Effects of metal cations on mild steel corrosion in 10 mM Cl⁻ aqueous solution

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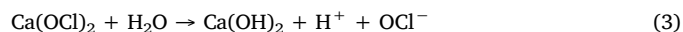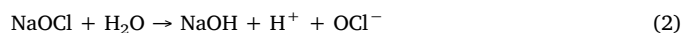
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ABSTRACT

The influences of metal cations on the corrosion of mild steel in 10 mM Cl⁻ aqueous solutions were investigated by electrochemical techniques and immersion tests. Immersion tests and electrochemical impedance spectroscopy (EIS) results showed that Zn^{2+} has a significant effect on corrosion inhibition. Surface morphological inspection also showed the smooth surface of specimen immersed in Zn^{2+} containing solution. Analysis of X-ray photoelectron spectroscopy showed that Zn^{2+} was incorporated in the oxide films by making a strong bond. It is supposed that Zn^{2+} forms a very effective shielding film which can inhibit the electrochemical reactions, and consequently lowers the corrosion rate.

1. Introduction

The stability of a metal when exposed to the environment depends on a multitude of factors that may vary greatly with the concentration of Cl⁻ and SO_4^{2-} of that environment. Mild steel is very popular and widely used metallic materials, and the corrosion of this steel is a serious problem in water supply pipes, storage tanks and circulating water pipes etc., and the corrosion behavior have been studied by many researchers [1–3]. The corrosion rate of mild steel can be accelerated by the presence of the compound that may contains Cl⁻ and SO_4^{2-} [4–6]. Large amount of chlorine compounds (Cl_2, NaOCl, $Ca(OCl)_2$ etc.) are used as disinfectants in the waste water treatment and bleach for both domestic and industrial purposes. These compounds are also widely used to disinfect drinking water and swimming pool water, and to control bacteria and odors in the food industry [7–9]. Enormous amount of chlorine compounds is also used in the laundry to bleach and wash the cloths. Chlorine compounds are listed as a known poison and it has an adverse effect on corrosion of the pipe line of water circulation system and other metallic equipment that exposed in that environment, and these compounds are dissociated into Cl⁻ and OCl⁻ in the aqueous solution as following reactions (1)–(3).

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \tag{1}$$

$$NaOCl + H_2O \rightarrow NaOH + H^+ + OCl^- \tag{2}$$

$$Ca(OCl)_2 + H_2O \rightarrow Ca(OH)_2 + H^+ + OCl^- \tag{3}$$

The oxide layer (passive film) of the steel is generally destroyed by

the penetration of Cl⁻ in aqueous solution [4,10–13]. Fig. 1(a) and (b) shows the penetration and film thinning mechanism of Cl⁻ into the oxide films [14–17]. After destruction of the passive films, the corrosion process starts with a coupled of electrochemical reactions [1,2,18]. Fig. 1(c) shows the anodic reaction of metal dissolution (reaction (4)) and cathodic reaction of oxygen reduction (reaction (5)).

$$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^- \tag{4}$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{5}$$

Otani et al. [18,19], Kato [20] and Takasaki [21] investigated the corrosion behavior of mild steel by emphasizing the effects of metal cations in model fresh water, and they found that Zn^{2+} and Al^{3+} have ability to inhibit the corrosion. Mahdavian et al. [22] investigated the corrosion inhibition of mild steel by some zinc complexes in sodium chloride solution. Prabhu et al. [23] investigated the corrosion behavior of metal surface treated with a new organic chelating inhibitor in acid solution. Jin-xia Xu et al. [24] investigated the steel corrosion in saturated calcium hydroxide solution with metal oxides and nitrates. For this reason, the effect of metal cations on the corrosion of mild steel should be considered in the Cl⁻ containing aqueous solution. The effect of metal cations on corrosion of mild steel in 10 mM Cl⁻ aqueous solution is not fully understood. Therefore, it is needed to clarify the effect of metal cations on corrosion behavior of mild steel in the solution that contains 10 mM Cl⁻ at an equal level of pH.

