High Temperature and High Pressure Corrosion of Titanium in Hydrometallurgical Applications

by

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Abstract

The corrosion characteristics of titanium (ASTM Grade 2) in copper pressure leaching environments are determined from room temperature and pressure up to high temperatures and pressures (230 °C, 430 psi). Anodic oxidation and controlled chemical oxidation methods are used to improve the corrosion resistance of Ti. Electrochemical and mass loss measurements are performed to evaluate the corrosion resistance of pre-oxidized titanium, compared to that of titanium with no prior oxidation, to generate a best practices guide for the hydrometallurgical industry.

The results at low temperature showed that H₂SO₄ solution is very corrosive for Ti with a freshly polished surface. The corrosion rates (CRs) of Ti are obtained using mass loss and electrochemical measurements in H₂SO₄ with Cl⁻, Cu²⁺ and Fe³⁺ additions up to 175 °C. It is found that the CRs of Ti are unaffected by the presence of Cl⁻ ions in H₂SO₄ solutions. CRs obtained from mass loss and electrochemical measurements confirm that Cu²⁺ and Fe³⁺ ions are good corrosion inhibitors for Ti. Iso-corrosion diagrams, with 0.1, 0.5 and 1 mm yr⁻¹ lines for Ti in 3-50 wt.% H₂SO₄ solutions with Cu²⁺ or Fe³⁺ additions from room temperature to 175 °C are constructed from immersion test data.

The effects of temperature (100-230 °C) and SO₄²⁻ concentration (0-0.5 mol L⁻¹) on the pitting corrosion of Ti are studied in neutral Cl⁻ containing solutions using cyclic potentiodynamic polarization and linear-sweep thermammetry measurements. A metastable pitting temperature threshold (MPTT) is defined for Ti as a function of sulfate to chloride mole ratio using linear-sweep thermammetry measurements.
Anodic oxide films (AOFs) are potentiostatically formed on Ti in 0.5 M H₂SO₄ solutions at various anodizing voltages (up to 80 V) at 25 °C. A new method is developed to fabricate chemically oxidized films (COFs) with high corrosion resistance by controlled chemical oxidation with H₂O₂ solutions at 90 °C. The corrosion behavior of the as grown AOFs and COFs is investigated in copper sulfide leaching solutions. It is confirmed that chemical oxidation with 2 M H₂O₂/0.1 M HCl solution leads to the best improvement of the corrosion resistance of Ti.
Preface

The following journal papers and conference presentations have been published from the research work presented in this dissertation. I am the primary author of all the published work. Professor Edouard Asselin and Professor Akram Alfantazi extensively helped with all the aspects of the research work.

Journal Papers


Conference Presentations with Proceeding


Conference Presentation and Poster

1. J. Liu, A. Alfantazi, E. Asselin, Influence of cupric, ferric and chloride on the corrosion of Ti in sulfuric acid solutions below 100 °C. February 2013, NACE Northern Area Western Conference, Victoria, BC, Canada.

2. J. Liu, A. Alfantazi, E. Asselin, Iso-corrosion diagrams and electrochemical properties of Ti in sulfuric acid solutions up to 175 °C. January 2014, NACE International Northern Area Western Conference, Edmonton, Alberta, Canada.
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Figure B-1 Autoclave assembly.

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Figure C-1 Immersion apparatus assembly.

Figure D-1 Controlled chemical oxidation assembly.
List of Symbols

A  sample area, cm$^2$
C$_j$  molar concentration of ion, mol L$^{-1}$
D  density, g cm$^{-3}$
D$_0$  diffusivity of defects, cm$^2$ s$^{-1}$
e  electron charge, C
E$_{Ag/AgCl}$  potential of the RE measured against the SHE at 25 °C, V
E$_b$  breakdown potential, V
E$_{corr}$  corrosion potential, V
E$_{FB}$  flatband potential, V
E$_{LJP}$  isothermal liquid junction potential, V
E$_{measured}$  measured potential, V
E$_{pp}$  primary passive potential, V
E$_{rp}$  repassivation potential, V
E$_{TLJ}$  thermal liquid junction potential, V
E$_{vs,SHE}$  potential of the WE reported against the SHE at 25 °C, V
F  Faraday’s constant, C mol$^{-1}$
f$_{m,j}$  activity coefficient on the mole fraction scale, 1
i$_{passive}$  passive current density, A cm$^{-2}$
iR  ohmic loss, V
k  Boltzmann constant, J K$^{-1}$
M  atomic mass, g mol$^{-1}$
n
n
valence state, 1

