen compound layer on the outer side and the inner nitrogen solid solution layer on the carbon steel were formed by the plasma nitriding treatment. The interface between the nitrogen compound and the nitrogen solid solution layers was defined at a depth of 7 μm from the surface. The nitrogen solid solution layer was assumed to be a carbon steel with interstitial nitrogen and no nitride precipitate.

Figure 3 shows the GD-OES nitrogen concentration depth profile of the plasma nitrided and the untreated carbon steels. The nitrogen concentration of the plasma nitrided carbon steel decreased gradually with depth from the surface. The nitrogen concentration in the nitrogen solid solution layer at a depth of 7 μm to 20 μm from the plasma nitrided carbon steel surface was 0.1–0.05 mass%, which was higher than that in the untreated carbon steel. The GD-OES depth profile of the plasma nitrided carbon steel polished with 6 μm and 1 μm diamond pastes to remove the nitrogen compound layer was also measured. The polished plasma nitrided carbon steel indicated 0.1–0.05 mass% nitrogen concentration, indicating that the nitrogen solid solution layer was exposed by the polishing.

Figure 4a displays the XRD patterns of the nitrogen compound layer, the nitrogen solid solution layer, and the untreated carbon steel. The peaks of the nitrogen compound layer were assigned to Fe$_4$N and Fe$_{16}$N$_2$ iron nitrides$^{30,31}$ and the untreated carbon steel, which corresponded to the ferrite phase ($\alpha$) of steel.$^{32}$ The slightly etched nitrogen enriched layer formed on the plasma nitrided carbon steel (Figs. 1 and 2) was confirmed to be the nitrogen compound layer, consisting of Fe$_4$N and Fe$_{16}$N$_2$ iron nitrides. All peaks of the nitrogen solid solution layer were identified as the ferrite phase (α) of steel,$^{32}$ indicating no nitride precipitate occurred. The positions of the peaks of the nitrogen solid solution layer shifted to lower angle than those of the untreated carbon steel. The diffraction peaks of the (110) body-centered cubic structure of the nitrogen solid solution layer and the untreated carbon steel were detected at $2\theta = 44.56^\circ$ and $44.84^\circ$, respectively (Fig. 4b). The calculated lattice parameters of the ferrite phase of the nitrogen solid solution layer and the untreated carbon steel were 2.88 Å and 2.86 Å, respectively. The lattice parameter of the nitrogen solid solution layer showed a ca. 0.7% increase over that of the untreated carbon steel. From the results of the no iron nitride peak and the expansion of the lattice parameter, the nitrogen solid solution layer was confirmed to be carbon steel with interstitial nitrogen with no nitride precipitate.
Figure 3. GD-OES nitrogen concentration depth profiles of plasma nitrided and untreated carbon steels.

Figure 5 shows the optical microscope and the SEM images of the specimen surfaces and the typical inclusions in the untreated carbon steel and the nitrogen solid solution layer. Elongated inclusions and dot-like inclusions are evenly dispersed in both the untreated carbon steel and the nitrogen solid solution layer (Figs. 5a–5f). The relative concentrations of Mn, S, Al, O, Si, P, Ti, and Fe, as determined by the EDS point analysis on the typical inclusions, are listed in Table II. Because the inclusions were thinner or smaller than the spread volume of the incident electron, it is likely that the high Fe concentrations are from the steel matrixes. The typical elongated inclusion in the untreated carbon steel (Fig. 5b) contained Mn and S in about 1:1 atomic ratio, implying an MnS inclusion. The typical dot-like inclusions in the untreated carbon steel were MnS inclusions, as was the case for the typical elongated inclusions and composite inclusions shown in Fig. 5c. The atomic ratio of the region with Mn and S was approximately 1:1, and in the region with Al and O, the atomic ratio was approximately 2:3 for typical composite inclusions, suggesting these inclusions were MnS-Al2O3. As in the case of the untreated carbon steel, the typical inclusions in the nitrogen solid solution layer were elongated or dot-like MnS inclusions (Figs. 5e and 5f) and dot-like MnS-Al2O3 composite inclusions. The results of the etching (Fig. 1) and the inclusion characterization (Fig. 5 and Table II) confirm that both the untreated carbon steel and the nitrogen solid solution layer had a ferrite-pearlite structure with inclusions. The grinding mark with