Incorporation of the metal cations in the passive films would be significant to clarify the influence of metal cations on the corrosion of
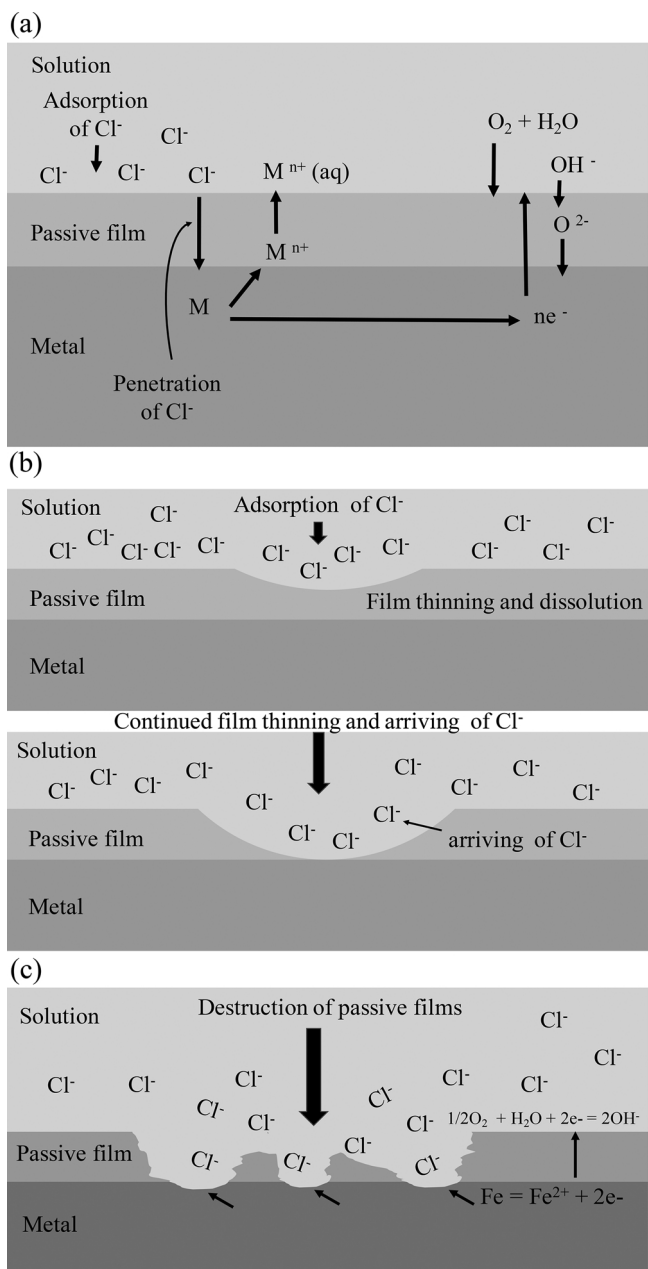
(a)

(b)

(c)

Fig. 1. Schematic representation of adsorption of Cl^- on the metal surface by (a) penetration, (b) film thinning, and (c) dissolution with electrochemical reactions on mild steel surface in 10 mM Cl^- aqueous solution.

mild steel in the 10 mM Cl^- aqueous solution. According to the Lewis concept regarding acid and bases, cations and anions act as acids and bases, respectively [25]. Further, acids and bases are categorized into 'hard' and 'soft' [26]. According to the hard and soft acid and base (HSAB) concept, soft acids react and form strong bonds with soft bases, whereas hard acids react and form strong bonds with hard bases. The metal cation hardness is based on the HSAB concept. The hardness of metal cations, X, is expressed (equation (6)) as follows [18,27,28]:

