

Effects of Sn and Sb on the Corrosion Resistance of AH 32 Steel in a Cargo Oil Tank Environment

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Effects of the alloying elements, Sn and Sb, on the corrosion resistance of modified AH 32 steel for the cargo oil tanks (COT) were examined using an electrochemical test and weight loss measurement. All experiments were carried out in acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C, simulating the inner bottom plate of COT. It was clearly found that the small amount addition of Sn and Sb improved the corrosion resistance of modified AH 32 steel, which is confirmed by the higher polarization resistance of AH 32 steel modified with Sn and Sb addition compared with that of the base steel. X-ray photoelectron spectroscopy analysis of the corroded surface after immersion of 72 h presented that the AH 32 steel modified with Sn and Sb addition created the protective corrosion products including SnO₂ and Sb₂O₅. These oxides act as high corrosion inhibitor to anodic corrosion reaction, and hence leading to the improvement in the corrosion resistance of the modified AH 32 steels.

Keywords: alloys, Sn, Sb, corrosion, electrochemistry

1. INTRODUCTION

AH 32 steel has been extensively used as a structural material for cargo oil tanks (COT) due to their excellent weldability and good mechanical properties. The AH 32 steel is required to have a yield strength of 315 N/mm² or more, 440~590 N/mm² of a tensile strength, an elongation of 22% or more and a carbon equivalent (C_{eq}) less than 0.36 according to the rules of classification society [1]. The weldability and mechanical properties of the AH 32 steel are determined by their C_{eq} value as expressed by Eq. 1.

$$C_{eq} = C + Mn/6 + (Cr + Mo + V)/5 + (Ni + Cu)/1 \quad (1)$$

The low alloy steel with lower C_{eq} showed better weldability as well as higher resistance to low-temperature brittleness. Therefore, the weldability and mechanical properties of

COT can be controlled by adjusting the C_{eq} of the steel, and it is one of the important parameter to be considered when we develop AH 32 steel for COT through compositional modification. Table 1 shows chemical composition of AH 32 steel suggested by classification society rules [2]. In Table 1, the alloying elements, C, Si and Mn, are added to improve the mechanical properties and weldability and P and S are impurities. The AH 32 steel has Al, Nb, V or other suitable grain refining elements used by either singly or in combination. When these are used singly, the specified minimum content of the grain refining element is required. The alloying elements, Cu, Cr, Ni and Mo, are added to improve the corrosion resistance of the AH 32 steel.

In general, the AH 32 steel of COT faces to a serious corrosion problem caused by crude oil environment. There are two types of corrosion problem depending on the location of COT. The general corrosion occurred on ceiling area of COT while the pitting corrosion occurred on inner bottom plate. These corrosion problems reduce the service life of COT

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Table 1. Chemical composition and C_{eq} of the AH 32 steel (wt%)

C	Si	Mn	P, S	Cu	Cr	Ni	Mo	Al	Ni	V	Ti	C_{eq}
<0.18	<0.50	0.90~1.60	<0.035	<0.35	<0.20	<0.40	<0.08	>0.015	0.02~0.05	0.05~0.10	<0.02	<0.36

including the increase of repair cost and the decrease of safety. In particular, observed maximum rate of pitting corrosion on the inner bottom plate is recorded as 4 mm/y, which is very acute corrosion rate. The pitting corrosion of inner bottom plate in COT occurs as follow processes; The high concentrated chloride ion and H_2S in remaining water after drainage in COT are originated from crude oil exist [3]. The inner bottom plate is fully covered with oil coating layer containing sludge and generally, oil coating led to decreases corrosion rate. Partial defects of the oil coating, however, would be happened caused by water washing and water drops from ceiling area [3,4]. Then the inner bottom plate is exposed to severe corrosion environment with concentrated chloride ion and H_2S and pits generated from these defects of the oil coating. Individual pits create the individual corrosion cell between defect (small anodic area) and steel surface beneath the oil coating around defect (large cathodic area). In addition to here, elemental sulphur that dripping down from ceiling area accelerates corrosion of inner bottom plate by the action as an oxidizer as follows [3],



The best way to retard the growth of pits might be clear cleaning and entire oil recoating on the surface of inner bottom plate.

A lot of researchers have reported the improvement methods of corrosion resistance of low alloy steels in various corrosive environments by adding minor alloying elements. Recently, the effects of Sn and Sb on the corrosion resistance of low alloy steels in acidic chloride solution are reported. Nam *et al.* [5] suggested that Sn created a protective SnO_2 layer on the steel surface, which inhibited steel dissolution in acidic chloride solution (5.5×10^{-3} M sodium chloride and 6.25×10^{-5} M sulphuric acid, pH 4.01). Lin *et al.* [6] reported that the presence of Sn decreased the corrosion rate of the X52 steel which is generally used for oil and gas transmission pipeline in 3.5% NaCl solution injected H_2S gas. Le *et al.* [7] reported that the addition of 0.10% Sb created not only a protective Sb_2O_5 oxide film on the steel surface, but also stimulated the development of high corrosion inhibiting to low alloy steel

for flue gas desulfurization system.

An important research goal is to evaluate the corrosion resistance of AH 32 steels modified with Sn and Sb addition using by electrochemical technique and immersion test. Then we find out the composition of the protective oxides formed on these steels. Thus, in this study, the objective is to elucidate the effect of Sn and Sb on the corrosion behaviour of AH 32 steel in simulated environment of inner bottom plate of COT.