N_D

density of defects, cm^{-3}

Q

constant phase element, \mu F \ cm^{-2} \ s^{-1}

R

resistance, \Omega

R_{p-LPR}

linear polarization resistance, \Omega

S^\circ

standard entropy, J \ K^{-1} \ mol^{-1}

S_{i}^*

entropy of transport, J \ mol^{-1} \ K^{-1}

t

time, s

T

absolute temperature, K

\text{t_i^*}

transport number, 1

u_i

ion mobility, cm^{2} \ V^{-1} \ s^{-1}

W

mass loss, mg

z_i

ion charge, C

\Delta E_{\text{SHE}}

the potential difference of the SHE thermal cell at T and 25 \ ^\circ\text{C}, V

\Delta \text{f} G^\circ

standard Gibb's free energy, kJ mol^{-1}

\varepsilon

dielectric constant, F \ m^{-1}

\varepsilon_0

vacuum permittivity, F \ m^{-1}

\lambda_i

individual ionic conductivity, cm^{2} \ \Omega^{-1} \ \text{equiv}^{-1}
**List of Abbreviations**

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AOF</td>
<td>anodized oxide film</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode</td>
</tr>
<tr>
<td>COF</td>
<td>chemically oxidized film</td>
</tr>
<tr>
<td>CPE</td>
<td>constant phase element</td>
</tr>
<tr>
<td>CPP</td>
<td>cyclic potentiodynamic polarization</td>
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<td>CPT</td>
<td>critical pitting temperature</td>
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<td>external pressure balanced reference electrode</td>
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<td>metastable pitting temperature threshold</td>
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<td>optical microscope</td>
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<td>standard hydrogen electrode</td>
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<tr>
<td>ToF-SIMS</td>
<td>Time of flight secondary ion mass spectrometry</td>
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<td>WE</td>
<td>working electrode</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
Acknowledgements

My utmost gratitude to Professor Edouard Asselin (supervisor) and Professor Akram Alfantazi (co-supervisor), whose sincere support and constant encouragement I will never forget. Without their guidance, this work would never have been completed.

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Dedication

This dissertation is dedicated to:

My beloved parents and my dear uncle;

最爱我的爸爸妈妈和我最爱的叔叔

For their encouragements to pursue my studies,

and their constant support throughout my life.

It’s a terrible thing, I think, in life to wait until you are ready.

I have this feeling now that actually no one is ever ready to do anything.

There is almost no such thing as ready.

This is only now.

And you may as well do it now.
1 Introduction

Traditionally, metals such as copper and nickel have been produced by pyrometallurgical processes from their concentrates. In recent decades, the metallurgical industry has been searching for a hydrometallurgical process as an alternative to pyrometallurgical treatment due to the high capital costs associated with smelting and some of the inherent advantages of hydrometallurgy. These advantages include the possibility of treating low-grade ores (increasingly more common in the case of copper) and easier waste control, with the attendant benefits to the environment (Córdoba et al., 2008).

Hydrometallurgical production of copper from its sulfide ores typically involves using concentrated sulfuric acid or a mixed sulfate-chloride system to extract the desired metal at elevated temperatures (Dreisinger, 2006; Jones, 1999; McDonald & Muir, 2007; Sahu & Asselin, 2011). For example, medium temperature chalcopyrite concentrate leaching processes may operate at temperatures of 125-150 °C and pressures of 800-2200 kPa (Dreisinger, 2006; Jones, 1999; McDonald & Muir, 2007; Sahu & Asselin, 2011). These conditions place extraordinary demands on the materials of construction of the autoclaves used in pressure leaching operations. In order to ensure the safety and working efficiency of hydrometallurgical production, equipment used in leaching processes should be made of materials that can provide suitable corrosion resistance, which leads to a long service life.

Ti and its alloys are the materials currently selected for many internal autoclave parts including the liner, where they are subjected to strong solutions of reducing acid, high temperature and high pressure (Grauman & Say, 2000; Reid, 2003; Vaughan, 2003a, 2003b). Increasing application of Ti in hydrometallurgical equipment warrants that further research into its
corrosion behavior under conditions relevant to hydrometallurgy be undertaken. During service, 
Ti is subjected to severe conditions of acidity, temperature, and pressure. The model system used 
here is that of medium temperature chalcopyrite leaching processes that take place in sulfuric 
acid with the presence of chloride, cupric and ferric ions in combination, and in many cases the 
chloride concentrations can be very high (Dreisinger, 2006; Sahu & Asselin, 2011). The 
temperature of these processes is typically 150 °C. Generally, Ti is thermodynamically unstable 
in sulfuric or hydrochloric acids, even in the presence of corrosion-inhibiting cations and oxygen 
(Blackwood et al., 1988; Vaughan & Alfantazi, 2006). Fortunately, the presence of many 
oxidizing species in the bulk solution ensures a passive rest potential for the Ti liner and parts. 
However, scale buildup on the autoclave liner and components provide the opportunity for 
localized corrosion. In addition, it has been reported that the pitting corrosion of Ti in chloride 
containing solutions is strongly temperature-dependent (Beck, 1973a). Therefore, Ti becomes 
susceptible to both uniform and pitting corrosion in this kind of environment (Armstrong et al., 
1970; He et al., 2002; Kelly, 1976, 1979; Shibata & Zhu, 1995; Thomas & Nobe, 1969; Vaughan 
& Alfantazi, 2006; Vaughan et al., 2010). Corrosion damage is expensive to repair and may 
cause severe safety problems.

