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Corrosion inhibition effects of metal cations on SUS304 in 0.5 M Cl^- aqueous solution

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ABSTRACT

The corrosion characteristics of SUS304 exposed to 0.5 M Cl^- aqueous solution containing different metal cations were studied with immersion tests, surface analysis and electrochemical tests. The mechanism of corrosion with metal cations was clarified by the XPS analysis results together with the hard and soft acid and base (HSAB) concept and the passive films structure. It is supposed that metal cations with large hardness make a layer by chemical bonding with the passive films. The passive films are protected by the metal cation layer from Cl^- attack, and consequently corrosion reactions are inhibited.

1. Introduction

SUS304 is very popular and widely used in applications requiring high corrosion resistance. However, corrosion of stainless steel is a serious problem in liquid supply pipes and storage tanks, ships, bridges and many other constructions. Corrosion of stainless steel has been investigated by many researchers [1–11]. The corrosion resistance property of stainless steel mostly depends on the stability of the passive films. In corrosive environment, the re-passivation properties of the passive films provide the key to the high corrosion resistance of stainless steels [12,13].

Corrosion of stainless steel depends on the various environmental factors. One of the important factor is presence of anions (Cl^- and SO_4^{2-}) in the aqueous solution. Cl^- plays a major role in corrosion of steel because the passive films are easily destroyed by this anion [14–18]. Corrosion reactions are initiated on the steel surface while the passive films are destroyed by Cl^- in the aqueous solution [14–20]. The passive films stability is decreased with increasing the Cl^- concentration in the aqueous solution. In other word, corrosion of steel is highly correlated with the Cl^- concentration [21–27]. There are reports that metal cations can change the corrosion behavior of steel in aqueous solution [21–29]. Islam et al. [21] studied the inhibiting effects of metal cations on mild steel corrosion in Cl^- containing aqueous solution. Otani et al. [22,23] investigated the effects of metal cations on steel corrosion in fresh water and they found that metal cations have an ability to make a layer on the passive films and protect the film from Cl^- attack in the solution. Zhang et al. [24] studied the inhibiting effect of metal cations and reported that some metal cations (Mn^{2+}, Ni^{2+} and Zn^{2+}) effectively inhibit the intergranular stress corrosion cracking of sensitized type 304 stainless steel in SO_4^{2-} (10^{-5} kmol/m^3) containing aqueous solution. They also clarified the effects of metal cations with hardness, *X*, which is based on the hard and soft acid and base (HSAB) concept. Khedr et al. [25] studied the role of metal cations in the corrosion and corrosion inhibition of aluminium in aqueous solutions of SO_4^{2-} and NO_3^-. O'dell et al. [28] reported that some metal cations exhibit inhibiting effects to the intergranular stress corrosion cracking of sensitized type 304 stainless steel in Cl^- containing aqueous solution. Drazic et al. [29] reported that Cd^{2+}, Mn^{2+} and Zn^{2+} inhibit the corrosion of iron in sulphuric acid solutions. Gatos [30] investigated the effects of metal cations on the corrosion of iron in acids. In some nuclear power reactors, metal cations are added into high temperature water for suppressing corrosion of the reactor component materials and avoiding accumulation of radioactive metal element [24,31]. Therefore, it has been confirmed that metal cations affect the corrosion of stainless steel in aqueous solution [24,32]. However, the effects of metal cations on corrosion of SUS304 in 0.5 M Cl^- aqueous solution remain unknown and the corrosion inhibition mechanism of metal cations with the passive films are not fully elucidated.

In this study, the effects of metal cations on corrosion of SUS304 in 0.5 M Cl^- aqueous solution were investigated by immersion tests, electrochemical tests, scanning electron microscope (SEM), atomic force microscope (AFM) and X-ray photoelectron spectroscope (XPS). The corrosion inhibition mechanism of metal cations with the passive films structure has also been clarified by the hardness of metal cation,

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X, based on the hard and soft acid and base (HSAB) concept.

2. Experimental

2.1. Specimens

SUS304 sheets were cut into small pieces (7 × 7 × 1 mm) and were used as specimens. In the case of electrochemical tests, a conductive wire was connected to each specimen to use as a working electrode. All the specimens were molded in epoxy resin (Struers Ltd., Epofix Resin) to carried out different tests [21]. The exposed surface of the molded specimen was grounded with SiC abrasive paper from #1000 to #4000 grit size. For immersion tests, the specimens were taken out from the resin after polished [21]. Before performing the tests, all the specimens were cleaned in ethanol and then in highly purified water using ultrasonic bath.

2.2. Solutions

Three 0.5 M Cl^- solutions with different metal cations were used as test solutions; 0.1 mM $MgCl_2$ (Mg_{sol}), 0.1 mM $ZnCl_2$ (Zn_{sol}), and 0.1 mM $AlCl_3$ (Al_{sol}) and their Cl^- concentration was adjusted to 0.5 M by NaCl. In this experiment, 0.5 M NaCl (Na_{sol}) was used as a reference solution. Water used in this study was highly purified; distilled two times and 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.

