

Gravimetric corrosion tests and surface analysis of SUS 310S in model seawater

ABSTRACT

The corrosion behaviors of SUS 310S in model seawater with different metal cations have been investigated by gravimetric tests and surface analysis. Different corrosion rates were observed in different solutions by the kinds of metal cations, and Zn^{2+} containing solution showed the lowest corrosion rate among used solutions. SEM observations showed the pits on the surface that were different from each other. White pits were observed on the specimen immersed in the Zn^{2+} containing solution. X-ray photoelectron spectroscopic results showed the presence of Zn^{2+} and Al^{3+} on the specimen immersed in the corresponding solution. Metal cations that have large X showed the tendency to form a fence layer on the specimen surface. Metal dissolution as well as chloride ions attacks were inhibited by the layer of metal cations with large X .

Keywords: Gravimetric test, SUS 310S; corrosion; seawater, SEM, XPS.

1. INTRODUCTION

Stainless steels that abundantly used in many areas are one of the good choices for the consumers. Among the numbers of stainless steels, SUS310S is famous for its durability against corrosion [1, 2]. Generally stainless steels have high corrosion resistant and possesses durability and sustainability. The durability of steels is mostly depended on the oxide film stability on the surface. Stainless steels have good corrosion resistance over mild steel because of stronger oxide film. However, in high chloride containing environment, the oxide film is destroyed by the chloride ions. It is recognized that chloride ions are very much aggressive and destroy the oxide film by film thinning, penetration and film rupture mechanisms [3-8]. Usually, metal dissolution is originated after the destruction of oxide film by the chloride ions [9-13]. Oxide film destruction rate is increased with increasing the chloride ion

concentration. Consequently, the metal dissolution rate is also increased [14, 15]. Fig. 1 shows the oxide film destruction by chloride ions and metal dissolution is accelerated.

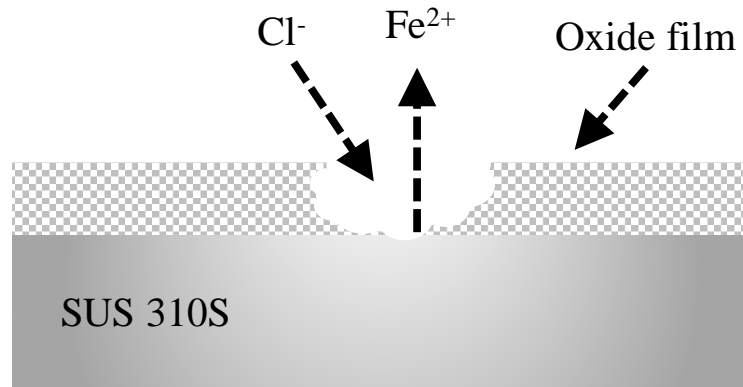


Fig. 1 Oxide film destruction by Cl^- and acceleration of metal dissolution

There are several studies have been carried out that metal cations have a tendency to inhibit the corrosion of steels in chloride aqueous solutions by forming a layer on the steel [9-12, 15, 16]. 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 as follows [9-12, 16, 17]:

$$X = [X_M^0 + (\sum I_n)^{1/2}]^2 / 10 \quad (1)$$

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. The hydroxyl groups of oxide film, which are categorized as hard bases, and metal cations with large X , which are categorized as hard acids, therefore easily bond together [9, 10]. 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 steel. Therefore, HSAB concept is very useful for understanding the incorporation of metal cations in the oxide films [9-12, 18]. The metal cation's hardness is shown in Table 1.

Table 1 Hardness of metal cations, X [16]

| Na^+ | Mg^{2+} | Zn^{2+} | Al^{3+} |
|---------------|------------------|------------------|------------------|
| 1.01 | 3.54 | 4.64 | 7.94 |

It has been recognized that metal cations significantly obstruct the corrosion of carbon steels, stainless steels and alloys in aqueous chloride solutions. However, in the case of specialized stainless steel 310S, the corrosion behavior in seawater with metal cations remains unknown. The present research purpose is to clarify the corrosion behavior of SUS 310S in model seawater with metal cations and propose a corrosion scenario with the oxide film.

