Interstitial Carbon Enhanced Corrosion Resistance of Fe-33Mn-xC Austenitic Steels: Inhibition of Anodic Dissolution

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Five Fe-33Mn-xC steels, referred to as 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels according to their carbon content in mass%, were prepared to clarify the effect of interstitial carbon on the dissolution behavior of steel. The 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels indicated a fully austenitic structure with no carbide precipitate. The lattice parameters of the 0.6 C, 0.8 C, and 1.1 C steels calculated from the γ(111) and γ(200) diffraction peaks increased by up to around 0.8% over that of the 0.3 C steel, suggesting that the added carbon was present as interstitial carbon in the steels. The 0.6 C, 0.8 C, and 1.1 C steels were passivated during the anodic polarization measurements in 0.1 M Na2SO4 solution at pH 12.0, whereas the 0 C and 0.3 C steels actively dissolved. The anodic polarization measurements in a buffer solution at pH 10.0 demonstrated a lower dissolution current density for the 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels with higher amounts of interstitial carbon. The dissolution current density at 0.3 V vs. Ag/AgCl (3.33 M KCl) of the 1.1 C steel was reduced to approximately 1 x 10^{-2} A m^{-2}, which is one hundredth that of the 0.3 C steel. The dissolution current density of the steels was not inhibited by the presence of 0.1 M CO3^{2-} ions, which is an expected dissolution product of interstitial carbon, implying that the interstitial carbon improved the electrochemical property of the steels themselves. The work function of the 1.1 C steel, which showed improved corrosion resistance with interstitial carbon, was 0.12 eV lower than that of the 0 C steel. The peak positions of the Fe 2p_{3/2} and Mn 2p_{3/2} spectra of the 1.1 C steel indicated the bonding energies were approximately 0.1 eV and 0.2 eV higher than those of the 0 C steel. This can likely be attributed to the partial chemical bonding of interstitial carbon to iron and manganese, respectively.

Interstitial carbon has been reported to successfully improve the corrosion resistance of austenitic stainless steels. Low-temperature carburizing treatments have been typically applied to introduce a substantial amount of interstitial carbon at the surface region of austenitic stainless steels to form a carbide precipitation free carbon super saturated solid solution layer.1,4 The carburizing treatments are known to dramatically improve the pitting corrosion resistance of austenitic stainless steels in chloride-containing environments. Anodic polarization measurements of the specimens with an exposed area of around 1 cm^2 indicated an increase in the pitting corrosion potential of the carburized stainless steels with interstitial carbon compared to untreated stainless steels.1,3-5 The microscopic anodic polarization measurements of the carburized stainless steel with a micro-scale electrode area (around 150 μm x 300 μm) containing an MnS inclusion, which is known to act as an initiation site of the pitting of stainless steels,10-21 demonstrated that no pitting was initiated on the carburized stainless steel despite the presence of the MnS inclusion.5 The micro-scale electrode area were in situ observed by an optical microscope with a water immersion objective lens (a lateral resolution of ca. 350 nm)10,22 during the microscopic anodic polarization. The microscopic polarization measurements revealed that the carburized stainless steel prevented the MnS inclusions from acting as pit initiation sites in chloride-containing environments, whereas pits were initiated at the MnS/steel boundaries on the untreated stainless steels. The stability of the Cr2O3-rich passive film formed on the surface of the carburized stainless steels has been proposed as an approach to improving the corrosion resistance of austenitic stainless steels with interstitial carbon.5,5 However, it has yet to be clarified whether or not the interstitial carbon improves the corrosion resistance of steels in general, such as steels without chromium. It is possible that, like interstitial nitrogen, interstitial carbon can be employed as an alloying element to enhance corrosion resistance not only for stainless steels but for all steels.

Nitriding treatments, which introduce super saturated interstitial nitrogen in austenitic stainless steels while avoiding nitride precipitates, are known to result in high localized corrosion resistance.22-28 It has been reported that the generation of hydroxide ions (OH^-) as a by-product of the dissolution of interstitial nitrogen in the exposed environment (alkalization) is one of mechanisms contributing to the improved localized corrosion resistance of austenitic stainless steels with interstitial nitrogen.29,30 The enhanced corrosion resistance of carbon steel with interstitial nitrogen was demonstrated in our previous work.31 Passivation occurred in carbon steel with approximately 0.1 mass% interstitial nitrogen in Na2SO4 solutions above pH 6.0 during anodic polarization measurements, whereas carbon steel without interstitial nitrogen actively dissolved in Na2SO4 solutions below pH 10.0. It was confirmed that the dissolution by-products and products of interstitial nitrogen, such as alkalization and nitrate ions (NO3^-), played important roles in improving the corrosion resistance of carbon steel, as in the case of austenitic stainless steels with interstitial nitrogen.