Ti is known to provide excellent corrosion resistance due to the chemically unreactive and 
mechanically strong oxide films formed on its surface (Donachie, 2000). Ti oxide forms instantly 
when a freshly polished Ti surface is exposed to air. The protective titanium oxide can be 
enhanced by three methods: thermal oxidation, anodic oxidation and chemical oxidation (Birch 
& Burleigh, 2000; Gaul, 1993; Kumar et al., 2010a; Kumar et al., 2009, 2010b; Schutz & 
Covington, 1981). Thermal oxidation is simple, but its reproducibility is poor and should be 
preceded by acid pickling to remove embedded surface contaminants, such as iron (McMaster,
Anodic oxidation is more consistent and can be effective as a single step if it is applied for a sufficient time to dissolve surface contamination (Cotton, 1970). Currently, it is industry practice to oxidize the Ti liner using sulfuric acid, ammonium phosphate or some other suitable solution to favor the formation of an artificially thick anodic oxide film at 25-80 V (Cotton, 1970; McMaster, 2001). Anodizing may be applied to autoclaves after installation, but it is a time consuming and laborious operation with potential safety problems. On the other hand, controlled chemical oxidation is an attractive technique for growing oxide layers on titanium substrates. Hydrogen peroxide (H₂O₂) is an oxidant that brings no external contamination. To the author’s knowledge, there is no chemical oxidation method that has been purposely developed for improving the corrosion resistance of titanium. It may be possible, and very useful, to control the properties of Ti surfaces, including the thickness of the oxide layers, by varying the conditions of the oxidizing treatment. This may lead to the creation of both chemically and mechanically strong surfaces designed to resist the aggressive pressure leaching environments. Nevertheless, the corrosion resistance of pre-oxidized and un-oxidized Ti in synthetic copper sulfide leaching solutions needs to be further understood to ensure the safety and working efficiency of hydrometallurgical copper production, but also to inform industry as to the best practices to follow.

As there is very little information pertaining to Ti corrosion in hydrometallurgical environments, the following study will present the results on the corrosion characteristics of Ti in synthetic pressure leaching solutions. While corrosion studies under high temperature high pressure conditions will eventually be presented, due to the paucity of information regarding the behavior of Ti in mixed sulfate-chloride systems, this study will begin by characterizing their electrochemical response at room temperature and then follow with results from successively
higher temperatures. For reasons to be discussed later, the pitting corrosion of Ti is studied in neutral sulfate–chloride systems at high temperatures. The corrosion behavior of anodized Ti will also be investigated, as anodizing is the one of the most cited methods to build an artificially thick anodic oxide film for hydrometallurgical applications. In the end, a new method will be developed to grow titanium oxide films for hydrometallurgical applications with high corrosion resistance by controlled chemical oxidation with H$_2$O$_2$ solutions at 90 °C.

In the following chapter (Chapter 2) the literature pertaining to this study will be discussed. Chapter 3 will present the objectives of this work. Chapter 4 discusses the results of experiments performed to study the effects of cupric, ferric and chloride on the corrosion of Ti in sulfuric acid solutions at low temperatures, below 100 °C. Chapter 5 presents the corrosion rates of Ti obtained by mass loss data and three new Iso-corrosion diagrams for Ti in sulfuric acid solutions. Chapter 6 discusses the corrosion rates of Ti obtained by electrochemical experiments at temperatures above 100 °C, and compares the corrosion rates obtained by mass loss and electrochemical measurements. Chapter 7 discusses the effects of temperature (100-230 °C) and sulfate ions on the pitting corrosion of Ti in neutral sodium chloride solutions. Chapter 8 discusses the potentiostatic formation of anodized Ti oxide films and characterizes the as formed oxide films for hydrometallurgical applications. Chapter 9 presents a method to grow titanium oxide films with high corrosion resistance by controlled chemical oxidation with H$_2$O$_2$ solutions at 90 °C. Finally, Chapter 10 presents the conclusions as well as more tentative findings, and finishes with recommendations for future work in this area.
2 Literature review

2.1 Medium temperature chalcopyrite leaching and autoclave liner materials

2.1.1 Medium temperature chalcopyrite leaching

Corrosion is the destructive attack of a material by reaction with its environment. Thus it is necessary to be familiar with both the material and its working environment in order to study the corrosion mechanism. The main subject of this study is the corrosion behavior of Ti, used as the autoclave liner, under medium temperature chalcopyrite concentrate leaching conditions.

