

Effect of Manganese on the Corrosion Behavior of Low Carbon Steel in 10 wt.% Sulfuric Acid

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This study examined the effect of manganese on the corrosion resistance of carbon steel in 10 wt.% sulfuric acid by using carbon steels containing three different manganese contents. From the results of electrochemical tests, it was confirmed that the increase of manganese in steel had a positive effect on the corrosion resistance and manganese content in steel changed the corrosion current density with the immersion time. From impedance spectroscopy and surface analysis, it was confirmed that the corrosion inhibiting effect of manganese in steel was attributed to the adsorption of manganese ions and the protective manganese products.

Keywords: Low carbon steel, manganese, sulfuric acid, electrochemical impedance spectroscopy (EIS)

1. INTRODUCTION

Corrosion of steel in sulfuric acid media is one of the main problems in many industrial systems including flue gas desulfurization system of thermal power plants. Especially, it is important to develop low alloy steels which have excellent corrosion resistance in severe environments and indicate relatively low cost compared to stainless steels or nickel alloys. To increase the corrosion resistance of low alloy steel in sulfuric acid, the effects of various elements and natural products on the corrosion resistance of low alloy steel have been studied widely [1-9] and the elements indicate positive or negative effects on the corrosion resistance with different mechanisms. Nevertheless, the well-known elements indicating positive effect on the corrosion resistance of low alloy steel are high in scarcity. In comparison with rare elements, Mn is one of the abundant elements on earth and it is added into steel in order to eliminate noxious sulfur by forming MnS inclusions. Mn in steel stabilizes austenite and it has a higher solubility in austenite than in ferrite. It is reported that MnS inclusion has

a negative effect on localized corrosion in steel. MnS inclusions are known to be the initiation sites of pitting corrosion in stainless steel [10] and diffusion paths for hydrogen in low carbon steel [11]. Krawiec [12] monitored the local current distribution around a pitting site in order to observe difference of potential between substrate and MnS inclusion and confirmed that MnS inclusion indicated anodic potential compared with carbon steel. Especially, in chloride-containing solution, many studies are reported that MnS inclusions play a leading role in the initial corrosion because chloride prefers to adsorb and accumulate at the MnS inclusions, resulting in localized corrosion [13,14]. In the case of stainless steel, it is reported that the increase of Mn content decreases the repassivation rate of the alloys in stainless steel [15] and Mn does not contribute the corrosion resistance in stainless steel because Mn is absent in the passive film although it is contained about 6% in stainless steel [16]. The effect of Mn on the corrosion behavior of low alloy steel in sulfuric acid has not been clearly reported and the mechanism for a small addition of Mn in steel is also not clear. Cleary [17] conducted weight loss test and the results indicated a poor corrosion resistance of low alloy steel in sulfuric acid solution when the Mn content of the steel was above 1.2%. However, the inhibitory effect of Mn ions on the hydrogen evolution reaction of iron in a sulfuric acid solution is also reported [18-19]. In this study, the alloying effects of Mn on the corrosion properties of low carbon steels in sulfuric acid were examined through electrochemical tests and surface analyses.

2. EXPERIMENTAL PROCEDURES

2.1. Materials and solution

In this study, low carbon steels containing three different amounts of Mn were used as specimens.

Table 1. Compositions of the specimens

Specimen	Composition (wt.%)					
	C	Mn	P	S	Al	Fe
0.7 % Mn steel	0.07	0.7	0.01	0.01	0.04	Balance
2.0 % Mn steel	0.07	2.0	0.01	0.01	0.04	Balance
5.0 % Mn steel	0.07	5.0	0.01	0.01	0.04	Balance

Table 1 lists the chemical compositions of the three specimens. The cast was heated at 1250 °C for 1 h, and annealed at 900 °C. After that, it was coiled at 650 °C for 1 h and cooled in the furnace. The thickness of each plate-type specimen is 0.35 cm and the exposed surface area is 2.25 cm². The surface of the specimens was ground by 600-grit SiC paper and cleaned with ethanol before electrochemical tests. All electrochemical tests and surface analyses were conducted in 10 wt.% H₂SO₄

solution and the solution was aerated with air at a flow rate of 10 cm³/min. The temperature of solution was adjusted to 25 °C.

2.2. Electrochemical tests

All electrochemical tests were performed by using multipotentiostat/galvanostat VMP2 equipment. A three-electrode cell was used for electrochemical measurements. The test materials were used as the working electrode and a pure graphite rod and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. All electrochemical tests were performed after open-circuit potential (OCP) of the specimen had stabilized. Potentiodynamic polarization tests were performed to observe corrosion behaviors of each specimen. The scan range of the polarization was established from -250 mV_{OCP} to 100 mV_{SCE} with a scan rate of 0.166 mV s⁻¹.