Corrosion reactions are mostly depended on the pH of the aqueous solution [33,34]. It is essential to control the pH of aqueous solution for better understanding the individual effect of metal cations on the corrosion of stainless steel. The pH of used solutions was adjusted between 5.7 and 5.8 by 0.1 M NaOH (Table 1) before the tests. The pH of the solutions before and after immersion tests were measured by the pH meter (Eutech Instruments Pte. Ltd., Cyber-Scan 6000).

2.3. Immersion tests

Specimens were immersed in the solutions at 25 °C for 56 d (8 weeks). During the immersion tests, the solutions were open to the air. The mass of the specimens was measured using a micro balance (METTLER TOLEDO MX5, Pro FACT) before and after the immersion tests, and the corrosion rates were calculated from the mass change [21].

Before and after the immersion tests, the surfaces of the specimens were observed by a digital camera (Nikon D80-DSLR) and scanning electron microscope using secondary electrons imaging (SEM, JEOL Ltd., JSL6510-LA). The surface of the immersed specimens was analyzed by X-ray photoelectron spectroscope (XPS, JEOL Ltd., JPS-9200) using a monochrome Al Kα X-ray source (1486.6 eV). The diameter of specimen surface analyzed by the XPS was 3 mm. The surface roughness was measured by atomic force microscope (AFM, SPA400) using dynamic force mode with the cantilever type, SI-DF40. Before the analysis, the immersed specimens were cleaned ultrasonically first in ethanol and then in highly purified water.

Table 1
pH of the solutions used for immersion tests, initial value (pH_{int}), after immersion of specimens (pH_{corr}).

Test solutions	pH_{int}	pH_{corr}
Na_{sol}	5.8	4.3
Mg_{sol}	5.7	4.2
Zn_{sol}	5.7	4.3
Al_{sol}	5.7	4.5

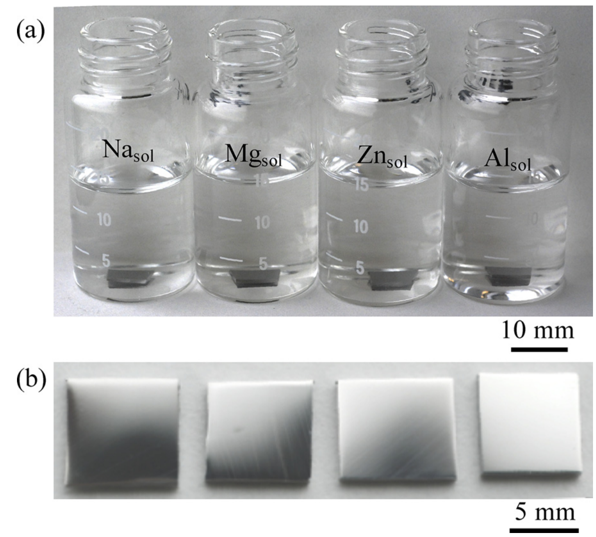

Fig. 1. Appearance of (a) solutions and (b) specimens after immersed in the solutions at 25 °C for 56 d.

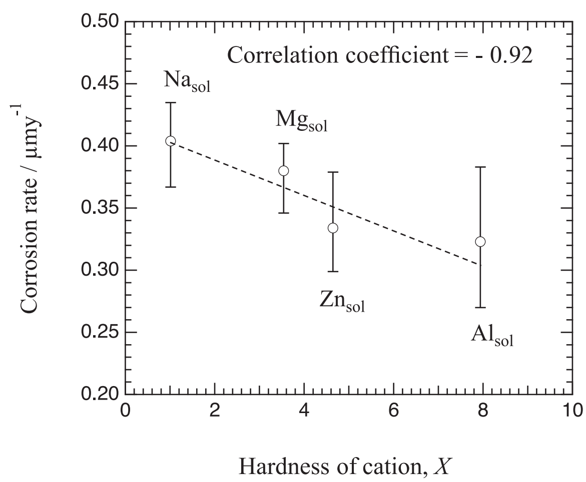

Fig. 2. Corrosion rate as a function of X.

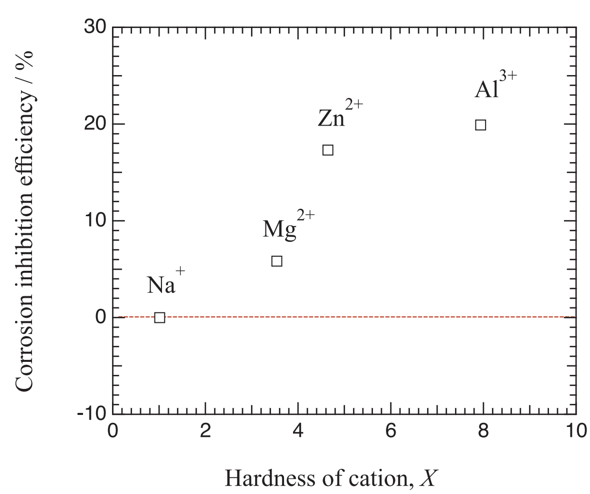

Fig. 3. Corrosion inhibition efficiency of metal cations as a function of X.

2.4. Electrochemical tests

Electrochemical tests were performed in a conventional three-electrode cell using a potentiostat (IVIUM TECHNOLOGIES, Pocketstat).