**Table II. Relative compositions (at%) of Points 1–7 shown in Fig. 5.**

| Point | Mn | S  | Al | O  | Si | P  | Ti | Fe |
|-------|----|----|----|----|----|----|----|----|
| 1     | 15 | 13 | <0.5| <0.1| <0.5| <0.1| 0.5 | 72 |
| 2     | 12 | 13 | <0.1| <0.1| <0.1| <0.1| 9   | 66 |
| 3     | 18 | 17 | 5  | 7  | <0.1| <0.1| 0.5 | 53 |
| 4     | 1  | 1  | 36 | 48 | <0.5| <0.5| <0.1| 13 |
| 5     | 9  | 8  | <0.5| <0.1| <0.5| <0.1| 0.5 | 38 |
| 6     | 12 | 12 | <0.1| <0.5| <0.5| <0.1| 0.5 | 75 |
| 7     | 7  | 7  | <0.5| <0.1| <0.5| <0.1| 0.5 | 86 |
SiC paper prior to the plasma nitriding treatment slightly remained on the rough surface nitrogen compound layer (Figs. 5g and 5h). The surface of the nitrogen compound layer lost its metallic luster, and no inclusions, neither MnS nor MnS-Al2O3, were observed on the surface.

**Anodic polarization behavior of untreated carbon steel, nitrogen solid solution layer, and nitrogen compound layer in 0.1 M Na2SO4.**—To clarify the effect of interstitial nitrogen on the anodic polarization behavior of carbon steel, the anodic polarization curves of the nitrogen solid solution layer and the untreated carbon steel were measured in 0.1 M Na2SO4 at pHs 4.0–12.0. The anodic polarization curves of the nitrogen compound layer were also measured in the same solutions. The anodic polarization curves are shown in Fig. 6, and the electrode surfaces after the polarization are shown in Fig. 7. The corrosion potentials of the untreated carbon steel in the solutions with a pH in the range of 11.0–12.0 were around 0.3 V (Figs. 6a and 6b). The anodic polarization curves of the untreated carbon steel measured in the solutions with the same pH indicated a passive current density of ca. $2 \times 10^{-2}$ A m$^{-2}$ in the potential range from 0 V to 0.7 V. The increases in the current densities at around 0.7 V and around 1.3 V can be attributed to the formation of soluble ferrate ions (FeO4$^{2-}$) and to oxygen generation, respectively. The silver and slightly stained appearance of the electrode surfaces after the polarization indicates the passivation of the untreated carbon steel in the solutions in the pH range of 11.0–12.0 (Fig. 7). The untreated carbon steel dissolved actively in the solutions in the pH range of 4.0–10.0 (Figs. 6c–6g). The corrosion potentials of the untreated carbon steel in the solutions in the pH range of 4.0–10.0 were ca. $0.4$ V or ca. 0.6 V, and were 100 mV or 300 mV less noble than those in the solutions with a pH of 11.0–12.0. The electrode surfaces after the polarization in the solutions in the pH range of 5.0–10.0 were non-uniformly dissolved (Fig. 7). This non-uniform dissolution initiated as spots and expanded in the direction of the gravitational force on the vertically placed electrode surface. It was assumed that this non-uniform dissolution was the result of the heterogeneous carbon steel surface with a ferrite-pearlite structure and inclusions, shown in Fig. 5. However, the electrode surface of the untreated carbon steel uniformly dissolved in the solution at pH 4. The nitrogen solid solution layer passivated in the solutions at pHs 11.0–12.0 as was the case in the untreated carbon steel (Figs. 6a, 6b, and 7). In the solutions with pHs ranging from 6.0 to 10.0 (Figs. 6c–6g), the corrosion potentials of the nitrogen solid solution layer were around −0.2 V, which was 200 mV more noble than those of the untreated carbon steel. A broad peak in the current density, which had the maximum value of ca. $1 \times 10^{-1}$ A m$^{-2}$ at around 0.2 V and then decreased to ca. $2 \times 10^{-2}$ A at around 0.4 V, was measured in the anodic polarization curves of the nitrogen solid solution layer in the solutions with a pH in the range of 6.0–10.0. The electrode surfaces of the nitrogen solid solution layer remained silver or were slightly stained after the polarization, indicating passivation in the solutions above pH 6.0 (Fig. 7). The failure of the nitrogen solid solution layer to passivate in the solution at pH 5.0 (Fig. 6h) resulted in a uniformly dissolved electrode surface (Fig. 7). The nitrogen solid solution layer dissolved actively in the solution at pH 4.0, as did the untreated carbon steel (Figs. 6i and 7). It is interesting to note that the nitrogen solid solution layer, which is the carbon steel with 0.05–0.1 mass% interstitial nitrogen, passivated in the solutions above pH 6.0 (neutral environments). The changes in the current densities at 0.2 V, as extracted from the anodic polarization curves in Fig. 6, are shown as a function of solution pH in Fig. 8. The active dissolution rates of the untreated carbon steel at 0.2 V in 0.1 M Na2SO4 at pHs 6.0–10.0 were higher than $1 \times 10^{2}$ A m$^{-2}$. The current densities of the nitrogen solid solution layer at 0.2 V in the solutions, at approx. $1 \times 10^{-1}$ A m$^{-2}$, were one thousandth that of the untreated carbon steel.