A considerable amount of interstitial carbon must be introduced to steels to examine the effectiveness of interstitial carbon on the corrosion resistance of steels in general. In this context, a high solid solubility limit of carbon is required, and thus, austenitic steel is preferred for this purpose. Therefore, an austenite-former element, such as manganese and nickel, must be alloyed with iron. Manganese has not been reported to enhance the corrosion resistance of iron alloys, while nickel is an alloying element in stainless steels known to do so. In order to clarify the effectiveness of interstitial carbon on the corrosion resistance of steels, manganese was considered preferable to nickel as an austenite-former in this case.

The purpose of this study was to investigate the effec of interstitial carbon content on the corrosion behavior of an austenitic steel in which Mn was alloyed as an austenite-former. Considerable amounts of carbon were introduced into Fe-33Mn-C steels and the carbon resided in the interstitial sites. Five Fe-33Mn-C steels with 0 mass% to 1.1 mass% interstitial carbon content were prepared in this study. The characterization of the five steels was carried out with Nital etching, 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 effectiveness of interstitial carbon on the corrosion resistance of the five steels. The improved corrosion resistance of the steels with interstitial carbon was analyzed in terms of the dissolution product of...
interstitial carbon. The differences of work function and electron binding energies of Fe and Mn in the steels with and without interstitial carbon were measured as properties accompanying the change in the electrochemical properties of the steels with interstitial carbon.

**Experimental**

**Specimens.**—Five ingots of Fe-33Mn-xC steels of various carbon contents were prepared by vacuum induction melting. The five Fe-33Mn-C steels are referred to as 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels according to their carbon content in this paper. The five ingots of the Fe-33Mn-C steels were forged and rolled at 1273 K into 20 mm in thickness, and then were heat-treated at 1273 K for 1 h and quenched in water. The chemical compositions of the steels are listed in Table I. The five steels used in the present study were the same as those used in the literature. After the heat-treatment, the five steel plates were cut into ca. 15 mm × 25 mm coupons parallel to the rolling direction.

Before taking measurements, the specimens were ground with SiC papers up to P-1200, and then polished with diamond pastes up to 1 μm. All the specimens were cleaned ultrasonically with ethanol.

**Microstructural and physical characteristics.**—The specimen surfaces were etched with 15% Nital solution (15 vol% HNO₃ in ethanol) to reveal the microstructures of the five Fe-33Mn-C steels. Rigaku MiniFlex 600 X-ray diffraction analysis (XRD), using Cu-Kα radiation (wavelength: λ = 1.5418 Å) with a Ni filter, was performed to identify the crystal structures and the lattice parameters of the five steels. The scanning speed and the step size were 4 degrees per minute and 0.02 degrees, respectively. The chemical compositions of inclusions in the five steels were analyzed using FEI Quanta 250 FEG field emission scanning electron microscope (FE-SEM) equipped with AMETEK EDAX Octane Elite energy-dispersive X-ray spectroscopy (EDS) system at an electron accelerating voltage of 20 kV.

The work functions of the five steels were obtained by RIKEN KEIKI AC-2 photoemission yield spectroscopy in air (PYS). The photoemission yields of the five steels were measured as a function of the incident photon energy (PYS spectra). 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,

\[ Y^{1/n} \propto (\hbar v - \epsilon), \]

where \( Y \) is the photoemission yield, \( n \) is a parameter dependent on the specimen type (metals: \( n = 2 \), semiconductors: \( n = 1-3 \)), organic materials: \( n = 3 \), \( \hbar v \) is the incident photon energy, and \( \epsilon \) 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.