2. EXPERIMENTAL

2.1 Specimens

SUS 310S sheet with 0.5 mm thickness was used as the specimens for this experiment. The specimen size was 7×7 mm. The chemical compositions of the specimen are mentioned in Table 2. Each specimen was embedded in epoxy resin leaving one side exposed surface. SiC abrasive paper was used to abrade the exposed surface of the specimen from #1000 to #4000 grit size. After surface abrasion, the specimens were removed from the resin and were cleaned in an ultrasonic bath with ethanol and highly purified water. The specimens were kept in a desiccator to avoid any types of contamination until the gravimetric tests.

Table 2 Chemical composition of SUS 310S (mass%)

| C | Si | Mn | P | S | Cr | Ni | Fe |
|------|------|------|-------|-------|-------|-------|------|
| 0.08 | 1.50 | 2.00 | 0.045 | 0.030 | 24~26 | 19~22 | Bal. |

2.2 Solutions

Four solutions were prepared that contains different cations. 500 mM NaCl solution (Na_{sol}), 0.1 mM MgCl_2 solution (Mg_{sol}), 0.1 mM ZnCl_2 solution (Zn_{sol}) and 0.1 mM AlCl_3 solution (Al_{sol}), and their Cl^- concentration was adjusted to 500 mM by NaCl. The Cl^- concentration of all solutions was 500 mM that is similar to the concentration of seawater [11, 12, 19]. The 500 mM NaCl was used as the reference solution. The experimental solutions were prepared by highly purified water (MILLIPORE, Simplicity UV). All the solutions were colorless and transparent before the gravimetric tests. The pH of the solutions was around neutral. The pH of the solutions is mentioned in Table 3. All of the chemicals used in this experiment were special analytical grade obtained from Kanto Chemical Co. Ltd.

2.3 Gravimetric Tests

The gravimetric tests were carried out for 12 weeks at 25°C. Each specimen was immersed in a vial that contains 20 mL solution. During the tests, the solutions were open to the air for the easy circulation of oxygen. The immersion tests were fully under stagnant condition and the temperature was maintained very carefully. After the tests, each specimen was cleaned carefully by ultrasonic bath and the mass was measured using a micro balance (METTLER TOLEDO MX5, Pro FACT). The corrosion rates were calculated based on the mass loss due to immersion in the solutions [9-12]. The pH of all solutions was also recorded after the immersion tests using a pH meter (Eutech Instruments Pte. Ltd., Cyber-Scan 6000). Each test was carried out with three replicates to get the reproducible data.

2.4 Surface Characterizations

Before and after the gravimetric tests, the testing solutions and specimen surfaces were observed by digital camera (Nikon D80). For the clear understanding and clarifying the corrosion situations, the specimen's surfaces were observed by scanning electron microscope (SEM, JEOL Ltd., JSL6510-LA). Surface analysis was carried out to clarify the specimen surface condition after immersion in the solutions. Ultrasonically cleaned specimen's surface after the immersion was analyzed by X-ray photoelectron spectroscope (XPS, JEOL Ltd., JPS-9200) using an Al K α X-ray source. The diameter of specimen surface analyzed by the XPS was 3 mm.

3. RESULTS AND DISCUSSION

3.1 Gravimetric Tests

Fig. 2 a) shows the appearance of solution and Fig. 2 b) shows the appearance of specimen's surface at the starting of immersion. The solutions are clear and transparent at the initial of the gravimetric tests.

