Influence of Metal Cations on Corrosion Behavior of Titanium in Sulfuric Acid Solutions

LIU XINXIN

Graduated School of Engineering

Hokkaido University

2024

Summary

The metallic Ti is well known for its physical properties, biological properties, and anti-corrosion ability especially in the acid environment. Currently, titanium-based materials are used as thermal power plants chimney lining materials due to their high corrosion resistance in acidic environments. Thermal power plants usually use mineral combustion to obtain energy, such as hard bituminous coal and brown coal. Fossil coals usually contain sulfur compounds, and they will convert into sulfur oxides (SO_x) during the combustion [1], and finally form the sulfuric acids with the moisture in the flue gas. As a result, the chimney environment in industrial settings is complicated due to the presence of acids, fluoride ions (F^-), and metal cations. It has been confirmed that a large number of fluoride ions and metal cations are present in exhaust gases and fly ash [2-6]. Although previous studies have shown that Ti undergoes severe corrosion in fluoride-containing acidic solutions [7-10], the effect of metal cations on the corrosion of Ti is unknown.

Due to the metal cations generally existing in the aqueous solution, being economical and environmentally friendly, and handling easily, understanding the effect of metal cations on the corrosion of Ti may provide help to industrialization application. Therefore, it is necessary to investigate the effect of metal cations on the corrosion of Ti and to understand the corrosion mechanism in acidic environments containing fluoride ions. Besides, to quantitatively analyze the corrosion effect of metal cations on metals, it is very important to select a suitable indicator. The indicator needs to be able to provide a clear classification or description of the metal cation and the anions.

This thesis concentrates on finding an indicator to evaluate the effect of the different metal cations on the corrosion of Ti in a room-temperature sulfuric acid solution containing fluoride ions, and clarifying the possible mechanisms by which metal cations accelerate or inhibit titanium corrosion.

Chapter 1 provided an overview of Ti corrosion. The corrosion factors (acid solution, fluoride ions and the metal cations) are also discussed in this chapter.

In Chapter 2, the influence of different metal cations on the corrosion of titanium in a room-temperature sulfuric acid solution containing fluoride ions was investigated. The goal was to find a suitable indicator for assessing the effect of metal cations on the corrosion of Ti.

1.68 mol L^{-1} H_2SO_4 containing 0.058 mol L^{-1} NaF was used as the standard solution. Nine metal cations (calcium ions, copper ions, ferrous ions, magnesium ions, manganese ions, nickel ions, aluminum ions, ferric ions, and zinc ions) were added to introduce the desired metal cations to the standard solution. The Ca^{2+} containing solution was saturated and the concentrations of the other metal cations was 0.2 mol L^{-1}. Samples were immersed in the test solutions (20 mL) for 7 d at room temperature. Before and after the immersion tests, a microbalance was used to measure the mass of the samples.

From the mass loss results, the solutions containing Fe^{3+}, Cu^{2+}, and Al^{3+}, show a significant decrease in mass loss compared to the standard solution, categorizing them as the inhibiting type. In solutions containing Ca^{2+} and Fe^{2+}, the mass loss is almost the same as in the standard solution, which is categorized as the no effect type. In the Ni^{2+}, Mn^{2+}, Zn^{2+}, and Mg^{2+}, the mass loss is significantly higher than in the standard solution, categorizing them as the accelerating type.

Standard electrode potential, hardness of metal cations, electronegativity and the stability constant of metal-fluorine complex were chosen as the potential indicators to categorize the influence of metal cations on Ti corrosion in standard solution. From the results, the stability constant of metal-fluorine complex as the indicator has the highest correlation coefficient which could be used as the indicator. The results in Chapter 2 also provide information on the further mechanism study.

In Chapter 3, according to the literature, the effects of Zn^{2+} on different metals are different: Zn^{2+} accelerates Mg corrosion through a displacement reaction [11] while Zn^{2+} inhibits the corrosion of mild steel in Cl^- containing solution by forming a Zn-layer [12]. Since the mechanism of Zn^{2+} accelerating the corrosion of Ti is unknown, the effect of zinc ion concentration on the corrosion of Ti in the sulfuric acid solution with fluoride ions was investigated by the immersion test and electrochemical impedance spectroscopy test. To clarify the mechanism of zinc ions accelerating the corrosion of Ti, the sodium fluoride solution and the sulfuric acid solution were chosen as the control groups.