Electrochemical impedance spectroscopy (EIS) was performed to evaluate the polarization resistance of Mn-containing steels. The frequency was ranged from 100 kHz to 10 mHz with a sinusoidal potential perturbation of 10 mV in amplitude. To ensure reproducibility, the measurements for each specimen were repeated three times.

2.3. Surface analysis

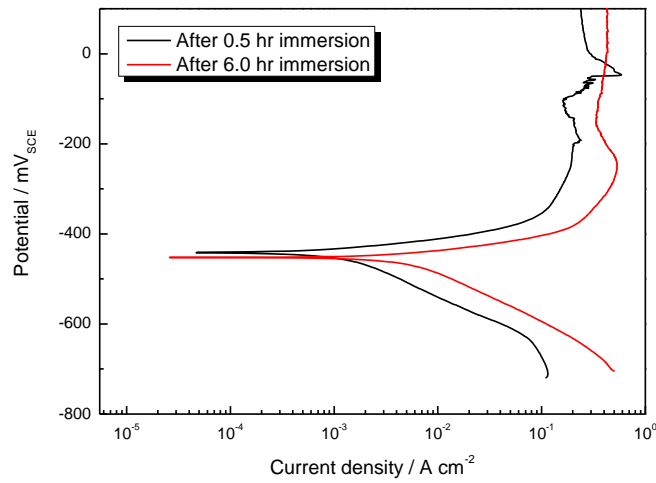
X-ray photoelectron spectroscopy (XPS) was conducted to analyze contents and intensities of corrosion products generated after 6 h immersion of Mn-containing steels by using Model SIGMA PROBE equipment. Electron probe microanalysis (EPMA) using Model JEOL JXA-8900R was performed to observe the distribution of corrosion products generated after 6 h immersion of Mn-containing steels.

3. RESULTS AND DISCUSSION

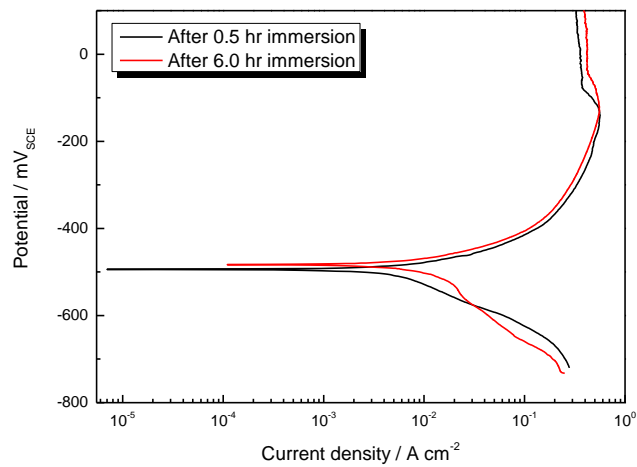
3.1. Potentiodynamic polarization test

Table 2. Electrochemical parameters of the potentiodynamic polarization tests in 10 wt.% H₂SO₄ solution

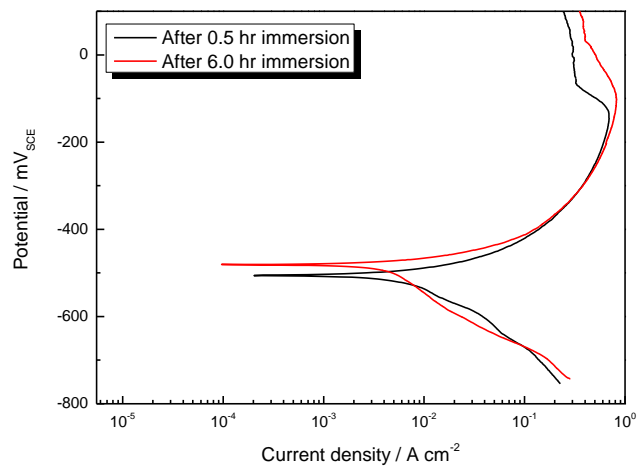
Specimen	Immersion time before test / hour	E _{corr} / mV	i _{corr} / mA cm ⁻²	β _a / mV dec ⁻¹	β _c / mV dec ⁻¹
0.7 % Mn steel	0.5	-444.00	1.25	38.40	106.09
	6.0	-453.99	6.09	38.60	114.25
2.0 % Mn steel	0.5	-494.78	4.77	41.70	103.80
	6.0	-481.20	6.96	53.16	148.20
5.0 % Mn steel	0.5	-507.00	4.97	45.39	104.89
	6.0	-484.70	3.85	41.70	129.50