The binding energies of Fe 2pₓᵧ and Mn 2pₓᵧ electrons of the 0 C and 1.1 C steels were measured using KRATOS AXIS-ULTRA DLD X-ray photo-electron spectroscopy (XPS) equipped with a monochromatic Al Kα excitation source (1486.69 eV). The binding energy axis was calibrated to give Au 4fₓᵧ and Cu 2pₓᵧ electrons of 84.0 eV and 932.7 eV, respectively. Both the 0 C and 1.1 C steels were sputtered with Ar⁺ ions for 120 s prior to the data collection in order to remove the air-formed oxide film on the specimen surfaces. The binding energy peak of O 1s electron disappeared after the Ar⁺ ions sputtering.

| Steel | C    | Si   | Mn   | P     | S     | Cu   | Fe   |
|-------|------|------|------|-------|-------|------|------|
| 0 C steel | 0.003 | 0.04 | 32.5 | <0.01 | 0.008 | <0.002 | Bal. |
| 0.3 C steel | 0.29  | 0.04 | 32.8 | <0.01 | 0.008 | <0.002 | Bal. |
| 0.6 C steel | 0.55  | 0.04 | 32.6 | <0.01 | 0.008 | <0.002 | Bal. |
| 0.8 C steel | 0.83  | 0.04 | 32.7 | <0.01 | 0.008 | <0.002 | Bal. |
| 1.1 C steel | 1.12  | 0.03 | 32.6 | <0.01 | 0.010 | <0.002 | Bal. |

**Figure 1.** Calculated phase diagram of Fe-33Mn-C (mass%).

**Results and Discussion**

**Microstructural characterization.**—Figure 1 represents the phase diagram of the Fe-33Mn-C system calculated by PANDAT software. Manganese is known for its role as an austenite former. The Fe-33Mn-C steels with 0 mass% to 1.1 mass% carbon content used in this study, which were heat-treated at 1273 K and quenched in water, were expected to form a fully austenitic structure with varying interstitial carbon content with no carbide precipitate. Figure 2 shows the optical microscope images of the five steels etched with 15% Nital solution. The surfaces of the steel specimens with the larger carbon content were stained brown during the etching. The grain size of the five steels was almost the same, at around 50 μm to 70 μm. Figure 3 displays the XRD patterns of the five steels. As expected, all peaks of the 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels were identified as the γ-austenitic phase of steel, indicating no carbide precipitate occurred. The peaks of the 0 C steel were assigned to γ-austenitic and ε-martensitic (hcp) phases of steel even though no martensitic structure was observed on the etched 0 C steel surface (Fig. 2a). It should be noted that ε-martensite can be induced by mechanical grinding around room temperature, such as grinding with SiC papers in water, in austenitic Fe-Mn-C steels with a low carbon content, such as the 0 C steel. The peaks of the ε-martensitic (hcp) phase of the 0 C steel were, therefore, considered to
Figure 2. Optical microscope images of (a) 0 C, (b) 0.3 C, (c) 0.6 C, (d) 0.8 C, and (e) 1.1 C steels etched with 15% Nital solution.

Figure 3. XRD patterns (Cu-Kα radiation) of 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels. The positions of the γ(111) and γ(200) diffraction peaks shifted to a lower angle with increasing in carbon content. The positions of these diffraction peaks, the calculated lattice parameters of the austenitic phase, and the expansions of the lattice parameter compared with the 0 C steel are listed in Table II. The lattice parameters of the 0.6 C, 0.8 C, and 1.1 C steels calculated from the γ(111) and γ(200) peaks showed increases of up to 0.78% and 0.82% over that of the 0.3 C and 0 C steels, respectively, indicating that the added carbon was present as an interstitial element in the steels. The lattice parameter of the 0 C steel was the same as that of the 0.3 C steel; this was likely due to the formation of ε-martensite in the 0 C steel. The formation of ε-martensite in the 0 C steel, which is accompanied by a contraction in volume, led the γ-austenite in the 0 C steel to expand to the same lattice parameter as that of the 0.3 C steel. From these results, it was confirmed that the 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels had a fully austenitic structure with varying interstitial carbon content and no carbide precipitate. The 0 C steel had the mechanical-grinding-induced ε-martensite in the austenite matrix. Figure 4 exhibits the optical microscope and the SEM images of the five steels. The field of view of the optical microscope was the same as that of the SEM for each of the steels. The surfaces of the five steels imply that the ε-martensite was induced during the wet-grinding with water prior to the XRD measurement. The positions of the γ(111) and γ(200) diffraction peaks shifted to a lower angle with increasing in carbon content. The positions of these diffraction peaks, the calculated lattice parameters of the austenitic phase, and the expansions of the lattice parameter compared with the 0 C steel are listed in Table II. The lattice parameters of the 0.6 C, 0.8 C, and 1.1 C steels calculated from the γ(111) and γ(200) peaks showed increases of up to 0.78% and 0.82% over that of the 0.3 C and 0 C steels, respectively, indicating that the added carbon was present as an interstitial element in the steels. The lattice parameter of the 0 C steel was the same as that of the 0.3 C steel; this was likely due to the formation of ε-martensite in the 0 C steel. The formation of ε-martensite in the 0 C steel, which is accompanied by a contraction in volume, led the γ-austenite in the 0 C steel to expand to the same lattice parameter as that of the 0.3 C steel. From these results, it was confirmed that the 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels had a fully austenitic structure with varying interstitial carbon content and no carbide precipitate. The 0 C steel had the mechanical-grinding-induced ε-martensite in the austenite matrix.