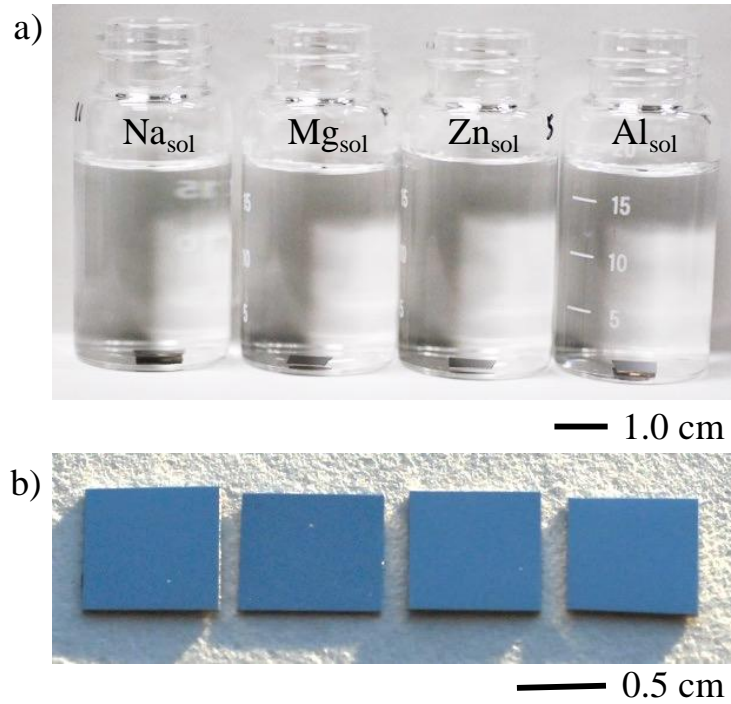


Fig. 2 a) Appearance of solution and b) appearance of specimen's surface at the starting of immersion

Fig. 3 a) shows the appearance of solution and Fig. 3 b) shows the appearance of specimen's surface after the immersion tests for 12 weeks at 25°C. There is no significant difference between the solutions at initial and after the tests. However, the surface conditions maybe changed that are not detectable by necked eye.

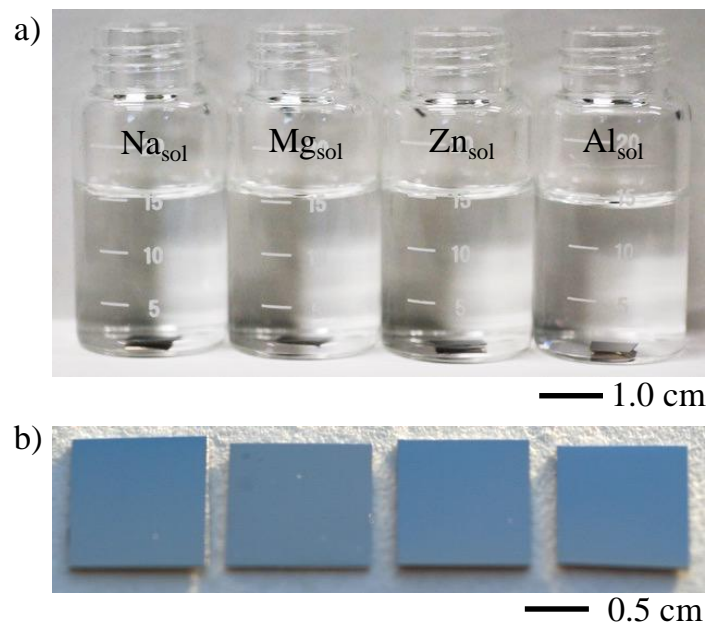


Fig. 3 a) Appearance of solution and b) appearance of specimen's surface after the immersion for 12 weeks at 25°C

Fig. 4 shows the corrosion rates as a function of cation hardness, X . From the Fig. 3 different corrosion rate are observed depending on the cations. There is a tendency to decrease the corrosion rate up to the hardness 6, and then again slightly increase the corrosion rate. However, Zn_{sol} shows the lowest corrosion rate among used solutions in this experiment. The recorded pH values are shown in Table 3. pH values are slightly increased after the immersion tests in all the cases. This was happened maybe due to the formation of hydroxide ion in the solutions [9-12].

Table 3 pH of solutions at the initial and after the immersion tests for 12 weeks at 25°C

| Solution | Initial pH | After Adjust pH | After Immersion tests pH |
|--------------------------|-----------------|-----------------|--------------------------|
| Na_{sol} | 5.88 ± 0.08 | 5.88 ± 0.08 | 6.45 ± 0.05 |
| Mg_{sol} | 5.72 ± 0.02 | 5.72 ± 0.06 | 6.42 ± 0.02 |
| Zn_{sol} | 5.74 ± 0.04 | 5.74 ± 0.05 | 6.88 ± 0.08 |
| Al_{sol} | 4.93 ± 0.12 | 5.74 ± 0.04 | 6.62 ± 0.02 |