(a)



(b)



(c)

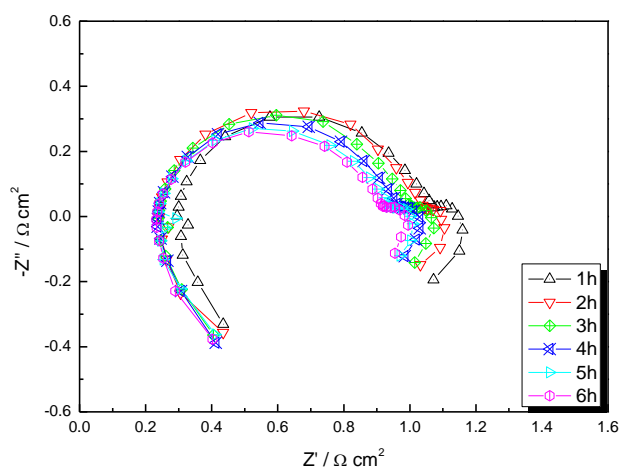
Figure 1. Potentiodynamic polarization curves of the Mn-containing steels in 10 wt.% H₂SO₄ solution: (a) 0.7 % Mn steel, (b) 2.0 % Mn steel and (c) 5.0 % Mn steel

Fig. 1 shows the polarization curves of the Mn-containing steels in sulfuric acid after 0.5 h and 6 h immersion. All specimens indicated active behaviors which is general corrosion behavior of low carbon steel in sulfuric acid.

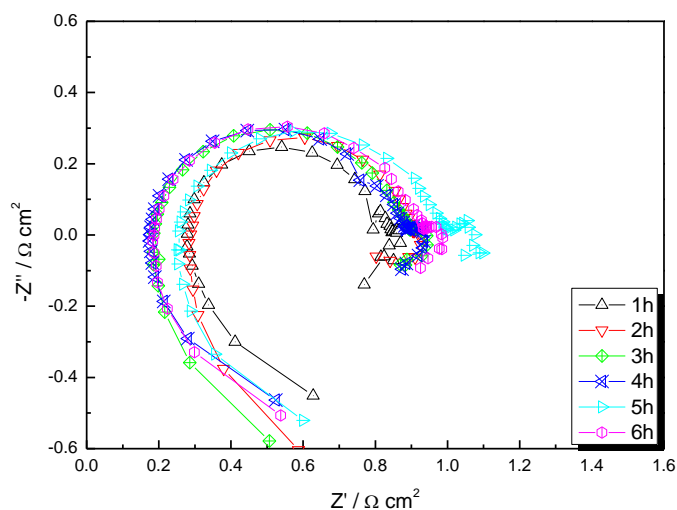
Table 2 shows the results of corrosion potential (E_{corr}), corrosion current density (i_{corr}) and Tafel constants (β_a, β_c) which were obtained from polarization curves. From the results of polarization tests performed after 0.5 h immersion, 0.7 % Mn steel indicated the highest corrosion potential and lowest corrosion current density among three specimens. However, the corrosion current density obtained from polarization curve performed after 6 h immersion indicated higher value than the corrosion current density obtained after 0.5 h immersion in Fig. 1 (a). On the contrary, in Fig. 1 (b), the polarization curves as a function of immersion time for 2.0 % Mn steel indicated analogous shape and the difference of two corrosion current densities of 2.0 % Mn steel after 0.5 and 6 h immersion was slight. In Fig. 1 (c), the corrosion density of 5.0 % Mn steel after 6 h immersion was lower than that after 0.5 h immersion. These results mean that the corrosion rate of Mn-containing steels was changed with immersion time. The corrosion potential among three Mn-containing steels resulted from the increase of oxidation reaction rate of Mn with increasing content of Mn. The corrosion probability of Mn is thermodynamically higher than that of Fe because electromotive force potential of Mn is lower than that of Fe [20].