Table II. Lattice parameters of 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels calculated from γ(111) and γ(200) diffraction peaks in Fig. 3.

| Steel   | γ(111) (degree) | γ(200) (degree) | γ(111) (Å)  | γ(200) (Å)  | Expansion of lattice parameter (%) |
|---------|----------------|----------------|-------------|-------------|----------------------------------|
| 0 C steel | 43.46          | 50.52          | 3.606       | 3.613       | 0       |
| 0.3 C steel | 43.46          | 50.52          | 3.606       | 3.613       | 0       |
| 0.6 C steel | 43.40          | 50.42          | 3.611       | 3.620       | 0.13    |
| 0.8 C steel | 43.30          | 50.32          | 3.619       | 3.627       | 0.36    |
| 1.1 C steel | 43.12          | 50.08          | 3.634       | 3.643       | 0.78    |
Figure 4. (a-e) Optical microscope and (f-j) SEM images of 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels ground with SiC paper up to P-1200, and then polished with diamond paste up to 1 μm.

Table III. Relative compositions (at%) of Points 1–5 shown in Fig. 4.

| Point | Mn   | S   | O   | Mg  | Al  | Si  | Ti  | Fe  |
|-------|------|-----|-----|-----|-----|-----|-----|-----|
| 1     | 53.8 | 27.6| 14.8| <0.1| 0.5 | 0.4 | <0.1| 2.9 |
| 2-1   | 46.2 | 0.2 | 42.2| 0.8 | 1.6 | 0.2 | <0.1| 8.8 |
| 2-2   | 50.4 | 20.4| 14.5| <0.1| 0.4 | 0.3 | 0.1 | 13.9|
| 3-1   | 50.7 | 25.3| 10.7| <0.1| 0.4 | <0.1| <0.1| 12.8|
| 3-2   | 46.0 | 20.4| 25.4| 0.2 | 2.7 | 0.2 | <0.1| 5.1 |
| 4     | 52.0 | 27.7| 16.0| 0.1 | 1.6 | 0.1 | <0.1| 2.4 |
| 5-1   | 47.6 | 6.1 | 42.2| 1.1 | 0.4 | <0.1| 0.2 | 2.3 |
| 5-2   | 51.8 | 28.8| 16.3| 0.9 | 0.2 | 0.2 | 0.2 | 1.7 |

slightly corroded non-uniformly after the mirror polishing, and the Areas 1–4 in Figs. 4f–4i show the typical corroded areas. With lower carbon content in the steels, the surface of the steels was more widely corroded after the polishing. Dot-like inclusions with a diameter of less than 10 μm were evenly dispersed in the five steels. The relative concentrations of Mn, S, O, Mg, Al, Si, Ti, and Fe, as determined by the EDS point analysis on the typical inclusions marked by Point 1–5 in Figs. 4f–4j, are listed in Table III. The five steels contained two kinds of inclusions: MnO and Mn-S-O.