Historically, sulfuric acid has been a common leach solution for sulfide ores because of its cost, relative environmental friendliness, and ease of regeneration. Unfortunately, the sulfate processes have a critical disadvantage because chalcopyrite leaches slowly in sulfate media. As well, high copper extractions are not attainable in a reasonable residence time unless the leaching temperature exceeds 200 °C or chalcopyrite is activated by a pretreatment method prior to leaching (Hackl et al., 1995). The reason for this, which has been identified by many investigators, is that a passivating layer forms on the mineral surface caused by the formation of an insulating layer of elemental sulfur (Dutrizac, 1981; Hackl et al., 1995; Munoz et al., 1979). In order to accelerate the oxidation of chalcopyrite, chloride ions are added to the sulfate solutions. The role of chloride may promote the formation of a more porous sulfur product on the mineral surface, thus permitting the dissolution reaction to proceed at a reasonable rate (Lu et al., 2000). Ferric ions and dissolved oxygen are the most often used oxidants for the oxidation of chalcopyrite in sulfuric acid. It has been proven that the leaching rate of chalcopyrite increased with an increase in $\text{Fe}_2(\text{SO}_4)_3$ concentration up to 0.1 mol L$^{-1}$, but at higher $\text{Fe}_2(\text{SO}_4)_3$ concentrations the leaching rate was only marginally dependent on the concentration of
Fe$_2$(SO$_4$)$_3$ (Hirato et al., 1987a). The leaching rate is faster with the higher oxygen partial pressure; pressure oxidation may be carried out under an oxygen partial pressure of 345-1725 kPa (Jones, 1995).

There are various hydrometallurgical processes for copper recovery from 80 to 220 °C (McDonald & Muir, 2007; Nazari et al., 2011). Medium temperature chalcopyrite leaching typically takes place at temperatures of 125 to 150 °C (Dreisinger, 2006; Jones, 1999; McDonald & Muir, 2007; Sahu & Asselin, 2011). It has been found that at high temperatures, 200-220 °C, leaching kinetics are rapid, however, the entire sulfide content is converted to sulfate leading to substantially higher oxygen consumption and higher acid generation, which might require neutralization in the down-stream processing of the leach solutions. Thus the preferable temperature of medium temperature chalcopyrite leaching is about 150 °C (Jones, 1995). The lixiviants typically contain 20 to 55 g L$^{-1}$ sulfuric acid, 8 to 12 g L$^{-1}$ Cl$^-$, 10-25 g L$^{-1}$ Cu$^{2+}$ (Jones, 1995; Jones, 1997; Jones, 1999), and less than 1 g L$^{-1}$ Fe$^{3+}$ (Defreyne et al., 2006b). The amount of these additions is determined by the grade of the ores and details are shown in Table 2-1 (Defreyne et al., 2006b; Jones, 1995; Jones, 1997; Jones, 1999).

Table 2-1 Typical additives' concentration

<table>
<thead>
<tr>
<th></th>
<th>Cu$^{2+}$</th>
<th>Cl$^-$</th>
<th>H$_2$SO$_4$</th>
<th>Fe$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range (g L$^{-1}$)</td>
<td>15-25(high grade ores); 10-15(low grade ores)</td>
<td>11-14</td>
<td>30-55(high grade ores); 20-30(low grade ores)</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Typical (g L$^{-1}$)</td>
<td>15</td>
<td>12</td>
<td>30</td>
<td>1.0</td>
</tr>
</tbody>
</table>
2.1.2 Autoclave liner materials

The two most useful properties of the metal are corrosion resistance and the highest strength-to-density ratio of any metallic element. In its unalloyed condition, Ti is as strong as some steels, but 45% less dense. The excellent resistance of Ti to general corrosion in most environments is well known. This is the result of a stable protective surface film, which consists basically of TiO$_2$. This thin oxide film passivates Ti as long as the film integrity is maintained. The resistance to local corrosion of Ti is also generally very high because of its protective oxide film and the virtual absence of inclusions (Lutjering & Williams, 2007).

Based on the above advantages and its ability to resist the high temperature corrosive slurries in many leaching processes, Ti is often chosen as an autoclave liner material (Grauman & Say, 2000; Reid, 2003; Vaughan, 2003b). Autoclaves used in the pressure leaching processes are often constructed of Ti-lined steel due to cost considerations in comparison with a solid Ti bomb. During service Ti liners are subjected to severe conditions of acidity, temperature and pressure (Reid, 2003; Vaughan, 2003b).

For Ti, the commercially pure (CP) grades are represented by their ASTM designations-Grades 1, 2, 3, and 4, since these are truly unalloyed, as shown in Table 2-2 (Donachie, 2000). It has been reported that the CP grades of Ti, have provided good corrosion resistance to oxidizing, sulfuric acid environments (Lamb & Thayer, 2001). The most widely used of all these CP Ti grades is Grade 2 (Mountford Jr, 2002). In general, the presence of many oxidizing species in the bulk solution ensures a passive rest potential for the Ti liner. However, Ti is not completely immune to corrosion, especially in sulfuric acid (Cobb & Uhlig, 1952; Kelly, 1976, 1979; Vaughan &
Alfantazi, 2006). A literature study of Ti corrosion in sulfuric acid is presented in the following section.