3.2. Electrochemical impedance spectroscopy

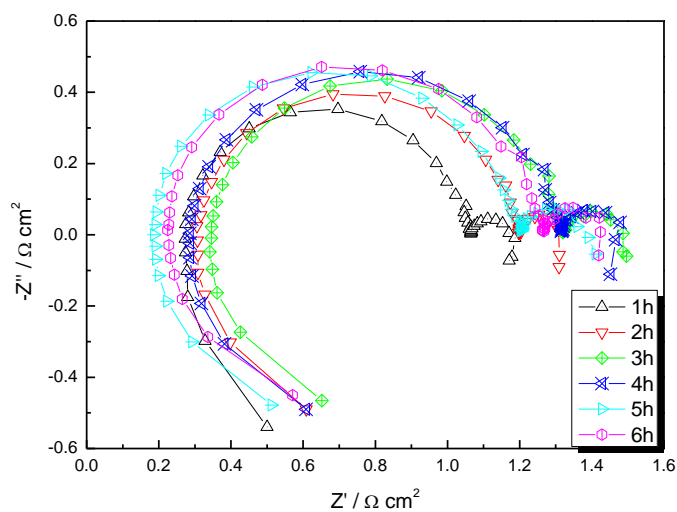
Electrochemical impedance spectroscopy was performed to observe the change of corrosion rates as a function of immersion time exactly. Fig. 2 shows Nyquist plots of EIS test results for the three specimens. EIS tests were performed at an interval of 1 h during 6 h. The equivalent circuit shown in Fig. 3 was used for fitting the EIS data. If the states of rust and substrate in the solution didn't have perfect capacitance values, the C value could be replaced by a constant phase element (CPE) value in order to improve the quality of the fit. R_s is the solution resistance of the test electrolyte between the working electrode and the reference electrode.



(a)



(b)



(c)

Figure 2. Impedance plots of the Mn-containing steels in 10 wt.% H₂SO₄ solution: (a) 0.7 % Mn steel, (b) 2.0 % Mn steel and (c) 5.0 % Mn steel

Meanwhile, CPE1 is constant phase element of rust capacitance and R_{rust} is rust resistance. CPE2 is constant phase element of the double layer capacitance at the solution/substrate interface. R_{ct} is the charge-transfer resistance of the substrate.

The polarization resistance, R_p, is equal to R_{rust} + R_{ct}. It is inversely proportional to the corrosion current density [21]:

$$R_p = \frac{\beta_a \beta_c}{2.3i_{corr} (\beta_a + \beta_c)} \quad (1)$$

EIS results of all specimens indicated obvious tendency of the polarization resistance with immersion time.

Table 3. Electrochemical parameters of the EIS test in 10 wt.% H₂SO₄ solution

Specimen	Immersion time / hour	R_s / $\Omega \text{ cm}^2$	$Y_{0,CPE1}$ / $\Omega^{-1} \text{ s}^n$	R_{rust} / $\Omega \text{ cm}^2$	$Y_{0,CPE2}$ / $\Omega^{-1} \text{ s}^n$	R_{ct} / $\Omega \text{ cm}^2$
0.7 % Mn steel	1	0.2836	0.0296	0.0157	0.0011	0.8145
	2	0.2255	0.0280	0.0206	0.0012	0.8400
	3	0.2275	0.0231	0.0158	0.0014	0.7954
	4	0.2246	0.0149	0.0207	0.0015	0.7430
	5	0.2396	0.0189	0.0007	0.0015	0.7248
	6	0.2257	0.0209	0.0140	0.0015	0.7081
2.0 % Mn steel	1	0.2302	0.0544	0.0519	0.0007	0.5977
	2	0.2248	0.0377	0.0707	0.0008	0.6484
	3	0.1648	0.0178	0.0283	0.0008	0.7280
	4	0.1487	0.0439	0.0326	0.0010	0.7572
	5	0.2424	0.0118	0.0210	0.0007	0.7497
	6	0.1663	0.0387	0.0264	0.0010	0.7937
5.0 % Mn steel	1	0.2268	0.0252	0.0540	0.0003	0.8172
	2	0.2740	0.0405	0.0408	0.0003	0.9673
	3	0.3091	0.0029	0.0433	0.0003	0.9734
	4	0.2428	0.0216	0.0520	0.0004	1.0810
	5	0.1928	0.4229	0.0498	0.0005	0.9527
	6	0.1813	0.1000	0.0463	0.0005	1.1990