The possibility that the passivation of the nitrogen solid solution layer in the solutions with pH above 6.0 results from the presence of undetectably small particles of Fe3N and Fe4N2 in the surface was precluded. The anodic polarization behavior of the nitrogen compound layer did not correspond to that of the nitrogen solid solution layer (Fig. 6). The corrosion potentials of the nitrogen compound layer

![Figure 5. Optical microscope (OM) and SEM images of specimen surfaces: (a, b, c) untreated carbon steel, (d, e, f) nitrogen solid solution layer, and (g, h) nitrogen compound layer. Enlarged SEM images: (b) Inclusions 1 in (a), (c) Inclusion 2 in (a), (e) Inclusions 3 in (d), and (f) Inclusion 4 in (d).](image-url)
Figure 6. Anodic polarization curves of the nitrogen solid solution layer, the nitrogen compound layer, and the untreated carbon steel in 0.1 M Na2SO4 at pHs 4.0–12.0.

in the solutions at pHs 11.0–12.0 were at around 0.5 V, which was 700 mV more noble than those of the nitrogen solid solution layer (Figs. 6a and 6b). The corrosion potentials of the nitrogen compound layer in the solutions in the pH range of 4.0–10.0 were around 0.1 V, which was similar to those of the nitrogen solid solution layer in the solutions in the pH range of 6.0–9.0; however, the anodic polarization curves of the nitrogen compound layer did not indicate the passive current density ca. $2 \times 10^{-2}$ A m$^{-2}$ (Figs. 6c–6i). The electrode surfaces of the nitrogen compound layer after the polarization in the solutions in the pH range of 4.0–12.0 were either almost the same as before the polarization or were slightly stained (Fig. 7). The results presented thus far clearly indicated that it was the 0.05–0.1 mass%
interstitial nitrogen which resulted in the passivation of the carbon steel in the neutral environments. The passivation mechanism of the nitrogen solid solution layer was analyzed in terms of the dissolution products of interstitial nitrogen and the work function of the carbon steel with interstitial nitrogen in the following sections.

Effect of dissolution products of interstitial nitrogen on anodic polarization behavior of carbon steel.—The dissolution products of interstitial nitrogen in carbon steel were predicted using the potential–pH diagram for N–H₂O system (Fig. 9). The standard chemical potentials of the species were obtained from the HSC Chemistry thermochemical database. The concentrations of soluble species were set to \(1 \times 10^{-5} \text{ mol/kg (H}_2\text{O)}\). Ammonium ions (\(\text{NH}_4^+\)), nitrite ions (\(\text{NO}_2^-\)), and nitrate ions (\(\text{NO}_3^-\)) were found to be thermodynamically stable in the passivation range of the nitrogen solid solution layer. Baba et al. suggested that interstitial nitrogen reacts with water (\(\text{H}_2\text{O)}\) and produces ammonium (\(\text{NH}_3\)) and hydroxide ions (\(\text{OH}^-\)) in the process of \(\text{NH}_4^+\) ion generation, suggesting that alkalization near the metal surface occurs on carbon steel with interstitial nitrogen. To confirm whether it is the combination of the alkalization and the generated ions which passivate the carbon steel with interstitial nitrogen in neutral environments, the anodic polarization curve of the nitrogen solid solution layer rotated at 200 rpm was measured in 0.1 M Na₂SO₄ at pH 6.0. The working electrode was rotated in order to prevent dissolution products from remaining near the surface of the electrode. Figure 10 shows the anodic polarization curves of the rotated nitrogen solid solution layer and the rotated untreated carbon steel in 0.1 M Na₂SO₄ at pH 6.0. Both the rotated untreated carbon steel and the untreated carbon steel which was not rotated (Fig. 6g) actively dissolved. The rotated electrode surface dissolved non-uniformly and was stained. The anodic polarization curve of the rotated nitrogen solid solution layer did not indicate the current density of \(2 \times 10^{-2} \text{ A m}^{-2}\), which was the passive current density of the nitrogen solid solution layer without the rotating (Fig. 6g). Therefore, it can be concluded that the rotated nitrogen solid solution layer failed to be passivated in 0.1 M Na₂SO₄.
at pH 6.0. The electrode surface of the rotated nitrogen solid solution layer dissolved non-uniformly and was stained in a similar manner to that of the rotated untreated carbon steel. This suggests that alkalization alone or the combination of alkalization with the ions generated from the dissolution of interstitial nitrogen resulted in the passivation of the nitrogen solid solution layer in the neutral environments. Since alkalization and NO$_3^-$ ions are expected to be the dissolution products of interstitial nitrogen (Fig. 9), they were observed carefully in this study.