2. EXPERIMENTAL PROCEDURE

Table 2 shows chemical composition of AH 32 steels modified with Sn and Sb in this work. The content of Cu, Ni, Cr and Al is blank due to the alloy design security of steel manufacture company. In order to obtain extremely low interstitial grade, the alloys were prepared by vacuum arc melting furnace, and then cast in the form of a button 8 mm thick. The casts were homogenized for 15 min at 1200 °C, and then hot rolled to 3 mm thick plate.

Specimens were prepared by cold rolling the heated plates to 1.5 mm thick sheets, and then they were solution annealed for 10 min at 920 °C, followed by water quenching. Sn and Sb content of the alloys were confirmed by energy dispersive spectrometer (EDS). The modified AH 32 steels were mounted on an epoxy resin with an expose area of 0.1256 cm^2 , and then ground to number 2000 grit SiC paper finally polished to a 1 μm diamond suspension and ultrasonically cleaned with ethanol. The modified AH32 specimens mounted on epoxy resin were used as working electrodes in electrochemical tests.

A conventional three-electrode cell of 1 L-multineck flask was used for electrochemical tests. The electrochemical cell was equipped with a platinum counter electrode, a saturated calomel reference electrode (SCE), and working electrode. All the electrode potentials were referenced against the SCE. All tests were carried out in acidic chloride solution composed of 0.14 M HCl and 10 wt% NaCl, pH 0.85 at 30 °C. Prior to each electrochemical test, the working electrode was cathodically cleaned for 100 s at -1.0 V to remove an air-formed oxide on the surface. After the working electrode had reached a

Table 2. Chemical composition of the modified AH 32 steels (wt%)

Modified AH32	Fe	C	Si	Mn	Cu	Ni	Cr	Al	Sn	Sb	C_{eq}
Base	balance	0.10	0.40	1.00	blank	blank	blank	blank	-	-	0.313
0.05Sn	balance	0.10	0.40	1.00	blank	blank	blank	blank	0.05	-	0.313
0.10Sn	balance	0.10	0.40	1.00	blank	blank	blank	blank	0.10	-	0.313
0.05Sb	balance	0.10	0.40	1.00	blank	blank	blank	blank	-	0.05	0.313
0.10Sb	balance	0.10	0.40	1.00	blank	blank	blank	blank	-	0.10	0.313

stable corrosion potential (1 h), potentiodynamic tests were performed at a scan rate of 1 mV/s with an initial potential of -150 mV versus open circuit potential (OCP). After the working electrode had reached the stable corrosion potential (3 h), the EIS measurements were conducted by an AC signal with amplitude of 10 mV peak to peak at the OCP and frequency ranging from 10^5 Hz to 1 Hz. All the EIS data were fitted to appropriate equivalent circuits using software program "Z-man" [8].

The immersion test was performed in an acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C, which was proposed for an accelerated corrosion test in inner environment of COT according to the regulation II-1/3-11 of the International Convention for the Safety of Life at Sea (SOLAS), 1974, as amended adopted by resolution MSC.291 (87), concerning alternative means of corrosion protection for cargo oil tanks of crude oil tankers [9]. This experimental test has been used in many previous studies as a classical and typical method for calculating corrosion rate [10-12]. Additionally, the test solution was changed every 24 h to minimize pH change of the test solution. The volume of the solution was controlled more than 20 ml per unit surface area of specimen (cm^2). The size of specimen was $25 \pm 1 \text{ mm} \times 60 \pm 1 \text{ mm} \times 0.5 \pm 1 \text{ mm}$ as shown in Fig. 1. The surface of the speci-

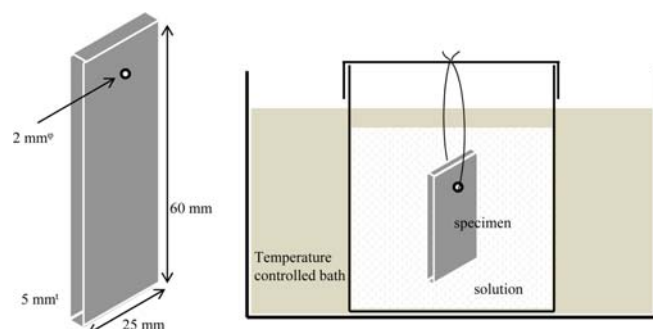


Fig. 1. Specimen size and simulated corrosion test apparatus for inner bottom plate of COT.

mens were polished to # 2000 grit SiC paper, then ultrasonically cleaned with ethanol, and finally, rinsed in distilled water. The specimens were hung in a solution from a nylon wire of 0.3 mm in diameter to avoid crevice-like and/or localized corrosion during 72 h. After the test, the specimens were cleaned chemically with 1000 mL hydrochloric acid mixture (HCl) mixed with 20 g antimony trioxide (Sb_2O_3) and 50 g stannous chloride (SnCl_2) for 5 min at 25 °C according to ASTM G1-03. The chemical solution was vigorously stirred during the cleaning of specimens. The cleaned specimens were rinsed with distilled water and dried in a desiccator for 12 h. The corrosion rate is calculated.

$$\begin{aligned} \text{Corrosion rate (mm/year)} \\ = \frac{365(\text{days}) \times 24(\text{hours}) \times W \times 10}{S \times 72(\text{hours}) \times D} \end{aligned} \quad (3)$$

where W is weight loss (g) of the specimen during the test, and S and D is surface area (cm^2) and density (g/cm^3) of the specimen, respectively.