$$X = X_M^0 + (\Sigma\, I_n)^{1/2}]^2/10 \qquad (6)$$

Where X_M^0 is the electronegativity of the metal atom, and I_n (eV) is the ionization potential from the neutral metal atom to the given oxidized state, n. Hard acids and hard bases can form stable bonds. Hydroxyl groups, which are categorized as hard bases, are located on the outermost layer of oxide film of mild steel and metal cations with large X, which are categorized as hard acids therefore easily bond with hydroxyl

groups on the mild steel. For this reason, the value of X indicates the tendency of formation of chemical bond between metal cations in the solution and hydroxyl groups on the mild steel surface. Therefore, HSAB concept is very useful for understanding the incorporation of metal cations in the oxide films [29]. Based on the HSAB concept, hardness of metal cation, X was introduced to explain the corrosion behavior of metals in fresh water [27]. However, X is not suitable corrosion indicator regarding corrosion of metals in fresh water [18]. It is still unknown the possibility of X as an indicator for corrosion of metals in the 10 mM Cl^- aqueous solution. The mechanism of corrosion inhibition of metal cations is also unknown. By considering the corrosion rate of mild steel that depends on the metal cations [18,19], Cl^- concentration, pH [30,31] and dissolved oxygen, the present research purpose is to find out the effects of metal cations on corrosion of mild steel, and the mechanism of corrosion inhibition in 10 mM Cl^- aqueous solution at an equal level of pH.

In this experiment, comparative conditions were used to study the influence of metal cations on corrosion of mild steel in 10 mM Cl^- aqueous solution. The fluctuations of environmental factors were controlled initially to obtain the effective influence of metal cations on corrosion. The influence of metal cations on corrosion of mild steel in the mentioned environment were investigated by electrochemical impedance spectroscopy (EIS), immersion tests, surface observation and analysis with scanning electron microscope (SEM), Energy dispersive X-ray spectroscope (EDS) and X-ray photoelectron spectroscope (XPS).

2. Experimental

2.1. Specimens

Mild steel sheets (7×7 mm in size and 0.7 mm in thickness) were used as specimens. The chemical composition of the mild steel is shown in Table 1. The methods used to prepare specimens for immersion tests and electrochemical measurements are shown in Fig. 2. To make an electrical contact, a wire was connected with each specimen to perform the electrochemical measurements. All the specimens were molded in epoxy resin (Struers Ltd., EpoFix Resin). The exposed surface of each molded specimen was grounded (Marumoto Struers S5629, LaboForce-3) with SiC abrasive papers from #400 to #4000 grit size, then finally polished by colloidal silica. Before the immersion tests, the specimens were taken out from the epoxy resin. All the specimens were ultrasonically cleaned (SIBATA ultrasonic cleaner, SU-2T) in ethanol and then in highly purified water. The specimens were kept in a desiccator to avoid any type of contamination and humidity.

2.2. Solutions

Five different salt solutions, 10 mM NaCl (Na_{sol}), 0.1 mM $MgCl_2$ (Mg_{sol}), 0.1 mM $ZnCl_2$ (Zn_{sol}), 0.1 mM $AlCl_3$ (Al_{sol}), and 0.1 mM $ZrOCl_2$ (Zr_{sol}) were used as test solutions. The Cl^- concentration of each solution was adjusted to 10 mM by NaCl. In this study, Na_{sol} was considered as a standard solution. Water used in this study was highly purified that was distilled two times and then further purified by water purifier (MILIPORE, Simplicity UV). All chemicals used in this study were special analytical grade and obtained from Kanto Chemical Co. Ltd.

Electrochemical reactions are mostly depended on the pH of the aqueous solution [30,31]. The pH of used solutions was controlled between 5.7 and 5.8 by 0.1 M NaOH (Table 2). The pH measurement of

Table 1
Chemical composition of specimen (mass%).

C	Si	Mn	P	S	Fe
0.020	0.010	0.180	0.015	< 0.01	Bal.