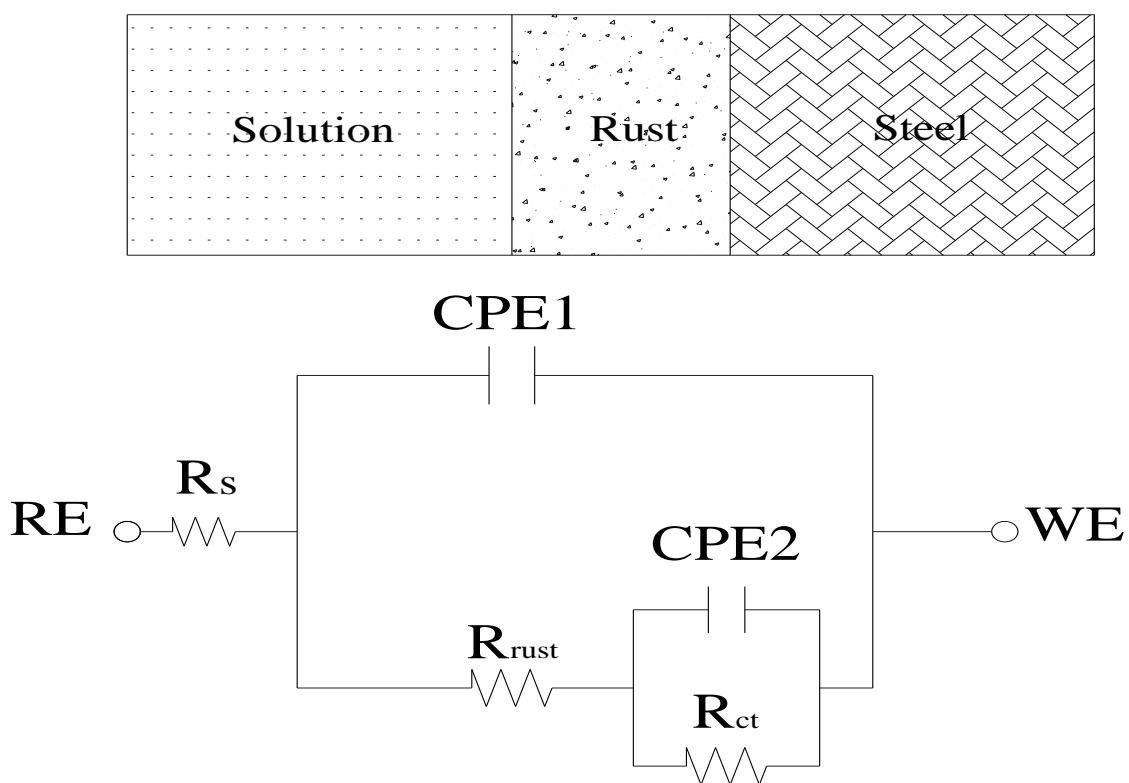


Figure 3. The equivalent circuit for fitting the EIS data

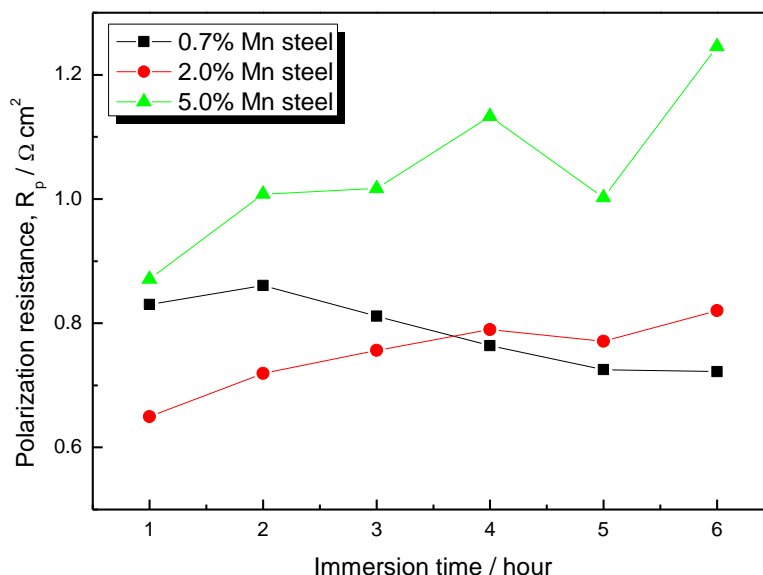


Figure 4. Polarization resistances of the Mn-containing steels as a function of time in 10 wt.% H₂SO₄ solution

Table 3 lists the polarization resistance of three specimens as immersion time. Fig. 2 (a) indicated the polarization resistance of 0.7 % Mn steel was decreased with increasing immersion time while the polarization resistances of 2.0 % and 5.0 % Mn steels were increased in Fig. 2 (b) and (c). Fig. 4 shows the polarization resistance of Mn-containing steels as a function of immersion time in 10 wt.% sulfuric acid. These results indicated protective products didn't exist only in 0.7 % Mn steel. The protective property of products formed by corrosion of 5.0 % Mn steel was the best among those of three Mn-containing steels.