After the immersion test, the corrosion products on the alloy surface were examined by X-ray photoelectron spectroscopy (XPS) to elucidate the effects of Sn and Sb on the corrosion behavior of AH 32 steel. The XPS measurements were performed using the monochromatic Al-K α x-ray source (15 kV, 20 mA, 300 W) and pass energy of 200 eV. On the other hand pass energy of each alloying elements (Fe, O, Sn, and Sb) was decreased to 50 eV in order to increase resolution and make narrow scan condition. XPS beam spot size was 400 μm and scan step size was 0.1 eV. XPS spectra were analysed using an XPS analysis software program, XPSPEAK41.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization response and EIS measurement

Figure 2 shows effects of Sn and Sb on the polarization response of the modified AH 32 steels in the acidic chloride

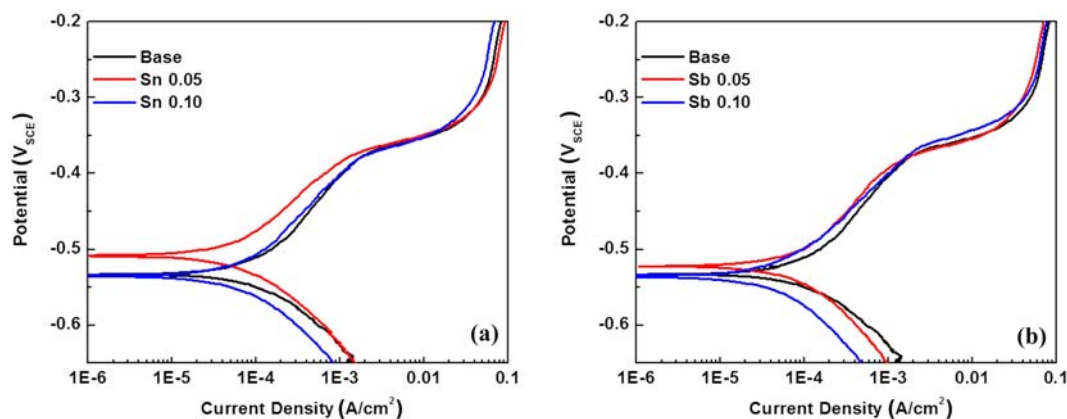
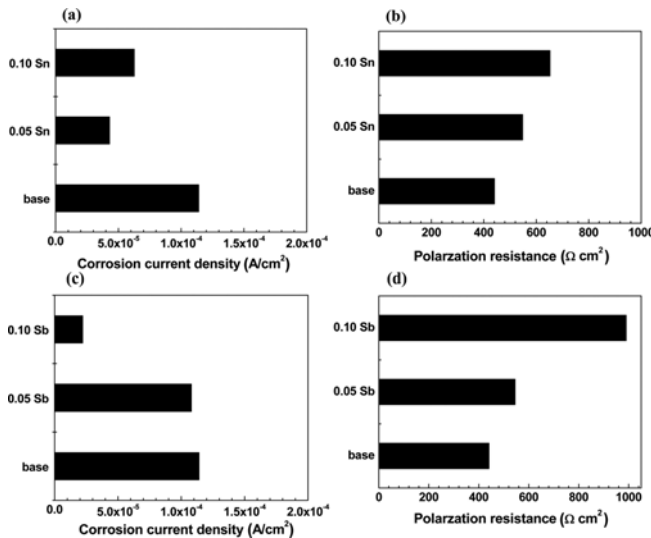


Fig. 2. Polarization response of the modified AH 32 steels in deaerated acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C. (a) Sn and (b) Sb.

Table 3. Corrosion properties of the modified AH 32 steels from potentiodynamic polarization tests

Specimen	E_{corr} (mV)	i_{corr} (A/Cm ²)	β_a (V/decade)	β_c (V/decade)	R_p ($\Omega \cdot \text{Cm}^2$)
Base	-532.3	1.14E-4	0.416	0.160	440.72
0.05 Sn	-520.6	4.30E-5	0.112	0.105	547.96
0.10 Sn	-535.7	6.27E-5	0.205	0.174	652.63
0.05 Sb	-522.7	1.08E-4	0.279	0.263	545.02
0.10 Sb	-535.5	2.22E-5	0.095	0.108	989.85

**Fig. 3.** Effect of Sn and Sb on the corrosion properties of modified AH 32 steels (a) i_{corr} of modified AH 32 steel with Sn, (b) R_p of modified AH 32 steel with Sn, (c) i_{corr} of modified AH 32 steel with Sb, and (d) R_p of modified AH 32 steel with Sb.

solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C. All the modified AH 32 steels exhibited an active corrosion behaviour in which the anodic current density continuously increased with applied potential. Evidently, the addition small amount (0.05 wt%) of Sn or Sb to the AH32 gave a beneficial effects on the corrosion behaviour of the modified alloys either by decreasing the anodic dissolution rate or by shifting the corrosion potential in the noble direction. The corrosion properties examined by potentiodynamic polarization tests were listed in Table 3.

Figure 3 presents the effect of Sn and Sb on the corrosion properties of the modified AH 32 steels. The corrosion current density (i_{corr}) determined using the Tafel extrapolation and polarization resistance (R_p) was calculated by following Eq. [13];

$$R_p = \frac{\beta_a \beta_c}{2.3 i_{corr} (\beta_a + \beta_c)} \quad (4)$$

where i_{corr} is the corrosion current density of each specimens and β_a is anodic Tafel slope and β_c is cathodic Tafel slope.

As a result of potentiodynamic polarization tests, the i_{corr} of AH 32 steel modified with Sn and Sb addition was lower

than that of base steel, and the i_{corr} decreased with increasing Sn and Sb content. The R_p of AH 32 steel modified with Sn and Sb addition was higher than that of base steel, and it increased with increasing Sn and Sb content.