Table 2-2 Composition summary of commercial Ti grades (Donachie, 2000).

<table>
<thead>
<tr>
<th>Designation</th>
<th>Impurity limits, (max) wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
</tr>
<tr>
<td>ASTM Grade 1</td>
<td>0.03</td>
</tr>
<tr>
<td>ASTM Grade 2</td>
<td>0.03</td>
</tr>
<tr>
<td>ASTM Grade 3</td>
<td>0.05</td>
</tr>
<tr>
<td>ASTM Grade 4</td>
<td>0.05</td>
</tr>
</tbody>
</table>

2.2 Ti corrosion

2.2.1 Equilibrium $E_h$–pH diagrams of the Ti–H$_2$O system

The usefulness of $E_h$–pH diagrams in the study of corrosion is widely recognized. Ti is one of the most important metals for use in corrosive environments, especially in chloride containing solutions. $E_h$–pH diagrams for Ti–H$_2$O system have been well developed and are particularly useful for studying the corrosion behavior of Ti (Lee, 1981; Macdonald et al., 1979c; Pourbaix, 1966; Vaughan & Alfantazi, 2006).

Macdonald et al., constructed the $E_h$–pH diagrams for Ti in high salinity brine (3.6 M NaCl) at 25 and 250 °C (Macdonald et al., 1979c). An increased domain of the Ti oxides in reducing acid is observed in the diagram of Macdonald, et al., at 250 °C (Macdonald et al., 1979c). Later, Lee
developed $E_h$–pH diagrams for the Ti–H$_2$O system from 25 to 300 °C (Lee, 1981). As shown in Figure 2–1, $E_h$–pH diagrams show that Ti oxides can be dissolved in reducing acids to form Ti$^{2+}$ or Ti$^{3+}$; the standard electrode potential for the Ti/Ti$^{2+}$ couple is −1.80 V at 25 °C and this potential becomes more negative with increasing temperature to a value of −1.90 V at 150 °C, which indicates that Ti is a very reactive material. Also, the stability of Ti and its oxides in acidic solutions increases with increasing temperature.

Thermodynamic $E_h$–pH diagrams for the Ti–H$_2$O, Ti–SO$_4$–H$_2$O, and Ti–Cl–H$_2$O systems at 25 °C were derived (Vaughan & Alfantazi, 2006). The ion activities used in their calculations were 0.1 for both SO$_4^{2−}$ and Cl$^−$. Sulfate ions and chloride ions complex with Ti(IV) to form TiO(SO$_4$)$_2^{2−}$ and TiOCl$_4^{2−}$, respectively. This extends the range of stability of Ti ions to lower acid concentrations (pH < ~3.5 and pH < ~1.5, respectively) (Vaughan & Alfantazi, 2006).
Figure 2-1 $E_h$–pH diagrams for the Ti–H$_2$O system at (a) 25 °C and (b) 150 °C (Lee, 1981).
2.2.2 Ti corrosion in sulfuric acid

As shown in the above $E_h$-$pH$ diagrams, Ti is thermodynamically reactive, but is nevertheless very corrosion resistant because of a highly resistant passive film. It corrodes only in solutions at low pH under reducing conditions. Many authors have previously published in the area of Ti corrosion in sulfuric acid solutions below 100 °C. In the early 1950s, the effect of aeration on the corrosion of Ti in sulfuric acid was studied. Ma and Peres observed that increasing the oxygen content decreased the corrosion rate of Ti (Ma & Peres, 1951). Golden et al. reported that the corrosion rates of Ti were lower in $N_2$-saturated solutions compared with these in air-saturated environments (Golden et al., 1952). Schlain et al. also noted that the presence of air inhibits the initiation of corrosion, but increases the corrosion rate once corrosion starts (Schlain et al., 1955).