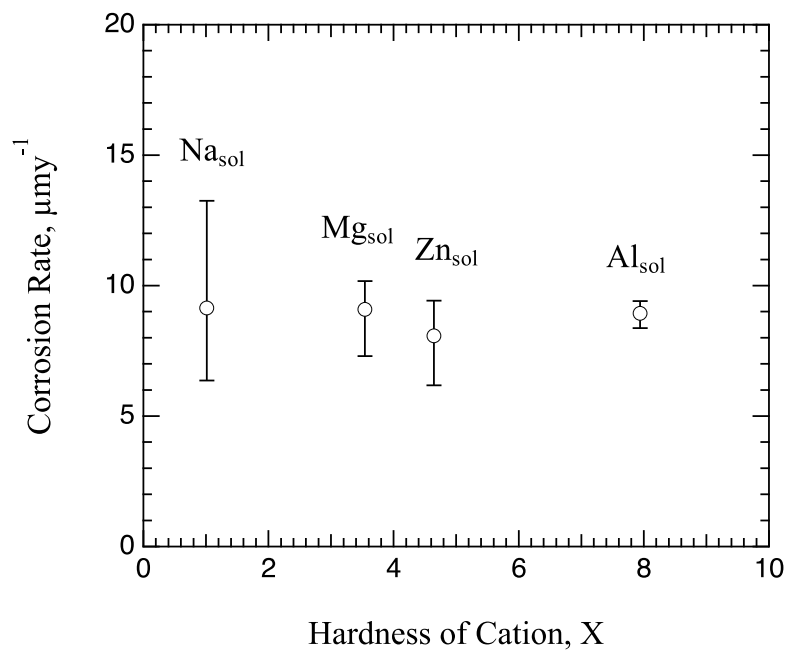


Fig. 4 Corrosion rate as a function of X

3.2 Surface Observation and Characterization

Surface investigation is the important criteria for explaining the corrosion scenario after the immersion tests. Fig. 5 shows the surface SEM images of specimen after the immersion tests for 12 weeks at 25°C. Some small pits are observed on the specimen immersed in Na_{sol} and Al_{sol} . Pits are also observed in the case of Mg_{sol} and Zn_{sol} . However, the pits are different in each other, and white pits are observed on the specimen immersed in Zn_{sol} .

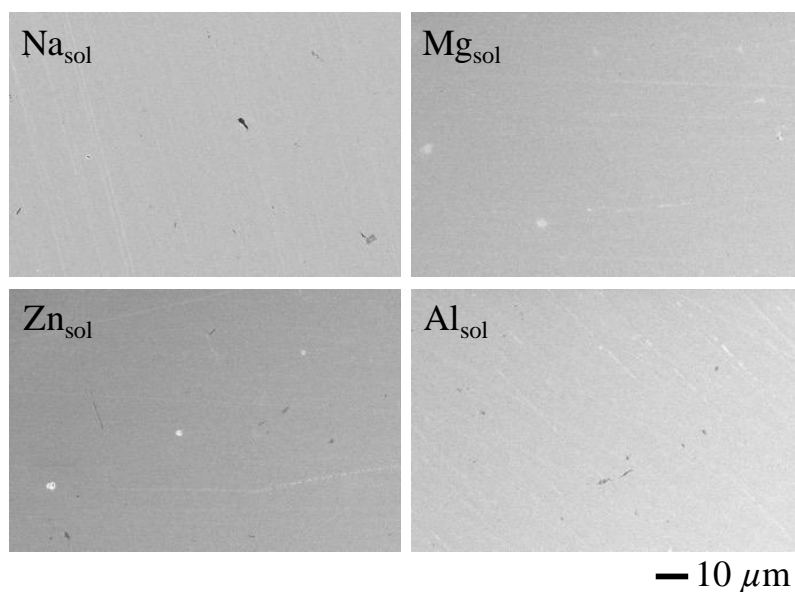


Fig. 5 Surface SEM images of specimen after immersion in the solution for 12 weeks at 25°C

The specimen surface was further investigated by XPS. Fig. 6 shows the XPS wide scan spectra of specimen immersed in the solution for 12 weeks at 25°C. From these wide scan spectra, $\text{Zn}2p_{3/2}$ and $\text{Al}2p_{3/2}$ peaks are observed in the case of corresponding specimen, whereas $\text{Na}1s$ and $\text{Mg}1s$ peaks are not observed. These results suggested that Zn^{2+} and Al^{3+} present on the surface after immersion in the corresponding solutions.