From EIS results, CPE values of Mn-containing steels are also related to the corrosion resistance. CPE is defined in impedance representation as:

$$Z(\text{CPE}) = Y_0^{-1} (j\omega)^{-n} \quad (2)$$

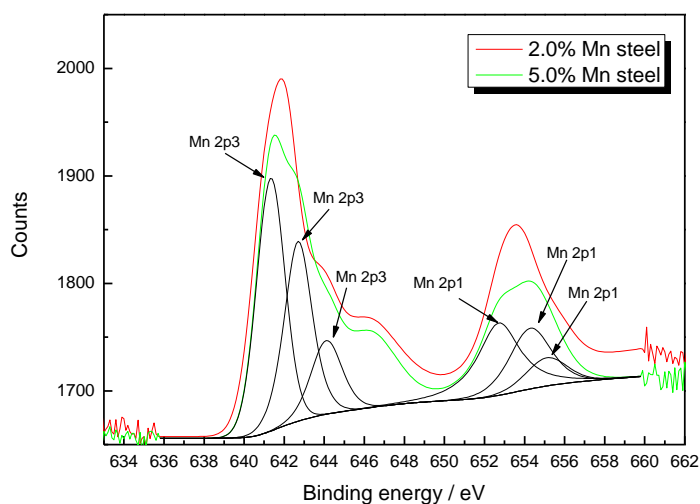
where Y_0 is the CPE constant, ω is the angular frequency (in rad s⁻¹), $j^2 = -1$ is the imaginary number and n is the CPE exponent. Depending on n , CPE can represent resistance ($Z(\text{CPE}) = R$, $n = 0$), capacitance ($Z(\text{CPE}) = C$, $n = 1$), inductance ($Z(\text{CPE}) = L$, $n = -1$) or Warburg impedance for ($n = 0.5$) [13, 16]. In this paper, we could convert $Y_{0,\text{CPE}2}$ into C_{dl} because the n values of CPE2 calculated from all impedance data of the three specimens were 1.

The capacitance value of double layer can be related to adsorption of ions [22]. When the adsorption of ions occurs at the surface, the capacitance is dropped because the area of the electrical double layer which functions as capacitor is decreased. It was confirmed that the higher content of Mn in steel indicated comparatively lower $Y_{0,\text{CPE}2}$ values in Table 3. The adsorption probability of Mn ions is related to the content of Mn in steel. The adsorption of Mn ions on the surface could affect the decrease of $Y_{0,\text{CPE}2}$ because the capacitance area on the surface was decreased by Mn ions. In addition, the adsorbed ions play a role in the inhibition of the penetration of aggressive ions. Therefore, R_{ct} was

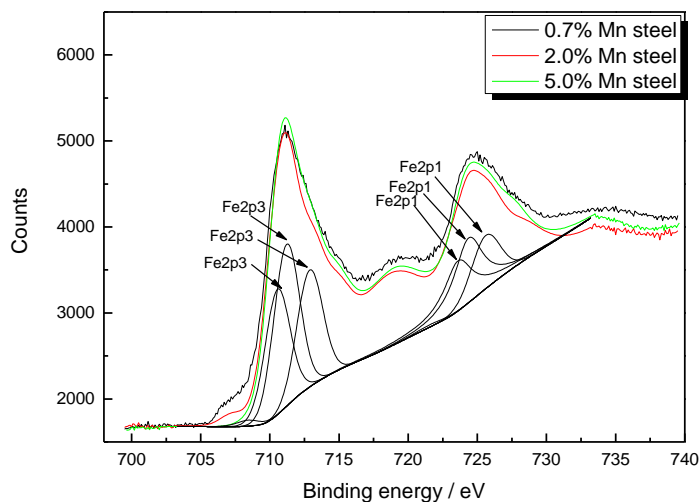
increased with increasing Mn content in steel. From these results, it could be suggested that dissolved Mn^{2+} ions were adsorbed on to the substrate surface and had a positive effect on the corrosion resistance of steel.