The EIS analysis provides kinetic information of the electrode and surface properties of the interested systems. Mechanical information can be obtained from the shape of the impedance diagram [14,15]. In present study EIS test were carried out in acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C every 24 h during 72 h under stable OCP condition. Figure 4 shows a nyquist plot for the modified AH 32 steels with or without Sn and Sb addition. Impedance spectra of after 3 h immersion showed single semi-circle independent of Sn and Sb addition and it clearly indicated the single step charge transfer phenomenon on the modified AH 32 steels in the presence of diffusion. The diameter of semi-circle was increased with the increase in Sn and Sb content. On the other hand, the impedance spectra of other conditions (24 h, 48 h and 72 h of immersion) showed additional shapes of plot with semi-circle part. The impedance spectra of the additional part showed various shapes such as linear and distorted half-ellipse or semi-circle. It clearly indicated that there was two or more charge transfer reaction on the modified AH 32 steels in the presence of diffusion. Consequently, the magnitude of overall impedance was decreased with immersion time independent of Sn and Sb content. From the impedance spectrum features of mentioned above, two types of equivalent circuits were established with immersion time (Fig. 5). The first type of equivalent circuit described the modified AH 32 steel specimens after 3 h immersion. It was composed of a solution resistance (R_s), a charge transfer resistance (R_{ct}) and a constant phase elements describing double layer interface of electrode. Second type of equivalent circuit was composed of R_s , R_{ct} , CPE1, CPE2 and a rust layer resistance (R_{rust}). CPE1 is constant phase elements on rust layer and CPE2 is constant phase elements on interface between rust and electrode. This system is for the modified AH 32 steel specimens after 24 h, 48 h and 72 h immersion.

The “Z man” program was used to fit the EIS data to determine the optimized values of the equivalent elements (R_s , R_{ct} , R_{rust}), which were listed in Table 4 and Fig. 6. The R_s of the modified AH 32 steel specimens was measured constant, regardless of the immersion time and Sn, Sb content and it was indicated that the solution conditions (pH and temperature)

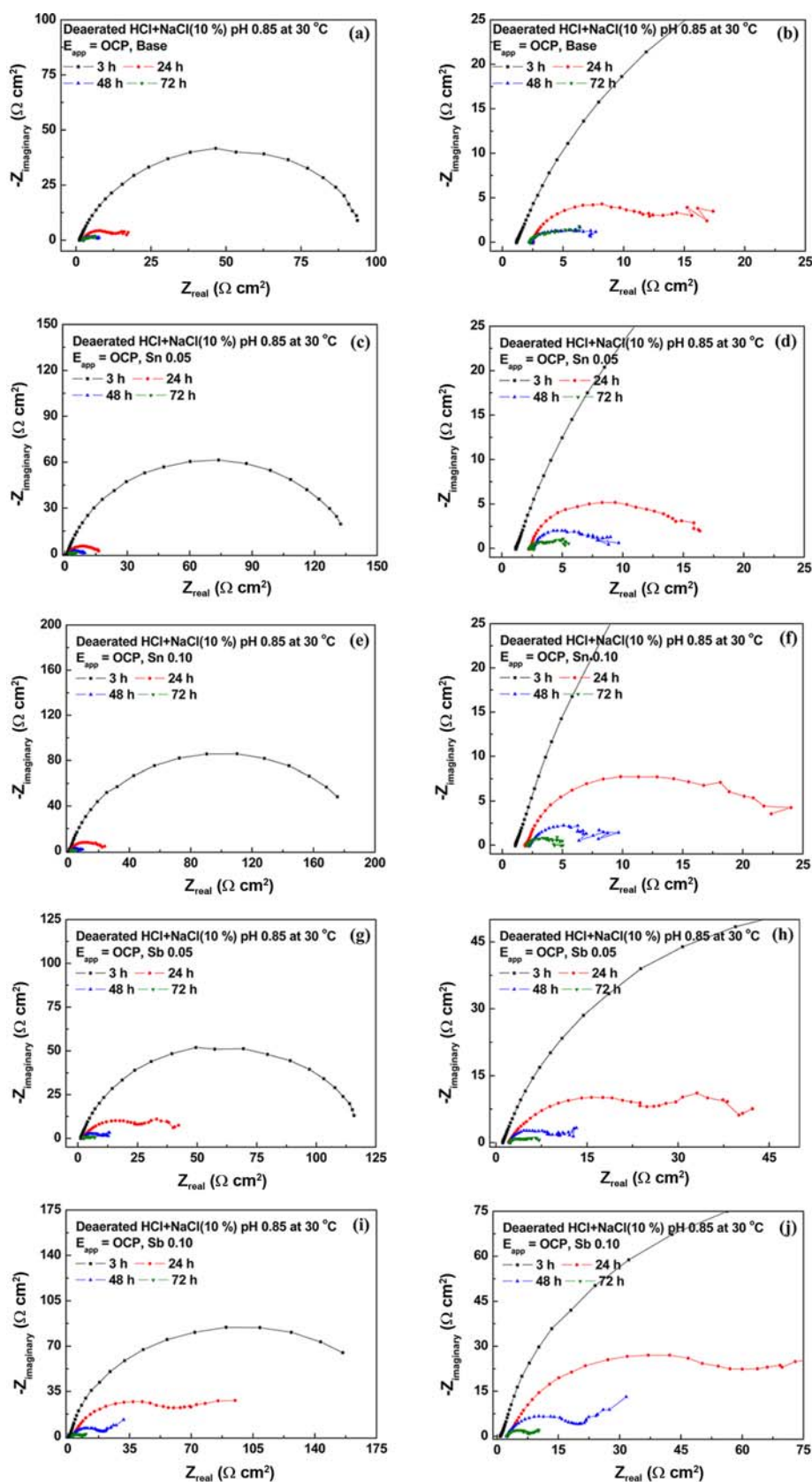


Fig. 4. Nyquist plot for the modified AH32 steels in acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C: (a, b) base, (c, d) 0.05 Sn, (e, f) 0.10 Sn, (g, h) 0.05 Sb, and (i, j) 0.10 Sb.

