学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

Influence of Metal Cations on Corrosion Behavior of Titanium in Sulfuric Acid Solutions
(硫酸環境中におけるチタンの腐食に及ぼす金属カチオンの影響)

Titanium-based materials are currently used as chimney lining materials due to their high corrosion resistance in acidic environments. It has been confirmed that a large number of fluoride ions and metal cations are present in exhaust gases and fly ash. Previous research has shown that titanium (Ti) undergoes severe corrosion in acidic solutions containing fluoride ions. However, few studies have been conducted on the effect of metal cations on the corrosion of Ti in aqueous environments. 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.

This thesis focuses on identifying 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, discussing its mechanisms and influencing factors.

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 identify a suitable indicator for evaluating the effect of metal cations on the corrosion of Ti. The effect of nine metal cations (calcium ions, copper ions, ferrous ions, magnesium ions, manganese ions, nickel ions, aluminum ions, ferric ions, and zinc ions) on the corrosion of Ti was investigated by the immersion tests. The results showed copper ions, aluminum ions and ferric ions significantly inhibit the corrosion of Ti. Nickel ions, manganese ions, magnesium ions and zinc ions accelerated the corrosion of Ti, while calcium ions and ferrous ions did not affect the corrosion of Ti. The stability constant of metal-fluorine complex was a suitable indicator to categorize the influence of metal cations on Ti corrosion in the acid solution with fluoride ions.

In Chapter 3, the effect of zinc ions concentrations 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 by which zinc ions accelerating the corrosion of Ti, the sodium fluoride solution and sulfuric acid solution were chosen as the control group. After the immersion tests, the surface of Ti specimens was observed by laser scanning confocal microscope and scanning electron microscope. The immersion test results showed that zinc ions accelerated the corrosion of Ti in the sulfuric acid solution with fluoride ions even at a low concentration. The dissolution of the titanium oxide film was the key factor in zinc ions accelerating the corrosion of Ti. An adsorption-dissolution model was used to study the effect of the zinc ions on the corrosion of Ti. The surface coverage by intermediate reaction products (titanium fluoride products) at steady state is reduced, indicating that the surface has more active sites for Ti dissolution.

In Chapter 4, the effect of corrosion-inhibiting metal cations (aluminium ions and ferric ions) on the corrosion of Ti in a sulfuric acid solution containing fluoride ions was clarified based on immersion tests and electrochemical tests. After the immersion tests, the surfaces of Ti specimens were observed using a scanning electron microscope and analyzed by X-ray photoelectron spectroscope. The surface observation results indicated aluminum ion and ferric ions 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 these metal cations improved corrosion resistance. As the concentration of added ferric ions 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 increased formation of intermediate reaction products at steady state suggested that fewer active sites were available for Ti dissolution.

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 was used to investigate the effects of zinc ions and ferric ions on the adsorption-dissolution process.