The anodic behavior of Ti in sulfuric acid was then reported by several investigators, and they all demonstrated that Ti exhibits an active-to-passive transition (Kelly, 1979; Levy, 1967; Stern & Wissenberg, 1959; Vaughan et al., 2010). Stern and Wissenberg reported that increasing acid concentration remarkably increases the critical current for passivity and the critical potential for passivity in boiling $H_2SO_4$ solutions (Stern & Wissenberg, 1959). Levy later observed that Ti−6Al−6V−2Sn exhibits an active−to−passive transition when the acid concentration is higher than 5 wt.% at 20 °C and the scan rate was 50 mV min$^{-1}$ (Levy, 1967). Similar behavior was also observed by Vaughan et al., i.e. that Ti Grade 2 (Ti−2) exhibits an active−to−passive transition when the acid concentration is higher than 30 g L$^{-1}$ at 21 °C with a scan rate of 0.5 mV s$^{-1}$, as shown in Figure 2−2 (Vaughan et al., 2010). Kelly thoroughly studied the effects of potential scan rate, temperature and pH on the anodic behavior of Ti in acid media (Kelly, 1979). Kelly noted that (1) with increasing scan rate, the active-to-passive transition became less distinct, the
maximum anodic current density \((i_m)\) increased and the corresponding potential \((E_m)\) became increasingly positive; (2) \(E_m\) was independent of temperature but \(i_m\) increased with increasing temperature; (3) \(i_m\) increased and \(E_m\) became increasingly positive as the pH decreased (Kelly, 1979). All the above studies concluded that Ti exhibits an active-to-passive transition in sulfuric acid solutions, which can be used advantageously to control the corrosion rate of Ti in sulfuric acids by ensuring potentials, remain in the passive region.

Figure 2-2 Anodic polarization of Ti−2 from −385 mV at 0.5 mV s\(^{-1}\), effect of acid concentration (Vaughan et al., 2010).
Chloride and other halide ions tend to increase the dissolution rate of many metals and alloys. Greene and Judd using potentiostatic anodic polarization found a relationship between the anodic dissolution kinetics of a metal in chloride media and its resistance to pitting corrosion (Greene & Judd, 1965). The ratio between dissolution current density in the presence and absence of chloride ion (the dissolution ratio) was inversely related to pitting resistance. Ti was unaffected by the presence of chloride (dissolution ratio = 1.0), which indicated its complete immunity to pitting or no susceptibility to chloride ions (Greene & Judd, 1965). Later, Levy reported that chloride ions reduce the critical current for passivity and that the critical current density was further reduced with increasing chloride ion concentration (Levy, 1967). These results are consistent with Thomas and Nobe's study on the effects of chloride ions on the anodic behavior of Ti in 1 N H₂SO₄ with different concentrations of NaCl at 24 ± 1 °C (Thomas & Nobe, 1969). In their study, it was also found that the passive current density decreased with an increase in chloride ion concentration (Thomas & Nobe, 1969). Thomas and Nobe further reported a comparison of the electrochemical parameters of Ti in HCl and H₂SO₄ at the same pH, which indicated the anodic dissolution of Ti in HCl is less than in H₂SO₄ (Thomas & Nobe, 1973). It could be concluded that chloride ions facilitated the anodic passivity of Ti in sulfuric acid solutions. However, the facilitating mechanism of chloride is not well understood. Also, this peculiarity makes Ti a suitable choice for the autoclave liner used in mixed chloride–sulfate pressure leaching.

Generally for Ti, oxidizing species such as cupric and ferric ions are known to be corrosion inhibitors (Cobb & Uhlig, 1952). An inhibitor as it pertains to this research can be defined as "a substance which can be added in microgram quantities to an environment to retard corrosion" (Holzworth & Louthan, 1968). Cobb and Uhlig reported that ferric and cupric ions are effective
inhibitors for the corrosion of pure Ti in boiling 10 wt.% sulfuric acid and ferric is more effective than cupric at the same concentration (Cobb & Uhlig, 1952). Levy also noted ferric and cupric ions inhibit the corrosion of Ti−6Al−6V−2Sn in 20 wt.% sulfuric acid at 65 °C (Levy, 1967). Been found that the addition of 1000 ppm of cupric reduces the corrosion rate of Grade 2 Ti by a factor of 1250 in 20 wt.% sulfuric acid at 100 °C (Been, 1998). Vaughan reported that the addition of a sufficient amount of ferric or cupric resulted in a large increase in the open circuit potential, 397 mV vs. NHE with 10 g L\(^{-1}\) Cu\(^{2+}\) at 80 °C (Vaughan, 2003b). Thus these metal ions inhibited the corrosion by polarizing Ti to a potential region where the passive TiO\(_2\) was thermodynamically stable (Vaughan, 2003b). Ti is known to spontaneously activate in deoxygenated sulfate solutions and would not be suitable for sulfide pressure leaching if it were not for the inhibitors’ effect. The nature of sulfide pressure leaching is such that oxidative conditions are usually maintained, however, upset conditions and plant shutdowns can result in inadvertent contact with reducing or non-oxidative solutions.

Although there have been numerous investigations of the electrochemical behavior of Ti in sulfate acid media, high temperature corrosion studies of Ti have been extremely limited in number, and few investigators have attempt to study the effects of cupric and ferric ions on anodic behavior of Ti at temperatures above 100 °C. Increasing application of Ti in hydrometallurgy places extraordinary demands on research of high temperature Ti corrosion.

### 2.2.3 Iso-corrosion diagrams of Ti

A common form of representing the uniform corrosion rate of materials is in the form of Iso-corrosion diagrams. An Iso-corrosion diagram is a graph showing corrosion rate as a function
of varying conditions such as temperature, solution concentration, or other environment compositions (Schweitzer, 1998).