3.3. Surface analysis

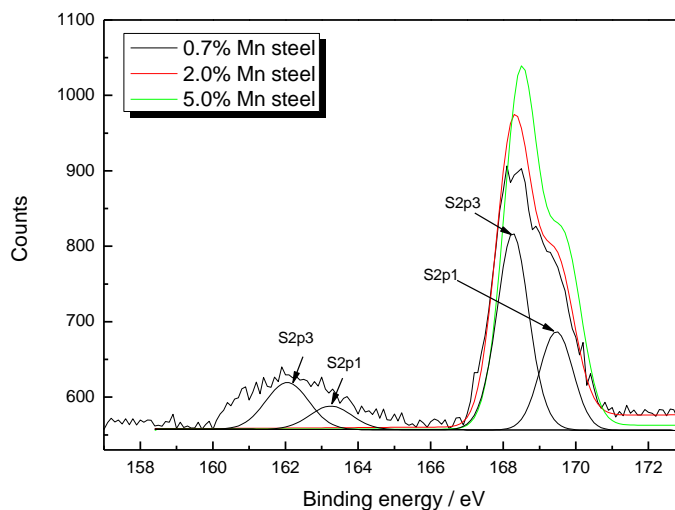
Fig. 5 shows the XPS spectra of Mn, Fe and S elements after 6 h immersion in 10 wt.% sulfuric acid and Table 4 lists compounds to be detectable in the results of XPS. Mn compounds were not observed on 0.7 % Mn steel (Fig. 5 (a)). This result means that the amount of Mn compounds formed by corrosion of 0.7 % Mn steel was not enough to increase the corrosion resistance of the steel. Mn compounds were detected in corrosion products of 2.0 % and 5.0 % Mn steels.



(a)



(b)



(c)

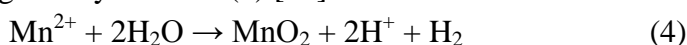
Figure 5. XPS spectra after 6 h immersion in 10 wt.% H₂SO₄ solution: (a) Mn, (b) Fe and (c) S**Table 4.** Binding energies of the components determined by XPS

Analyses of XPS spectra	Standard chemicals	Binding energy / eV
The spectrum of Mn 2p	MnO ₂	642.7, 643.4, 653.9
	Mn ₂ O ₃	641.5, 642.8, 653.7
	Mn ₃ O ₄	641.1, 653.1
	MnSO ₄	642.7
The spectrum of Fe 2p	FeOOH	711.5, 724.3
	Fe ₂ O ₃	711.5, 724.0
	Fe ₂ (SO ₄) ₃	713.5
The spectrum of S 2p	MnSO ₄	168.1, 169.6
	MnS	162.00

The corrosion products formed by Mn dissolution were manganese oxides and manganese sulfates. In acid solution, Mn is oxidized to Mn²⁺ ions as given by reaction (3):



Mn²⁺ ions and water molecules produce Mn dioxide (MnO₂) and hydrogen ions and hydrogen gas as given by reaction (4) [23]:



In sulfuric acid, iron and manganese in Mn-containing steel react with SO₄²⁻ ions and form iron sulfate (FeSO₄) and manganese sulfate (MnSO₄). In addition, the reaction of manganese dioxide with ferrous sulfate and excess acid can take place as following reaction (5) [24]:



From XPS analyses, it was proved that manganese oxide and sulfate could be formed by above reactions from Mn-containing steels in sulfuric acid solution. It was confirmed that these products protected the substrate and the protective property was intensified as time passed from EIS results.

The standard potential E_0 of reaction (3) is about -1.179 V and this potential is lower than that of iron ($\text{Fe} = \text{Fe}^{2+} + 2e^-$, $E_0 = -0.440$ V) [20]. Through the results of potentiodynamic test and XPS, it was confirmed that the increase of manganese content in steel decreased the corrosion potential of steel by increasing manganese dissolution reaction and formed more manganese corrosion products. From Figs. 1 (b) and (c), the increase of potential as a function of time means that the reaction (3) was decreased with increasing immersion time. It is reported that Mn^{2+} ions in sulfuric acid solution inhibits the dissolution of iron to a considerable extent and this inhibition effect of Mn^{2+} ions is attributed to their blocking nature of these metal cations to the iron dissolution reaction [19].