Anodic polarization behavior of the Fe-33Mn-C steels.—To clarify the effect of interstitial carbon on the dissolution behavior of steel, anodic polarization curves of the 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels were measured in 0.1 M Na₂SO₄ solutions at the pH ranges 11.0 to 13.0 (Fig. 5). The five steels were passivated in the solution at pH 13.0 in the same manner (Fig. 5a). The 0 C and 0.3 C steels dissolved actively, whereas the 0.6 C, 0.8 C, and 1.1 C steels were passivated in the solution at pH 12.0 (Fig. 5b). The five steels dissolved actively in the solution at pH 11.0 (Fig. 5c). The corrosion potential of the five steels in the solution at pH 11.0 tended to be noble with increased carbon content with the exception of the 0.3 C steel. Reproducibility was obtained for the anodic polarization behavior of the 0.3 C steel in the solution at pH 11.0, which had a more noble corrosion potential than that of the 0.6 C and 0.8 C steels and a rapid increase in the current density. It is interesting to note that the Fe-33Mn-C steels with more than 0.55 mass% carbon content, such as the 0.6 C, 0.8 C, and 1.1 C steels, were passivated in 0.1 M Na₂SO₄ solution at pH 12.0, indicating that the interstitial carbon improved the corrosion resistance of the Fe-33Mn-C steels. In order to ascertain more about the effect of interstitial carbon on the dissolution current density of the Fe-33Mn-C steels, anodic polarization curves of the five steels were measured in a buffer solution.

Figure 6 shows the anodic polarization curves of the five steels measured in 0.05 M Na₂B₄O₇-NaOH buffer solution at pH 10.0 with 0.1 M Na₂SO₄. Because the buffer solution prevents the pH value from decreasing with the hydrolysis reaction of metal ions released from metal dissolution, the anodic polarization measurements in the buffer solution were expected to emphasize the effect of the interstitial carbon.

Figure 5. Anodic polarization curves of 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels in 0.1 M Na₂SO₄ at pH ranges 11.0-13.0.
carbon content on the dissolution current density of the steels. The current density of the five steels in the buffer solution increased with the potential. It is clear that the dissolution current density of the steels decreased as the amount of interstitial carbon content in the steels increased, except in the case of the 0 C steel. The dissolution current density at 0.3 V of the 1.1 C steel was reduced to about $1 \times 10^{-2}$ A m$^{-2}$, which is one hundredth that of the 0.3 C steel (about 1 A m$^{-2}$). A new finding demonstrated here is that a higher content of interstitial carbon in the Fe-33Mn-C steels resulted in a stronger inhibition of the dissolution current density of the steels (Fig. 6), and therefore an improvement in the corrosion resistance (Fig. 5b).

Figure 6. Anodic polarization curves of 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels in 0.05 M Na$_2$B$_4$O$_7$–NaOH buffer solution (pH 10.0) with 0.1 M Na$_2$SO$_4$.

Carbon polarization measurements displayed in Figs. 5b and 6. In order to clarify the effect of the CO$_3^{2-}$ ions as a dissolution product of the interstitial carbon on the anodic polarization behavior of the 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels, the anodic polarization curves of the five steels were measured in Na$_2$CO$_3$–NaHCO$_3$ buffer solution (0.1 M CO$_3^{2-}$) at pH 10.0 with 0.1 M Na$_2$SO$_4$ (Fig. 7). The five steels actively dissolved in the buffer solution with CO$_3^{2-}$ ions. The dissolution current density of the five steels measured in the buffer solution at pH 10.0 with CO$_3^{2-}$ ions was higher than that in the buffer solution at pH 10.0 without CO$_3^{2-}$ ions (Fig. 6). This suggests that rather than inhibiting the dissolution current density of the five steels, the CO$_3^{2-}$ ions accelerated it. The inhibition effect of CO$_3^{2-}$ ions as a dissolution product of interstitial carbon on the dissolution current density of stainless steels has been discounted in another study on a Type 304 stainless steel. Interstitial carbon has been reported to improve the pitting corrosion resistance of the stainless steel in NaCl solutions; however, it was demonstrated that there was no difference between the active dissolution rates of the stainless steel in solutions with and without CO$_3^{2-}$ ions. This evidence is that the decrease in the dissolution current density of the Fe-33Mn-C steels as a function of the interstitial carbon content (Fig. 6) is not the effect of the formation of CO$_3^{2-}$ ions in solutions but the effect of the interstitial carbon itself in the steels.