1.68 mol L^{-1} H_2SO_4 containing 0.058 mol L^{-1} NaF was used as the mixed solution (S_{mixed}). The control groups are defined as S_{NaF} and S_{acid}. Four different concentrations of Zn^{2+} were added to these solutions. Samples were immersed in the test solutions (20 mL) for 7 d at room temperature. Before and after the immersion tests, the microbalance was used to measure the mass of samples. After immersion tests, the surface were observed and analyzed by a scanning electron microscope (SEM) and a laser scanning confocal microscope (LSCM). The electrochemical test were carried out in a three-electrode system using a potentiostat: a platinum plate was used as the counter electrode and an Ag/AgCl electrode (SSE) immersed in a saturated KCl solution was used as the reference electrode. The electrochemical impedance spectroscopy (EIS) tests were carried out in a frequency range from 10 kHz to 10 mHz, and the modulation amplitude was 10 mV. After the immersion tests, the surface of Ti samples was observed by laser scanning confocal microscope and scanning electron microscope.

The immersion test results showed that zinc ions could accelerate the corrosion of Ti in the sulfuric acid solution with fluoride ions even at a low concentration. The EIS test results are consistent with the mass loss results. In the control groups (S_{NaF} and S_{acid}), the addition of Zn^{2+} does not change the corrosion behavior of Ti. A possible explanation is that the titanium oxide film, which is generally believed to be the protective film, may

dissolve in S_{mixed}. As a result, the Zn^{2+} may accelerate the corrosion of the Ti substrate. The dissolution of the titanium oxide film is the key factor in zinc ions accelerating the corrosion of Ti.

An adsorption-dissolution model was used to study the effect of zinc ions on the corrosion of Ti. The adsorption/desorption kinetic parameter of indeterminate titanium fluoride products and the surface coverage by the indeterminate titanium fluoride products were calculated based on this model. From the results, at steady state, the surface coverage by intermediereate reaction products (titanium fluoride products) decreases, indicating that the surface has more active sites for Ti dissolution.

In Chapter 4, based on Chapter 2, the Al^{3+} and Fe^{3+} could be categorized as the inhibiting metal cations. However, the effects of Al^{3+} and Fe^{3+} on the surface morphology of Ti is unknown. Moreover, the mechanism of Fe^{3+} more efficiently enhances the corrosion resistance than Al^{3+} remains unknown. To investigate this, the surface observation and analysis and the electrochemical test were carried out.

1.68 mol L^{-1} H_2SO_4 containing 0.058 mol L^{-1} NaF was used as the S_{mixed}. In Al^{3+} case, the control groups are defined as S_{NaF} and S_{acid}. 0.2 mol L^{-1} Al^{3+} were added to the S_{mixed}, S_{NaF} and S_{acid}. In Fe^{3+} case, the control group is S_{acid}, and five different concentrations of Fe^{3+} (0.02 mol L^{-1}, 0.06 mol L^{-1}, 0.1 mol L^{-1}, 0.16 mol L^{-1} and 0.2 mol L^{-1}) were added to the solution. The surface were observed and analyzed by a scanning electron microscope (SEM) and an X-ray photoelectron spectroscopy (XPS). the electrochemical impedance spectroscopy (EIS) tests (in a frequency range from 10 kHz to 10 mHz, and the modulation amplitude was 10 mV) were carried out in these solutions.