Figure 2-3 Effect of ferric ions on the corrosion of Grade 2 Ti, 0.127 mm yr\(^{-1}\) Iso-corrosion line (Schutz & Covington, 1984).

Schutz and Covington have reported Iso-corrosion diagrams for Ti in pure naturally–aerated HCl and H\(_2\)SO\(_4\) media (Schutz & Covington, 1984). In their work, a corrosion rate of (> 76.2 mm yr\(^{-1}\)) was observed on Ti in boiling 10 wt.% H\(_2\)SO\(_4\), while the corrosion rate of Ti was reduced to 0.069 mm yr\(^{-1}\) in boiling 10 wt.% H\(_2\)SO\(_4\) in the presence of 500 ppm Fe\(^{3+}\). They also
presented the effect of different Fe$^{3+}$ additions to the HCl media on the corrosion resistance of Ti, as shown in Figure 2-3. Ti−2 showed corrosion resistance to 5 wt.% boiling HCl in the presence of 75 ppm Fe$^{3+}$, whereas, Ti−2 was severely attacked by 0.5 wt.% boiling HCl in the absence of Fe$^{3+}$ (Schutz & Covington, 1984). Mountford recently published 5 mpy Iso-corrosion lines for Ti Grade 2, 7 and 12 in sulfuric acid from room temperature to the boiling point (Grade 7: unalloyed titanium plus 0.12% to 0.25% palladium; Grade 12: Ti alloy with 0.3% molybdenum and 0.8% nickel) (Mountford Jr, 2002), as shown in Figure 2-4. It can be concluded that Grade 2 Ti will be attacked by severe corrosion in less than 5 wt.% boiling HCl or H$_2$SO$_4$.

Figure 2-4 Iso-corrosion diagram of Ti alloys in naturally aerated H$_2$SO$_4$ solutions (Mountford, 2002).
Iso-corrosion diagrams illustrate the resistance of metallic materials to general corrosion. Unfortunately, Iso-corrosion diagrams of Ti in sulfuric acid are limited in number, and to the author's knowledge, there is no Iso-corrosion diagram of Ti in sulfuric acid at temperatures above 100 °C. According to the standards for relative corrosion resistance in mm yr\(^{-1}\) from Jones, corrosion rates below 0.1 and 0.5 mm yr\(^{-1}\) are defined as excellent and good, respectively; corrosion rates above 1 mm yr\(^{-1}\) are defined as poor (Jones, 1996). Iso-corrosion diagrams with 0.1, 0.5 and 1.0 mm yr\(^{-1}\) Iso-corrosion lines will be very useful as guidance for material selection with respect to general corrosion. It is also necessary to improve the Iso-corrosion diagrams of Ti due to its use in a diverse and growing number of applications in sulfate related environments.

**2.2.4 Pitting corrosion of Ti**

The resistance to local corrosion of Ti is also generally very high because Ti normally does not contain inclusions, such as oxides, carbides, and sulfides, which leads to a greater resistance to pitting corrosion. (Lutjering & Williams, 2007; Virtanen & Curty, 2004) As well, many researchers agreed that chloride ions facilitated the anodic passivity of Ti in sulfuric acid solutions. Therefore, Ti is very suitable for hydrometallurgical applications. Although Ti is resistant to these aggressive environments, it is not totally immune and can be susceptible to pitting corrosion. (Gorynin, 1999; Shoesmith *et al*., 2000; Vaughan & Alfantazi, 2006) It has been reported that the pitting corrosion of Ti in chloride (Cl\(^{-}\)) containing solutions are strongly temperature-dependent (Beck, 1973a). Since Ti is commonly used in very aggressive environments containing high Cl\(^{-}\) concentration at high temperature, the pitting corrosion of Ti is a major concern for industry and engineers (Cotton, 1972; Shoesmith *et al*., 2000).
Halide solutions are noted for their ability to induce pitting on metals. For many other metals and alloys, a large amount of research have been carried out on the pitting corrosion in Cl\(^-\) containing solutions (Deng et al., 2008; Moayed & Newman, 2006; Pistorius & Burstein, 1992). In the case of Ti, there are few publications focusing on the pitting corrosion of Ti in Cl\(^-\) containing solutions (Burstein & Souto, 1995; Dugdale & Cotton, 1964). The effects of halide type and temperature on the pitting corrosion of Ti have been studied, as shown in Figure 2-5.
Beck, 1973a, 1973b; Dugdale & Cotton, 1964; Virtanen & Curty, 2004). Dugdale and Cotton found that the breakdown potential \( E_b \) of Ti is around 90 V vs. SHE in \( \text{F}^- \), 14 V vs. SHE in \( \text{Cl}^- \), 3.5 V vs. SHE in \( \text{Br}^- \), and 4.2 V vs. SHE in \( \Gamma^- \) containing solutions at room temperature (Dugdale & Cotton, 1964). Many researchers have agreed that \( \text{Br}^- \) anions are the most aggressive halides in triggering pitting corrosion of Ti (Basame & White, 2000; Casillas et al., 1994; Dugdale & Cotton, 1964). Beck reported that the of Ti in halide solutions decreased dramatically as the temperature increased (Beck, 1973a). Burstein and Souto observed that passive Ti showed evidence of microscopic instability at potentials well below the pitting potential in acidic \( \text{Cl}^- \) containing solutions (Burstein & Souto, 1995). Later, Neville and Xu found that pitting is the main type of localized corrosion for commercially pure (CP) Ti and Ti alloys in hydrochloric acid (HCl) solutions; they also defined a critical pitting temperature (CPT) for CP Ti and Ti alloys by potentiostatic polarization measurements in HCl solutions up to 100 °C (Neville & Xu, 2001). Most recently, Jiang et al. proved that \( \text{Cl}^- \) concentration had an effect on the metastable pitting intensity; their X-ray photoelectron spectroscopy (XPS) results also revealed that \( \text{Cl}^- \) was present in the outer oxide layer, but scarce in the inner oxide layer (Jiang et al., 2011b). Nevertheless, there is less information as it pertains to the pitting corrosion of Ti in \( \text{Cl}^- \) containing solutions at temperatures above 100 °C (Beck, 1973a; McKay & Mitton, 1985).