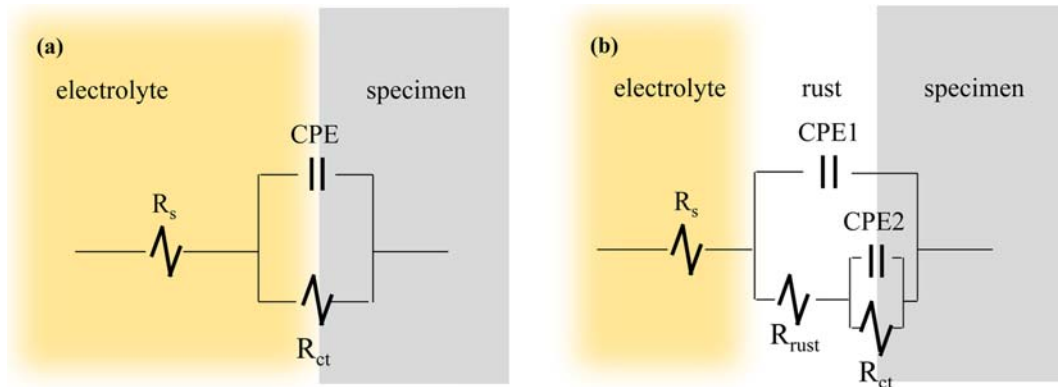


Fig. 5. Equivalent circuit for EIS data fitting (a) 3 h of immersion and (b) 24, 48, 72 h of immersion.

Table 4. Impedance parameters of the modified AH 32 in steels in deaerated acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C with immersion time

Modified AH32	Time (h)	R_t ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	R_{rust} ($\Omega \cdot \text{cm}^2$)
Base	3	1.329	96.407	-
	24	2.454	5.253	10.356
	48	2.416	0.670	4.617
	72	2.221	1.935	0.282
0.05 Sn	3	1.302	139.153	-
	24	2.328	1.362	13.063
	48	2.525	1.815	4.877
	72	2.469	1.904	1.10
0.10 Sn	3	1.246	199.593	-
	24	1.971	3.26	19.08
	48	2.255	0.993	5.247
	72	2.135	0.707	2.106
0.05 Sb	3	1.225	119.924	-
	24	2.196	13.171	27.377
	48	2.116	1.414	9.128
	72	2.284	3.316	2.144
0.10 Sb	3	0.962	197.624	-
	24	3.077	71.802	37.146
	48	2.312	25.156	19.053
	72	2.442	2.357	5.634

were maintained constant during EIS measurements. The R_{ct} and R_{rust} of the modified AH 32 steel specimens decreased with the immersion time. Contrary the R_{ct} and R_{rust} of the modified AH 32 steel specimens increase with the increase in Sn and Sb content at the same immersion time. Exceptionally, the R_{ct} of AH 32 steel modified with Sn addition at 24~72 h of immersion was almost same value than that of base steel.

The sum of the R_{ct} and the R_{rust} defined a total resistance (R_t), indicating the total corrosion resistance of the AH 32 steels. Figure 7 shows the change of the R_t according to the immersion time for modified AH 32 steel specimens. As a result, the R_t of the modified AH 32 steel specimens decreased with immersion time and increased with the increase in Sn and Sb content at the same immersion time. Especially in case of 3 h of immersion, the R_t ratio to each other modified AH 32 alloy

(0, 0.05 Sn, 0.10 Sn and 0, 0.05 Sb 0.10 Sb) was similar to the R_p ratio to each other confirmed by the results of potentiodynamic polarization test. These results were due to the same single charge transfer reaction of each test (EIS test and potentiodynamic polarization test) which is caused by similar environment at initial stage. However, the other cases (24 h, 48 h, and 72 h of immersion), the R_t ratios to each other are different to the R_p ratio to each other confirmed by the results of potentiodynamic polarization test. In this case, the electrode surface state of the each modified AH32 steel specimens was changed which causes two or more charge transfer in the presence of diffusion and ion diffusion in the rust was formed on the surface of AH32 steels.

3.2. Immersion test on simulated inner bottom plate

Immersion tests on simulated inner bottom plate were conducted in acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C for 72 h which is same solution composition of the electrochemical experiments. The corrosion rate of the AH32 steel specimens was determined using by formula which was mentioned experimental part. The calculated results were given in Table 5. The corrosion rate of AH 32 steel modified with Sn and Sb addition was lower than that of base steel, and the corrosion rate decreased with the increased in Sn and Sb content. The ratio of corrosion rate of each specimen from the immersion test was not similar to the ratio of corrosion current density of each specimen from the potentiodynamic polarization test. The reason of ratio difference was considered that the corrosion rate of AH32 steel specimens from the results of the immersion test is the summation of anodic corrosion reaction at every moment during immersion. On the other hand, corrosion current density of specimens from the results of the potentiodynamic polarization test is the summation of anodic corrosion reaction at instant initial stage (~1 h immersion).