On the basis of the possibility that the alkalization of the environment near the metal surface results in the passivation of the carbon steel with the 0.05–0.1 mass% interstitial nitrogen in the neutral environments, it was considered possible that rather than passivating in a buffer solution at pH 6.0, the nitrogen solid solution layer actively dissolves. Figure 11 displays the anodic polarization curves of the nitrogen solid solution layer and the untreated carbon steel in 0.125 M CH$_3$COONa–0.0062 M CH$_3$COOH buffer solution at pH 6.0 with 0.1 M Na$_2$SO$_4$. The polarization was initiated at $-1.2$ V subsequent to cathodic treatment at $-1.2$ V for 600 s to remove the air-formed film on the steel surfaces. As expected, the nitrogen solid solution layer dissolved actively in the buffer solution at pH 6.0, as was the case in the untreated carbon steel. Because the nitrogen solid solution layer was not passivated in the buffer solution at pH 6.0, it can be concluded that the alkalization of the environment near the metal surface due to the dissolution of interstitial nitrogen resulted in the passivation of the nitrogen solid solution layer in 0.1 M Na$_2$SO$_4$ at pH 6.0 (Fig. 6).

The anodic polarization curves of the untreated carbon steel and the nitrogen solid solution layer measured in 0.15 M H$_3$BO$_3$–0.0375 M Na$_2$B$_4$O$_7$ buffer solution at pH 8.45 with 0.1 M Na$_2$SO$_4$ are shown in Fig. 12. The polarization began at $-1.2$ V subsequent to cathodic treatment at $-1.2$ V for 600 s. A buffer solution at pH 8.45 was used to avoid the alkalization of the environment near the metal surface and to clarify the effect of the other dissolution products of interstitial nitrogen, such as NO$_3^-$ ions, on the anodic polarization behavior of the carbon steel. The untreated carbon steel was passivated in the buffer solution at pH 8.45 (Fig. 12a), whereas in 0.1 M Na$_2$SO$_4$ solutions

Figure 10. Anodic polarization curves of the rotated nitrogen solid solution layer and the rotated untreated carbon steel at 200 rpm in 0.1 M Na$_2$SO$_4$ at pH 6.0.

Figure 11. Anodic polarization curves of the nitrogen solid solution layer and the untreated carbon steel in 0.125 M CH$_3$COONa–0.0062 M CH$_3$COOH buffer solution (pH 6.0) with 0.1 M Na$_2$SO$_4$. The anodic polarization curves were measured subsequent to cathodic treatment at $-1.2$ V for 600 s.