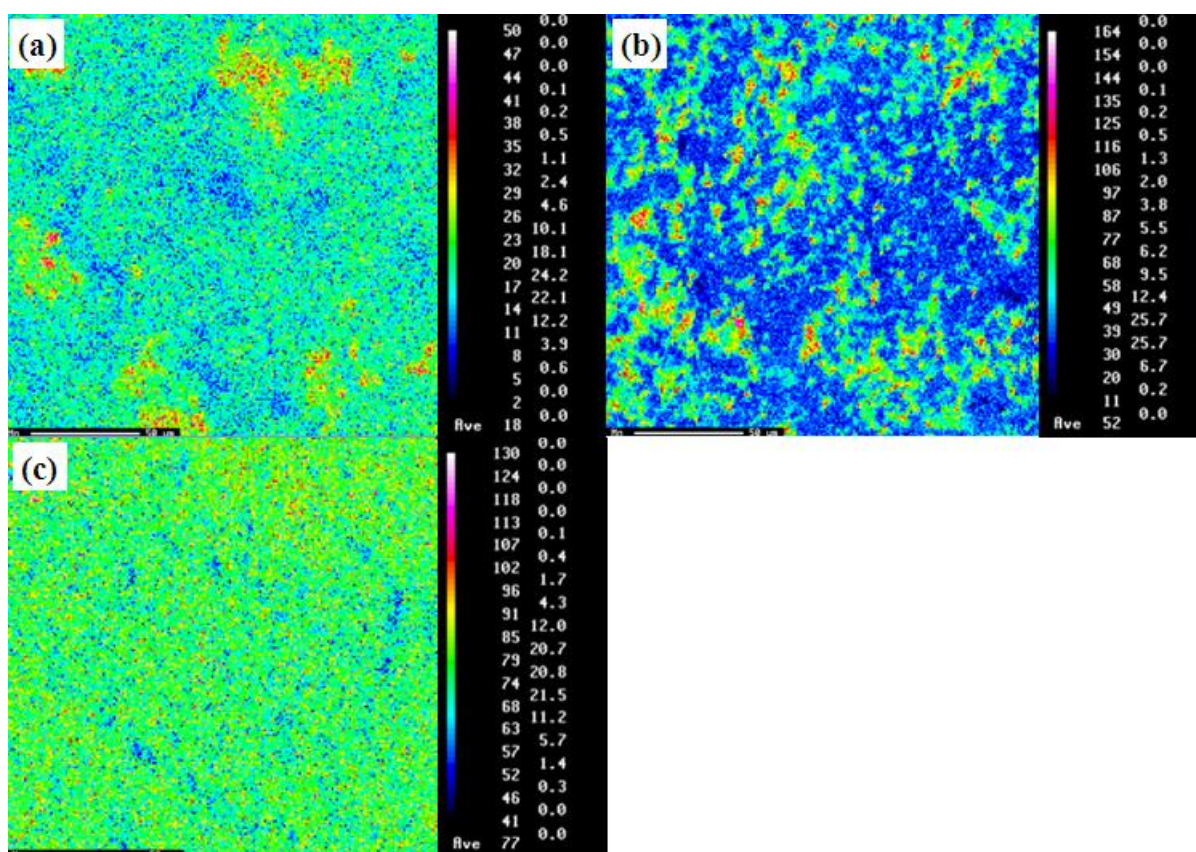


Figure 6. Mapping analyses of manganese element by EPMA after 6 h immersion: (a) 0.7 % Mn steel, (b) 2.0 % Mn steel, (c) 5.0 % Mn steel

EPMA analysis was performed to observe corroded surface of the Mn-containing steels. Fig. 6 presented the manganese mapping data after 6 h immersion in 10 wt.% sulfuric acid. Fig. 6 (a) shows manganese compounds of 0.7 % Mn steel also presented but indicated low intensity. It was confirmed that the amount of manganese corrosion products generated from 0.7 % Mn steel could not have an effect on the corrosion inhibition property through EPMA and electrochemical tests. In the case of 5.0 % Mn steel, the generated manganese products were distributed uniformly on the surface but corrosion

products generated by other steels indicated localized distribution. It could be suggested that the uniformity of manganese on the surface also contributed to the changes of polarization resistance as shown in Fig. 4 because the presence of corrosion products on localized surface could induce the galvanic corrosion with the other area. From this paper, it was confirmed that 5.0 % Mn is the best content on the corrosion resistance in sulfuric acid solution.

4. CONCLUSIONS

The corrosion resistances of 0.7 %, 2.0 % and 5.0 % Mn-containing steels in 10 wt.% sulfuric acid were studied using electrochemical tests and surface analyses. From potentiodynamic test results, corrosion current density of low alloy steel after 0.5 h immersion was inversely proportional to the manganese content of steel. However, the results after 6 h immersion indicated that manganese in steel had a positive effect on the corrosion resistance. Through the difference of CPE2 value which was calculated by EIS test among three Mn-containing steels, adsorption of Mn^{2+} ions on to the surface inhibited the corrosion of Mn-containing steel. It was confirmed through XPS analysis that corrosion products generated by manganese were mainly manganese oxides and sulfate. In the case of 0.7 % Mn steel, the amount of manganese corrosion products was not enough to protect the corrosion surface and 5.0 % Mn steel had the best manganese compounds increasing corrosion resistance due to inhibition effect of Mn^{2+} ions.

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