Effect of interstitial carbon on work function of the Fe-33Mn-C steels and binding energy of Fe and Mn.—The inhibition of the dissolution current density of the Fe-33Mn-C steels, which varies according to the amount of interstitial carbon content in the steels, can likely be attributed to the improvement in the electrochemical properties of the steels with the interstitial carbon themselves. There is a possibility that change in the electrochemical properties of steels with interstitial carbon brings about some changes in the work function and the chemical bonding of the metal elements in the steels. The work function is the energy required to remove an electron from the surface of a solid substance. In the study on different kinds of metals, Schmutz and Frankel demonstrated a proportional relationship between the corrosion potential and the work function measured as the Volta potential by Kelvin probe force microscopy. This implies that there is a relationship between the electrochemical properties, such as
the corrosion potential, and the work function. Asami and Hashimoto reported that the nature of chemical bonding of metal elements can be estimated using the chemical shift in the electron binding energy measured by XPS. It has been revealed that the pitting corrosion resistance of austenitic stainless steels is improved with interstitial nitrogen to chromium in the improved stainless steel was proposed based on the chemical shift in Cr 2p3/2 electron binding energy measured by XPS. The influence of the interstitial carbon in the Fe-33Mn-C steels on the work function and the binding energies of Fe 2p3/2 and Mn 2p3/2 was, therefore, analyzed.

Figure 8a shows the photoemission yields of the 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels as a function of the incident photon energy (PYS spectra). The change in the work functions of the five steels, defined as the photoelectric threshold energies in the PYS spectra, is described in Table IV and Fig. 8b as a function of the carbon content. The work functions of the Fe-33Mn-C steels with more than 0.29 mass% interstitial carbon, such as the 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels, were 0.09 eV to 0.16 eV lower than that of the 0 C steel, which was without interstitial carbon. The difference in the work functions can be attributed to the properties of the bulk metals because the incident photon energy, which was in the ultraviolet region, went through the air-formed oxide films on the surfaces of the five steels. A difference of about 0.1 eV in work function indicates different kinds of metals, and the interstitial carbon clearly resulted in a decrease in the work function of the Fe-33Mn-C steels. An increase in the work function of a carbon steel with interstitial nitrogen was demonstrated in a previous study; however, the interstitial carbon led to a decrease in the work function of the Fe-33Mn-C steels in this study.

Figure 9 exhibits the Fe 2p3/2 and Mn 2p3/2 X-ray photo-electron spectra of the 0 C and 1.1 C steels. Both the 0 C and 1.1 C steels were sputtered with Ar+ ions for 120 s prior to the data collection to remove the air-formed oxide film on the specimen surfaces. The peaks in the Fe 2p3/2 spectra of the 0 C and 1.1 C steels were at 706.62 eV and 706.75 eV, respectively (Fig. 9a). The peak position of the Fe 2p3/2 spectrum of the 1.1 C steel had a binding energy approximately 0.1 eV higher than that of the 0 C steel. The peaks in the Mn 2p3/2 spectra of the 0 C and 1.1 C steels were at 638.42 eV and 638.65 eV, respectively (Fig. 9b). The peak position of the Mn 2p3/2 spectrum of the 1.1 C steel had a binding energy approximately 0.2 eV higher than that of the 0 C steel. The magnitude of the chemical shift measured in the Fe 2p3/2 electron binding energy differed from that in the Mn 2p3/2 electron binding energy, clarifying that the origin of the differences in the peak positions of the Fe 2p3/2 and Mn 2p3/2 spectra measured with the 0 C and 1.1 C steels was not the surface charging effect. The chemical shifts of approximately 0.1 eV higher in the Fe 2p3/2 electron binding energy and approximately 0.2 eV higher in the Mn 2p3/2 electron binding energy measured for the 1.1 C steel were likely due to the presence of the chemical bonding of the interstitial carbon to iron and manganese, respectively. The peak positions of iron carbides, such as FeC and Fe3C, in the Fe 2p3/2 spectra were reported to indicate a binding energy 0.2 eV higher than that of pure iron metal. Interstitial carbon, which formed no carbide precipitate in the Fe-33Mn-C steels (Fig. 3), is considered to provide partial chemical bonding to iron and manganese in the γ-austenitic structure.