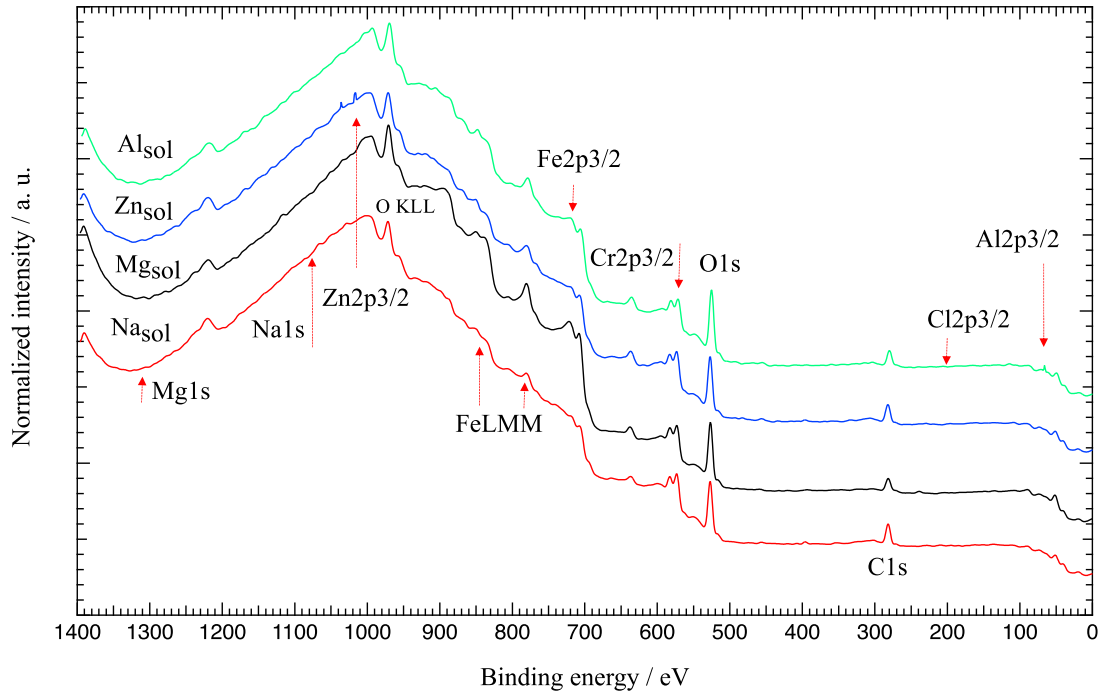


Fig. 6 XPS wide scan spectra of specimen immersed in the solution for 12 weeks at 25°C

3.3 Corrosion Scenario

Based on the experimental results, a corrosion scenario could be suggested. According to the HSAB concept, metal cations with large X , incorporate in the oxide film and attract the electron pair of oxygen atom in H_2O or OH^- in the film, and finally stimulates the deprotonation process [12, 18]. It is considered that the protons are replaced with the hard metal cations and form a metal cation layer on the oxide film. The layer of metal cation protects the oxide film from Cl^- attack and inhibits the corrosion reactions of steel. The metal cations with small X , do not have the ability to make a layer with the oxide film, and thus Cl^- can arrive on the steel surface by destroying the oxide film and initiate the metal dissolution reactions [9-12, 18].

The metal cations (Na^+ and Mg^{2+}) that have small X , may not have the ability to form hydroxide layer with the oxide film. As a consequence, the chloride ions easily destroy the oxide film and accelerate the metal oxidation. Fig. 7 represents the corrosion scenario with metal cations that have small X . For this reason, the solutions that contains Na^+ and Mg^{2+} ions showed the high corrosion rate as compared to the other solutions. Surface SEM images (Fig. 5) also supports these corrosion consequences.