3.3. Surface analysis

After 72 h of immersion in acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C, the corrosion

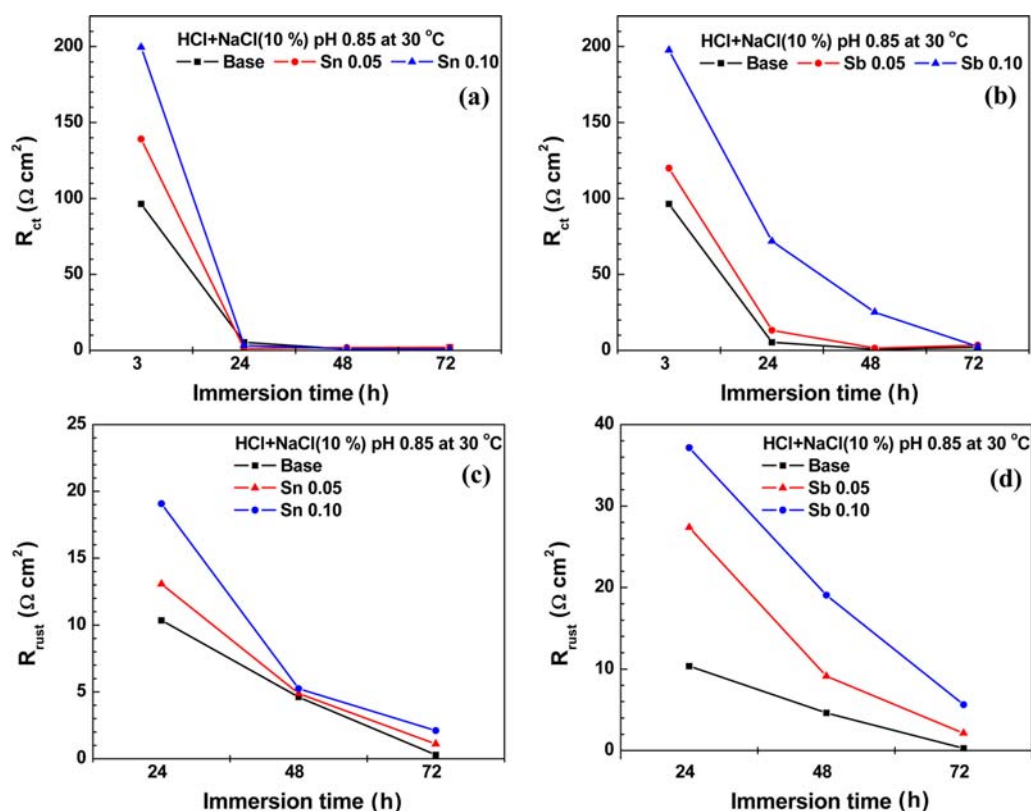


Fig. 6. Impedance parameters of the modified AH 32 steels in deaerated acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C with immersion time (a) R_{ct} with Sn, (b) R_{ct} with Sb, (c) R_{rust} with Sn, and (d) R_{rust} with Sb.

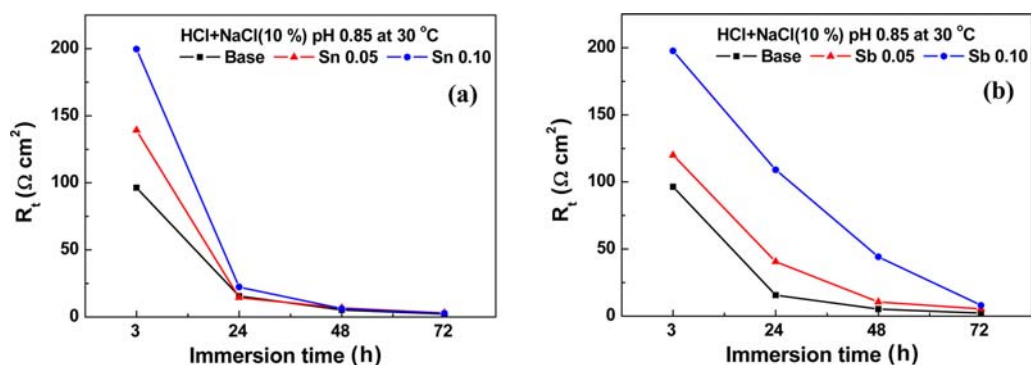


Fig. 7. Effect of Sn, Sb contents and immersion time for R_t from EIS test in deaerated acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85) at 30 °C. (a) Sn and (b) Sb.

Table 5. Results of immersion test on simulated inner bottom

Specimen	Base	0.05 Sn	0.10 Sn	0.05 Sb	0.10 Sb
Corrosion rate (mm/y)	3.30	1.90	1.50	2.20	1.20

products of surface were examined by XPS and survey spectra were described in Fig. 8. The XPS spectra of AH 32 steel modified with Sn showed Sn 3d, O 1s, Fe 2p and Cu 2p peaks (Fig. 8a) and those of AH 32 steel modified with Sb showed Sb 3d, O 1s, Fe 2p and Cu 2p peaks (Fig. 8b). These peaks clearly indicated the existence of Sn oxide, Sb oxide, Fe oxide

and Cu oxide, either singly or combination. XPS peak 41 program was used to obtain the binding energy of each XPS peak and were listed in Table 6 [13-19].