Conclusions

1. Five Fe-33Mn-C steels with 0 mass% to 1.1 mass% carbon content, which were referred to as the 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels, were prepared in this study. XRD patterns of the five steels clearly indicated that the 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels had a fully austenitic structure with no carbide precipitate, and the 0 C steel had a mechanical-grinding-induced ε-martensite in

| Table IV: Work functions of 0 C, 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels defined as photoelectric threshold energy in PYS spectra (Fig. 8). |
|---------------------------------|-------------------|
| Steel                          | Work function (eV) |
| 0 C steel                      | 4.88              |
| 0.3 C steel                    | 4.79              |
| 0.6 C steel                    | 4.77              |
| 0.8 C steel                    | 4.72              |
| 1.1 C steel                    | 4.76              |
2. The 0.6 C, 0.8 C, and 1.1 C steels, which are the Fe-33Mn-C steels, resulted in a stronger inhibition of interstitial carbon in the steels. Dot-like inclusions with a diameter of less than 10 μm were evenly dispersed in the five steels. The compositions of the typical inclusions in the five steels were MnO and Mn-S-O.

3. The dissolution current density of the Fe-33Mn-C steels was not inhibited by CO$_3^{2-}$ ions, the expected dissolution product of the interstitial carbon, during the anodic polarization in Na$_2$CO$_3$-NaHCO$_3$ buffer solution (0.1 M CO$_3^{2-}$) at pH 10.0 with 0.1 M Na$_2$SO$_4$. This confirmed that the decrease in the dissolution current density of the Fe-33Mn-C steels as a function of the interstitial carbon content measured in 0.05 M Na$_2$B$_4$O$_7$-NaOH buffer solution at pH 10.0 with 0.1 M Na$_2$SO$_4$ was not the effect of the formation of CO$_3^{2-}$ ions in the solution.

4. The work functions of the Fe-33Mn-C steels with more than 0.29 mass% interstitial carbon, such as the 0.3 C, 0.6 C, 0.8 C, and 1.1 C steels, determined by the PYS spectra were 0.09 eV to 0.16 eV lower than that of the 0 C steel, which had no interstitial carbon.

5. The XPS analysis of the 1.1 C steel detected the chemical shifts approximately 0.1 eV higher in the Fe 2$p_{3/2}$ electron binding energy and approximately 0.2 eV higher in the Mn 2$p_{3/2}$ electron binding energy compared with the peak positions of the Fe 2$p_{3/2}$ and Mn 2$p_{3/2}$ spectra measured for the 0 C steel. This result implies the partial chemical bonding of the interstitial carbon to the iron and manganese provided in the γ-austenitic structure.