Figure 12. Anodic polarization curves of (a) the untreated carbon steel and (b) the nitrogen solid solution layer in 0.15 M H$_3$BO$_3$–0.0375 M Na$_2$B$_4$O$_7$ buffer solution (pH 8.45) with 0.1 M Na$_2$SO$_4$. (c) Anodic polarization curve of the untreated carbon steel in 0.1 M NaNO$_3$ added to 0.15 M H$_3$BO$_3$–0.0375 M Na$_2$B$_4$O$_7$ buffer solution (pH 8.45) with 0.1 M Na$_2$SO$_4$. 
with pHs of 8.0 and 9.0, active dissolution behavior was observed (Figs. 6d and 6e). The maximum current density measured in the passive potential range was ca. $5 \times 10^{-3}$ A m$^{-2}$. The electrode surface of the untreated carbon steel was slightly stained after the polarization. The active dissolution, which initiated as spots and expanded in the direction of the gravitational force on the vertically placed electrode surface during the polarization in 0.1 M Na$_2$SO$_4$ at pHs 8.0 and 9.0 (Figs. 6d and 6e), was inhibited in the buffer solution at pH 8.45. The dissolution expansion, and therefore active dissolution, was likely attributed to the decrease in pH caused by the hydrolysis reaction of ferrous ions (Fe$^{2+}$) released from the dissolution at the initial spot stage. The passivation of the untreated carbon steel in the buffer solution at pH 8.45 was thought to be the result of the pH buffer action, which inhibited the decrease in pH. The nitrogen solid solution layer was passivated in the buffer solution at pH 8.45 (Fig. 12b), with no broad current peak measured in 0.1 M Na$_2$SO$_4$ at pHs 8.0 and 9.0 (Figs. 6d and 6e). The electrode surface remained silver after the polarization. The passive current density of the nitrogen solid solution layer was ca. $1.5 \times 10^{-2}$ A m$^{-2}$, which was less than one tenth that of the untreated carbon steel in the buffer solution. Wang et al. reported similar results with austenitic stainless steels: the passive current density of the plasma nitrided stainless steel in a borate buffer solution at pH 8.4 was reported to be one tenth that of untreated stainless steel.\textsuperscript{34} The difference between the passive current density of the untreated carbon steel and the nitrogen solid solution layer in the buffer solution at pH 8.45 suggests that, besides alkalization (OH$^-$ ions), the other dissolution products of interstitial nitrogen, such as NO$_3^-$ ions, had an effect on the anodic polarization behavior of the nitrogen solid solution layer.\textsuperscript{10}

The electrode surface of the untreated carbon steel remained silver. It is clear that NO$_3^-$ ions passivated the carbon steel surface, which led to a decrease in the passive current density. Judging from the results of the polarization measurements (Figs. 10–12), it is reasonable to conclude that both the alkalization of the environment near the metal surface and the NO$_3^-$ ions are the result of the dissolution of the interstitial nitrogen, and that the combination of both results in the passivation of the carbon steel with interstitial nitrogen (the nitrogen solid solution layer) in the neutral environments.

**Effect of interstitial nitrogen on work function of carbon steel.**—As mentioned above, it is possible that the solid solution metals do not easily dissolve in aqueous environments because of the presence of interstitial elements, such as nitrogen. In order to quantify the effect of interstitial nitrogen on the carbon steel itself, the work functions of the untreated carbon steel and the nitrogen solid solution layer were measured. The work function is the energy required to remove an electron from the surface of a solid substance, and the metal dissolution reaction requires these electrons to be removed to form metal ions. Therefore, it is understood that metals with a high work function do not easily dissolve in aqueous environments. In the work on different kinds of metals, Schmutz and Frankel demonstrated that there is a proportional relationship between the corrosion potential and the work function, measured as the Volta potential by a Kelvin probe force microscopy, implying that the resistance of metals to dissolution in aqueous environments can be quantified by their work function.\textsuperscript{35} The photoemission yields of the untreated carbon steel, the nitrogen solid solution layer, and the nitrogen compound layer are shown in Fig. 13 as a function of the incident photon energy (PYS spectra). The work functions of the untreated carbon steel, the nitrogen solid solution layer, and the nitrogen compound layer, defined as the photoelectric threshold energies in the PYS spectra, were 5.02, 5.10, and 5.28 eV, respectively (Table III). Since the nitrogen compound layer is not metal, its work function was much higher than that of the untreated carbon steel and the nitrogen solid solution layer. It should be noted that the work function of the nitrogen solid solution layer was 0.08 eV higher than that of the untreated carbon steel. The PYS spectra measurements were repeated three times, and the obtained work function of the nitrogen solid solution layer was ca. 0.08 eV higher than that of the untreated carbon steel. The difference in work function is assumed to be attributed to the properties of the bulk metals because the incident photon energy, which was in ultraviolet region, went through the air-formed oxide films on the surfaces of the nitrogen solid solution layer and the untreated carbon steel. The difference of about 0.1 eV in work function indicates different kinds of metals,\textsuperscript{36,37} and the interstitial nitrogen (0.05–0.1 mass%) clearly resulted in a significant improvement in the work function of the carbon steel. The results shows that the carbon steel with interstitial nitrogen does not easily dissolve in aqueous environments, resulting in the passivation of the nitrogen solid solution layer in the solutions with a pH above 6.0 (Fig. 6). It was revealed that the passivation of the carbon steel with the interstitial nitrogen (0.05–0.1 mass%) in the neutral environments is due to the alkalization effect of interstitial nitrogen on the exposed environments and the generation of NO$_3^-$ ions and also because of the increase in the work function of the carbon steel itself.