From the mass loss results, the addition of Al^{3+} only reduce the mass loss in the S_{mixed}, while the addition of Fe^{3+} reduce the mass loss in S_{mixed} and S_{acid}. The surface observation results indicated Al^{3+} and Fe^{3+} could change the surface morphology after immersion tests. Surface analysis detected peaks of ferric and fluorine, suggesting that the presence of ferric

ions reducing the activity of fluoride ions. Electrochemical test results indicated that the addition of Al^{3+} and Fe^{3+} enhanced the corrosion resistance of Ti in S_{mixed}. As the concentration of added Fe^{3+} increased, the corrosion resistance of Ti improved. An adsorption-dissolution model was used to study the effect of ferric ions on the corrosion of Ti. The possible indeterminate titanium product is titanium oxide products. From the Chapter 3, the oxide film is the key factor on Ti corrosion. According to this, the importance of titanium oxide film formation should be taken into consideration. At the steady state, the adsorption kinetic parameter of indeterminate titanium oxide products is larger than desorption kinetic parameter, which indicates the Fe^{3+} could improve the protective film formation.

Chapter 5 is the summary of Chapter 2 to Chapter 4. This thesis investigated the effect of different metal cations on the corrosion of Ti in a room-temperature sulfuric acid solution containing fluoride ions. A proper indicator, the stability of metal fluoride complex, was proposed to evaluate the effect of the metal cations on the corrosion of Ti in a room-temperature sulfuric acid solution containing fluoride ions. The larger stability constant of the metal-fluoride complex indicates that the activity of fluoride ions was reduced, which in turn decreased the dissolution of the naturally formed titanium oxide film. The adsorption-dissolution model could be used to investigate the effects of zinc ions and ferric ions on the adsorption-dissolution process.

Reference

1. Bordzilowski, J. and Darowicki, K. (1998) "Anti-corrosion protection of chimneys and flue gas ducts." Anti-Corrosion Methods and Material 45(6): 388-396.
2. Nishitani, T., Fukunaga, I., Itoh, H. and Nomura, T. (1999) "The relationship between HCl and mercury speciation in flue gas from municipal solid waste incinerators." Chemosphere 39(1):1-9.
3. Álvarez-Ayuso, E., Querol, X. and Tomás, A. (2006) "Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products." Chemosphere 65(11): 2009-2017.
4. Ruth, L. A. (1998) "Energy from municipal solid waste: A comparison with coal combustion technology." Progress in Energy and Combustion Science 24(6): 545-564.
5. Pavageau, M. P., Pécheyran, C., Krupp, E. M., Morin, A. and Donard, O. F. X. (2002) "Volatile metal species in coal combustion flue gas." Environmental Science & Technology 36 (7): 1561-1573
6. Vassilev, S. V., Vassileva, C. G., Karayigit, A. I., Bulut, Y., Alastuey, A. and Querol, X. (2005) "Phase–mineral and chemical composition of composite samples from feed coals, bottom ashes and fly ashes at the Soma power station, Turkey." International Journal of Coal Geology 61(1–2): 35-63.
7. Saiful Islam Md., Otani K. and Sakairi, M. (2018) "Corrosion inhibition effects of metal cations on SUS304 in 0.5 M Cl^- aqueous solution." Corrosion Science 140: 8-17.
8. Kartsonakis, I.A., Balaskas, A.C., Koumoulos, E.P., Charitidis, C.A. and Kordas, G. (2012) "Evaluation of corrosion resistance of magnesium alloy ZK10 coated with hybrid organic–inorganic film including containers." Corrosion Science 65: 481-493.
9. Michailidou, E., McMurray, H.N. and Williams, G. (2018) "Quantifying the role of

transition metal electrodeposition in the cathodic activation of corroding magnesium." Journal of The Electrochemical Society 165(5): C195-C205.

10. Lindgren, M., Huttunen-Saarivirta, E., Peltola, H., Romu, J., Sarikka, T., Hänninen, H. and Pohjanne, P. (2018) "Crevice corrosion of stainless steels 904L, 2205 and 2507 in high-temperature sulfuric acid solution containing chlorides: Influence of metal cations." Corrosion 74(2): 225–240.
11. Saiful I. Md. and M. Sakairi. (2019) "Effects of Zn^{2+} concentration on the corrosion of mild steel in NaCl aqueous solutions." Journal of The Electrochemical Society166 (2): C83-C90.
12. Huang, J., Song, G .L., Wang, Z., Zhu, Y. and Zheng, D. (2020) "The Zn^{2+} destabilized surface film and accelerated corrosion of magnesium." Journal of The Electrochemical Society 167: 161508.