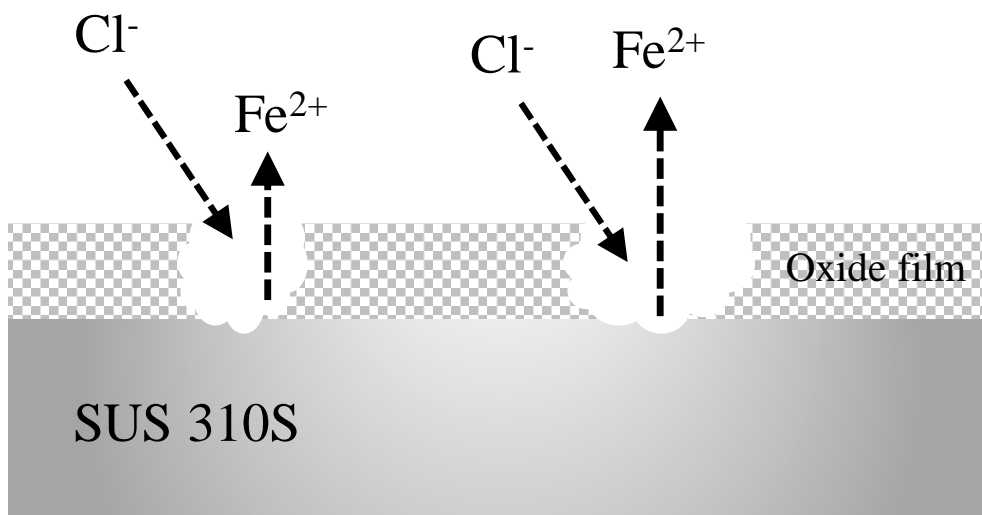


Fig. 7 Acceleration of corrosion by Cl^- in presence of metal cation with small X

On the other hand, the metal cations (Zn^{2+} and Al^{3+}) that have large X have a tendency to form a layer of hydroxide with the oxide film. Fig. 8 represents the corrosion scenario with metal cations that have large X . The layer of metal cation act as a barrier for the chloride ions as well as for the corrosion reactions. Due to the layer of metal cation, chloride ions cannot destroy the layer and the oxide film. As a result, corrosion reactions are inhibited in the case of Zn^{2+} and Al^{3+} containing solution. The Al^{3+} containing solution showed corrosion rate higher than Zn^{2+} containing solution. This is because of the layer of Al^{3+} may not stable properly [12, 18] in that pH of the solution (Table 2). According to the Pourbaix diagram and present solution concentration, there is a possibility to form aluminum hydroxide at the pH lower than 6 [20, 21]. However, the solution pH was higher than 6, and the layer of Al^{3+} may not formed properly. According to the experimental condition, Zn^{2+} containing solution has the ability to form hydroxide on the steel surface [22]. For these reasons Zn^{2+} containing solution showed the lowest corrosion rate as compared to the other solutions.

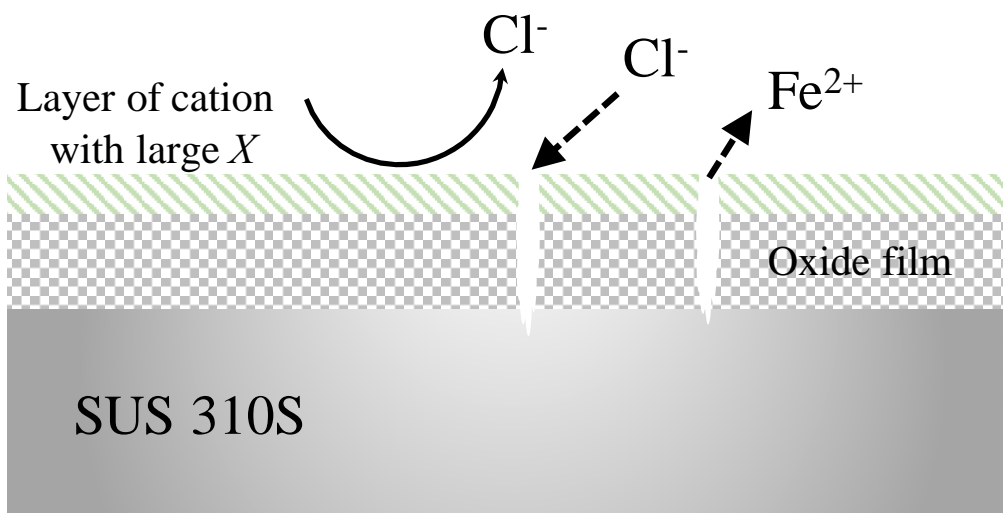


Fig. 8 Corrosion and Cl⁻ inhibition by a layer of metal cation with large X

4. CONCLUSION

The corrosion behaviors of SUS 310S in model seawater with different metal cations have been investigated by gravimetric tests and surface analysis, and the following conclusions can be drawn:

- Different corrosion rates were observed in different metal cationic solutions
- SEM observations showed the pits on the surface that were different from each other
- XPS wide scan spectra showed the presence of Zn²⁺ and Al³⁺ on the surface
- Metal cations that have large X, showed the tendency to form a barrier layer on the surface
- Metal dissolution and chloride ions were inhibited by the layer of metal cations with large X

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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