Consequently, the SnO_2 was observed at the corroded surface of AH 32 steel modified with Sn and it act as protective oxide against corrosion and inhibited the anodic corrosion

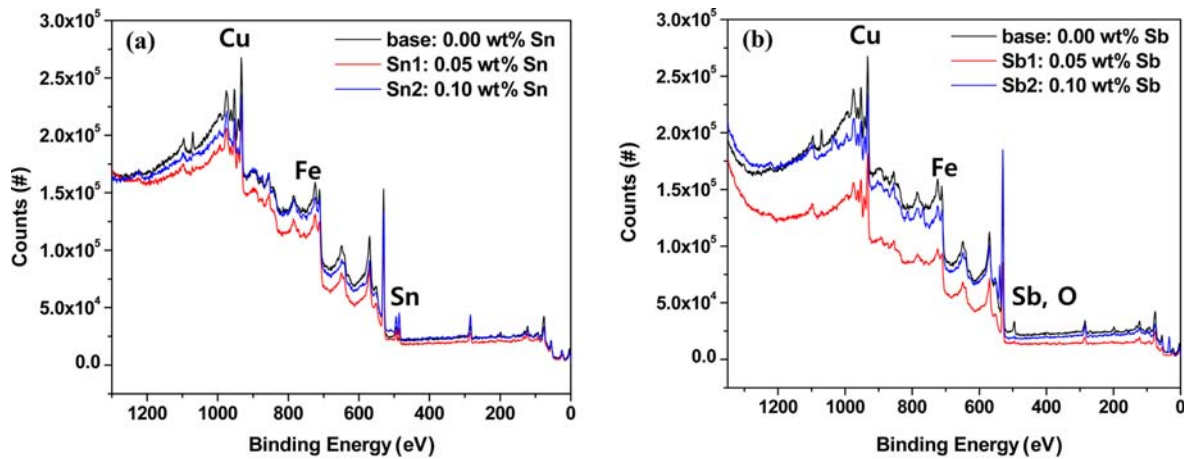


Fig. 8. Full range XPS survey from corroded surface of the modified AH32 steels (a) Sn addition modified AH 32 steels and (b) Sb addition modified AH 32 steels.

Table 6. XPS peak analysis for surface corrosion product of the modified AH32 steels

Specimen	Peak	Binding Energy (eV)	Product	Ref
Base	Cu 2p _{3/2}	934.72	Cu(OH) ₂	16
	Cu 2p _{1/2}	952.57	Cu ₂ O	17
	Cu 2p _{3/2}	934.49	Cu(OH) ₂	16
0.05 Sn	Cu 2p _{1/2}	952.59	Cu ₂ O	17
	Sn 3d _{5/2}	486.65	SnO	18
			SnO ₂	19
0.10 Sn	Sn 3d _{3/2}	495.09	SnO ₂	20
	Cu 2p _{3/2}	934.23	Cu(OH) ₂	16
	Cu 2p _{1/2}	952.59	Cu ₂ O	17
0.10 Sn	Sn 3d _{5/2}	486.73	SnO	18
			SnO ₂	19
	Sn 3d _{3/2}	495.17	SnO ₂	20
0.05 Sb	Cu 2p _{3/2}	934.63	Cu(OH) ₂	16
	Cu 2p _{1/2}	952.54	Cu ₂ O	17
	Sb 3d _{5/2}	530.13	Sb ₂ O ₅	20
0.10 Sb	Cu 2p _{3/2}	934.54	Cu(OH) ₂	16
	Cu 2p _{1/2}	952.64	Cu ₂ O	17
	Sb 3d _{5/2}	530.23	Sb ₂ O ₅	21
	Sb 3d _{3/2}	539.78	Sb ₂ O ₅	22

reaction. Thus, AH 32 steel modified with Sn showed low corrosion rate in immersion test and high polarization resistance in electrochemical test. Figure 9(a) presented XPS peaks of Sn 3d_{3/2} and Sn 3d_{5/2}, respectively. The magnitude of XPS peaks of Sn 3d was increased with increase in Sn content. The SnO₂ content of corrosion product on the surface was increased with the increase in Sn content in the modified AH 32 steels.

On the other hand, the Sb₂O₅ is known for element to give corrosion protectiveness and to inhibit the anodic corrosion reaction. The results indicated that AH 32 steel modified with Sb showed low corrosion rate in immersion test and high polarization resistance in electrochemical test. Figure 9(b) presented XPS peaks of Sb 3d_{3/2} and Sb 3d_{5/2}, respectively. In case of AH 32 steel modified with 0.05 Sb additions, XPS peak of Sb 3d_{3/2} was not observed. However, AH 32 steel modified with 0.10 Sb additions, XPS peak of Sb 3d_{3/2} was observed and overall magnitude of XPS peaks of Sb 3d was higher than those of AH 32 steel modified with 0.05 Sb additions. The amount of Sb₂O₅ in corrosion product on the surface was increased with the increase in Sb content in the modified AH 32 steels.