**Conclusions**

1. Low temperature plasma nitriding treatment at 603 K for 12 h was performed to a carbon steel, resulting in the formation of an outer nitrogen compound layer with a maximum thickness of ca. 7 μm and an inner nitrogen solid solution layer. The original ferritepearlite structure of carbon steel remained in the nitrogen solid solution layer. Analyses by EPMA, GD-OES, and XRD clearly indicated that the nitrogen solid solution layer contained 0.05–0.1 mass% (0.2–0.4 at%) interstitial nitrogen with no precipitation,
which resulted in a ca. 0.7% expansion of the lattice parameter. The inclusion distribution and the compositions of the typical inclusions in the nitrogen solid solution layer were almost the same as those of the untreated carbon steel. The inclusions were evenly dispersed, and were typically elongated or dot-like MnS inclusions and dot-like Al2O3–MnS composite inclusions.

2. The nitrogen solid solution layer, which is a carbon steel with 0.05–0.1 mass% interstitial nitrogen, passivated during the anodic polarization in 0.1 M Na2SO4 above pH 6.0, whereas the untreated carbon steel actively dissolved during the anodic polarization in 0.1 M Na2SO4 below pH 10.0. The nitrogen solid solution layer remained silver or were slightly stained after the polarization. The different anodic polarization behavior of the nitrogen compound layer and the nitrogen solid solution layer precluded the possibility that an undetectable surface covering with iron nitride precipitates was responsible for the passivation of the nitrogen solid solution layer in the neutral environments.

3. When rotated at 200 rpm, the nitrogen solid solution layer was not passivated during the anodic polarization in 0.1 M Na2SO4 at pH 6.0. The nitrogen solid solution layer (the working electrode) was rotated to avoid the accumulation of dissolution products of the interstitial nitrogen at the environment near the electrode surface. It was confirmed that the dissolution products of interstitial nitrogen were relevant to the passivation of the nitrogen solid solution layer in 0.1 M Na2SO4 above pH 6.0.

4. As was the case with the untreated carbon steel, the nitrogen solid solution layer actively dissolved during the anodic polarization in 0.125 M CH3COONa–0.0062 M CH3COOH buffer solution at pH 6.0 with 0.1 M Na2SO4. The active dissolution of the nitrogen solid solution layer confirmed that the alkalization of the environment near the metal surface due to the dissolution of the interstitial nitrogen resulted in the passivation of the nitrogen solid solution layer in 0.1 M Na2SO4 above pH 6.0.

5. The untreated carbon steel and the nitrogen solid solution layer passivated during the anodic polarization in 0.15 M H2BO3–0.0375 M Na2B4O7 buffer solution at pH 8.45 with 0.1 M Na2SO4. However, the maximum current density measured in the passive potential range of the untreated carbon steel was ca. 5 × 10⁻¹ A m⁻², which was more than tenfold the passive current density of the nitrogen solid solution layer. The different passivation current densities of the untreated carbon steel and the nitrogen solid solution layer suggest that besides alkalization, the other dissolution products of the interstitial nitrogen affect the anodic polarization behavior of the nitrogen solid solution layer. The anodic polarization curve of the untreated carbon steel measured in the buffer solution at pH 8.45 with NO3⁻ ions, one of the likely dissolution products of the interstitial nitrogen, corresponded to that of the nitrogen solid solution layer in the buffer solution at pH 8.45. The decrease in the passive current density of the untreated carbon steel was brought about the NO3⁻ ions.

6. The work functions of the untreated carbon steel, the nitrogen solid solution layer, and the nitrogen compound layer were 5.02, 5.10, and 5.28 eV, respectively. The work function of the carbon steel increased by 0.08 eV with 0.05–0.1 mass% interstitial nitrogen.

Acknowledgments

This work was supported by Japan Society for the Promotion of Science (JSPS) KAKENHI grant number 16K18269.

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