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References

1. F. J. Martin, E. J. Lemieux, T. M. Newbauer, R. A. Bayles, P. M. Nathans, H. Kahn, G. M. Michal, F. Ernst, and A. H. Heuer, Electrochim. Solid-State Lett., 10, C76 (2007).
2. Y. Sun, Surf. Coat. Technol., 204, 2789 (2010).
3. Y. Sun, Corros. Sci., 52, 2661 (2010).
4. F. J. Martin, P. M. Nathans, 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).
5. A. H. Heuer, H. Kahn, F. Ernst, G. M. Michal, D. B. Hovis, R. J. Rayne, F. J. Martin, and P. M. Nathans, Acta Mater., 60, 716 (2012).
6. A. Chiba, S. Shibukawa, I. Muto, T. Doi, K. Kawano, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 162, C270 (2015).
7. Y. Cao, F. Ernst, and G. M. Michal, Acta Mater., 51, 4117 (2003).
8. G. M. Michal, F. Ernst, H. Kahn, Y. Cao, F. Oba, N. Agrawal, and A. H. Heuer, Acta Mater., 54, 1597 (2006).
9. G. M. Michal, F. Ernst, and A. H. Heuer, Metall. Mater. Trans. A, 37A, 1819 (2006).
10. Z. Szklarska-Smialowska, Pitting corrosion of metals, p. 69, NACE, Houston, TX (1986).
11. G. S. Ekland, J. Electrochem. Soc., 121, 467 (1974).
12. T. Suter, E. G. Webb, H. Bohni, and R. C. Alkire, J. Electrochem. Soc., 148, B174 (2001).
13. J. O. Park, S. Matsch, and H. Högni, J. Electrochem. Soc., 149, B34 (2002).
14. E. G. Webb and R. C. Alkire, J. Electrochem. Soc., 149, B272 (2002).
15. H. Krawiec, V. Vignal, and R. Oltra, Electrochim. Commun., 6, 655 (2004).
16. H. Krawiec, V. Vignal, V. Heinzt, R. Oltra, and J. Olive, J. Electrochem. Soc., 152, B213 (2005).
17. I. Muto, Y. Izumiya, and N. Hara, J. Electrochem. Soc., 154, C439 (2007).
18. I. Muto, D. Ito, and N. Hara, J. Electrochem. Soc., 156, C355 (2009).
19. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 159, C341 (2012).
20. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, J. Electrochem. Soc., 160, C511 (2013).
21. A. Chiba, I. Muto, Y. Sugawara, and N. Hara, Mater. Trans., 55, 857 (2014).
22. M. Kadowski, I. Muto, Y. Sugawara, T. Doi, K. Kawano, and N. Hara, J. Electrochem. Soc., 164, C261 (2017).
23. Y. Sun, Surf. Eng., 26, 114 (2010).
24. Y. Sun, X. Y. Li, and T. Bell, J. Mater. Sci., 34, 4793 (1999).
25. H. Baba, T. Kodama, and Y. Katada, Corros. Sci., 44, 2593 (2002).
26. D. Kuroda, S. Hiromoto, T. Hanawa, and Y. Katada, Mater. Trans., 43, 3100 (2002).
27. C. X. Li and T. Bell, Corros. Sci., 46, 1527 (2004).
28. J. Flis and M. Kuczynska, J. Electrochem. Soc., 151, B573 (2004).
29. A. Fossati, B. Forni, E. Galvanetto, and T. Bacci, Corr. Sci., 48, 1513 (2006).
30. J. Flis-Kabulska, Y. Sun, and J. Flis, Electrochim. Acta, 104, 208 (2013).
31. A. Chiba, A. Nagataki, and T. Nishimura, J. Electrochem. Soc., 164, C17 (2017).

Figure 9. (a) Fe 2$p_{3/2}$ and (b) Mn 2$p_{3/2}$ X-ray photo-electron spectra of 0 C and 1.1 C steels sputtered with Ar$^+$ ions for 120 s.
32. M. Koyama, Y. Shimomura, A. Chiba, E. Akiyama, and K. Tsuzaki, *Scr. Mater.*, **141**, 20 (2017).
33. E. O. Kane, *Phys. Rev.*, **127**, 131 (1962).
34. G. W. Gibbons and F. G. Allen, *Phys. Rev.*, **127**, 141 (1962).
35. M. Kochi, Y. Harada, T. Hirooka, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **43**, 2690 (1970).
36. J. M. Ballantyne, *Phys. Rev. B*, **6**, 1436 (1972).
37. Powder Diffraction File (PDF) Card No. 00-033-0397.
38. M. Koyama, T. Sawaguchi, T. Lee, C. S. Lee, and K. Tsuzaki, *Mater. Sci. Eng. A*, **528**, 7310 (2011).
39. M. Koyama, T. Sawaguchi, and K. Tsuzaki, *Philos. Mag.*, **92**, 3051 (2012).
40. M. Kadowaki, I. Muto, Y. Sagawara, T. Doi, K. Kawano, and N. Hara, *J. Electrochem. Soc.*, **164**, C962 (2017).
41. A. Roine, *HSC Chemistry Thermo-chemical Database*, Version 9, Outotec Oy, Pori, Finland (2016).
42. P. Schmutz and G. S. Frankel, *J. Electrochem. Soc.*, **145**, 2285 (1998).
43. K. Asami and K. Hashimoto, *Corros. Sci.*, **17**, 559 (1977).
44. J. P. Riviere, M. Cahoreau, and P. Melheust, *J. Appl. Phys.*, **91**, 6361 (2002).
45. H. B. Michaelson, *J. Appl. Phys.*, **21**, 536 (1950).
46. N. D. Lang and W. Kohn, *Phys. Rev. B*, **3**, 1215 (1971).
47. A. R. Sethuraman, J. M. Stencel, A. M. Rubel, B. Cavin, and C. R. Hubbard, *J. Vac. Sci. Technol. A*, **12**, 443 (1994).