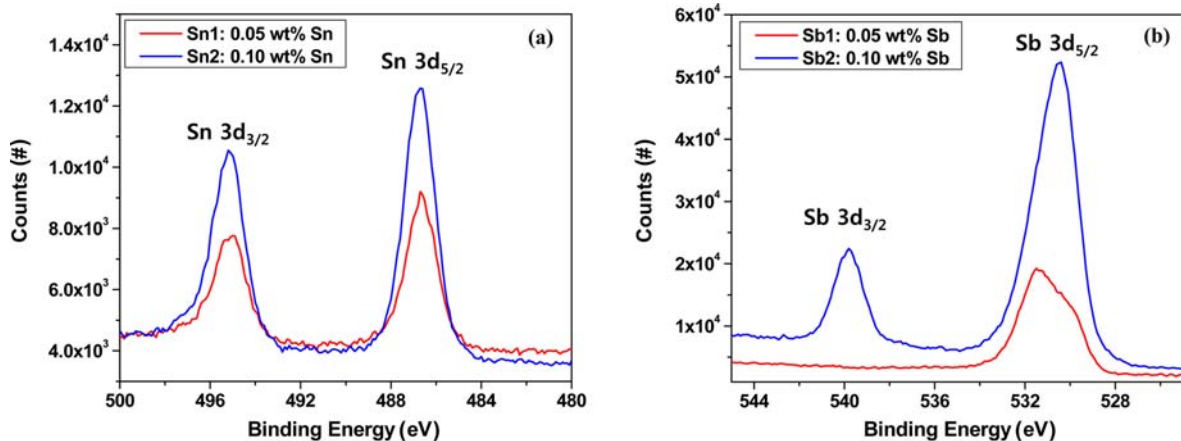


Fig. 9. Effect of Sn, Sb contents of XPS data from corroded surface of the modified AH32 steel (a) Sn and (b) Sb.

4. CONCLUSIONS

1. All the modified AH 32 steels exhibited active corrosion behaviour in acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85, 30 °C) which is described inner bottom plate corrosion environment of COT. As Sn and Sb content increases, the polarization resistance (R_p) of the modified AH 32 steels was increased as confirmed by calculated results from potentiodynamic polarization test.

2. The effects of Sn and Sb on the charge transfer kinetics of the modified AH 32 steels in acidic chloride solution (0.14 M HCl and 10 wt% NaCl, pH 0.85, 30 °C) were examined by the EIS test. The total resistance (R_t) of the modified AH 32 steels decreased with increasing immersion time and increased with increasing Sn and Sb content at the same immersion time.

3. The corrosion rates of the modified AH 32 steels decrease with with increasing Sn and Sb content according to weight loss measurement from immersion test on simulated inner bottom plate corrosion environment of COT.

4. The addition of Sn or Sb created the protective surface corrosion products on modified AH 32 steels including SnO₂ and Sb₂O₅. These oxides operated as high corrosion inhibitor to anodic corrosion reaction then it makes low corrosion rate of the modified AH 32 steels.

REFERENCE

1. IACS committee, *No 47 Shipping and Repair Quality Standard, rev.6*, p.8, IACS (2012).
2. Korean Register of Shipping Technical Rules Committee, *Rules for the Classification of Steel Ships, Part 2 Materials and Welding*, p.11, Korean Register of Shipping (2015).
3. K. Kashima, Y. Tanino, S. Kubo, A. Inami, and H. Miyuki, *Shipbuilding Technology ISST 2007*, pp.5-10, JASNAOE-RINA, Osaka, Japan (2007).
4. H. Shiomi, M. Kaneko, K. Kashima, H. Imamura, and T. Komori, *TSCF 2007 Shipbuilders Meeting*, pp.1-8, Busan, Korea (2007).
5. N. D. Nam, M. J. Kim, Y. W. Jang, and J. G. Kim, *Corros. Sci.* **52**, 14 (2010).
6. H. Lin, J. Wang, and E. Han, *Mater. Sci. Forum* **734-744**, 607 (2013).
7. D. P. Le, W. S. Ji, J. G. Kim, K. J. Jeong, and S. H. Lee, *Corros. Sci.* **50**, 1195 (2008).
8. Zive lab, *Zman Ver. 2.3.2*, <http://www.zivelab.com/zman/enindex.htm> (accessed June 29, 2015).
9. *Performance Standard for Alternative Means of Corrosion Protection for Cargo Oil Tanks of Crude Oil Tankers*, pp.11-14, SOLAS Reg. II-1/3-11(MSC.291(87)) (1974).
10. H. R. Riazi, I. Danaee, and M. Peykari, *Met. Mater. Int.* **19**, 224 (2013).
11. S.-A. Park, S.-H. Kim, Y.-H. Yoo, and J.-G. Kim, *Met. Mater. Int.* **21**, 470 (2015).
12. D. H. Cho, J. H. Nam, B. W. Lee, J. Y. Park, H. J. Shin, and I. M. Park, *Korean J. Met. Mater.* **53**, 220 (2015).
13. D. A. Jonse, *Principles and Prevention of Corrosion*, p.146, Printice-Hall, NJ (1996).
14. W. J. Lorenz and F. Mansfeld, *Corros. Sci.* **21**, 647 (1981).
15. E. Barsoukov and J. R. Macdonald, *Impedance Spectroscopy*, p. 70, John Wiley & Sons (2005).
16. M. G. Cook and N. S. Mc Intyre, *Analytical Chemistry*, **47**, 2208 (1975).
17. G. Haemers, J. J. Verbist, and S. Maroie, *Applications of Surface Science*, **17**, 463 (1984).
18. D. Briggs and M. P. Seah, *Practical Surface Analysis*, 2nd ed., p.201, John WILEY & SONS. (1993).
19. M. V. Zeller, P. A. Grutsch, and T. P. Fehlner, *Inorg. Chem.* **12**, 1431 (1973).
20. T. Tateishi, Y. Ito, and Y. Okazaki, *Mater. Trans.* **38**, 78 (1997).
21. C. D. Wagner, J. F. Moulder, L. E. Davis, and W. M. Riggs, *Handbook of X-ray Photoelectron Spectroscopy*, 1st ed., p.190, Perkin-Elmer Corporation, Physical Electronics Division (1979).
22. J. R. V. Wazer, W. E. Morgan, and W. J. Stec, *Inorg. Chem.* **12**, 953 (1973).