Based on the above discussion, temperature is critical parameter in the pitting corrosion of Ti. Regarding temperature, the concept of CPT has been introduced and widely used as a criterion for the pitting susceptibility of stainless-steel alloys (Brigham & Tozer, 1973; Deng et al., 2008; Frankel, 1998). In addition, plots of breakdown potential \( E_b \) vs. temperature are often used to define the CPT for stainless-steel alloys (Moayed & Newman, 2006; Ovarfort, 1989). It has been well accepted for stainless steels that the plot of \( E_b \) vs. temperature typically presents as an
“backwards S-shaped” curve and the position of the steep decrease in $E_b$ is referred to as the CPT for a given alloy, as shown in Figure 2-6 (Moayed & Newman, 2006; Ovarfort, 1989). It has been proven by previous researchers, that Ti and its alloys do not exhibit this “backwards S-shaped” curve in halide solutions (Beck, 1973a; Posey & Bohlmann, 1967). Therefore, potentiodynamic polarization is likely not the best technique for determining the CPT of Ti. The CPT is related to stable pitting. Each instance of stable pitting is the result of nucleation and stable growth of metastable pits on the sample surface (Burstein et al., 2005; Pistorius & Burstein, 1992). Metastable pitting can, and does, form at potentials between $E_b$ and $E_{rp}$ as the precursor for stable pitting (Burstein et al., 2010; Burstein et al., 2005; Frankel et al., 1987; Kelly et al., 2002). As well, metastable pitting can be observed as the transient fluctuations of current density before the onset of stable pitting under potentiostatic control at potentials between breakdown potential $E_b$ and repassivation potential $E_{rp}$ (Burstein et al., 2005; Kelly et al., 2002). It has been pointed out by Burstein et al. that metastable pitting has not been sufficiently examined in terms of its temperature dependence (Burstein et al., 2010).
Figure 2-6 Plot of breakdown potential vs. test temperature for 904LSS in potentiodynamic polarization experiments (Moayed & Newman, 2006).

The inhibition effects of oxygen-containing anions, such as SO$_4^{2-}$, chromate (CrO$_4^{2-}$), and hydrogen phosphate (HPO$_4^{2-}$), on the pitting corrosion of certain metals in halide solutions have been investigated by several workers (Anderson & Hocking, 1958; Dugdale & Cotton, 1964; Lee & Isaacs, 2008; O'Connor et al., 1956; Pistorius & Burstein, 1992). These inhibition effects have also been explained in terms of various theories. Connor et al. and Anderson and Hocking suggested that CrO$_4^{2-}$ and HPO$_4^{2-}$ ions competed with Cl$^-$ ions for adsorption sites on aluminum oxide (Anderson & Hocking, 1958; O'Connor et al., 1956). Pistorius and Burstein reported that
the inhibition effect of SO$_4^{2-}$ on the pitting of stainless steels was due to its ability to lower the solubility of the metal cation in the pit anolyte (Pistorius & Burstein, 1992). In the case of Ti, Dugdale and Cotton proposed that SO$_4^{2-}$ ions should be adsorbed in preference to halide ions, which would lead to lower halide concentrations on the surface oxide and in turn inhibit the pitting corrosion of Ti in mixed halide/SO$_4^{2-}$ solutions; however, they also hypothesized that the inhibiting effect was enhanced by the formation of two extremely stable compounds, \textit{i.e.}, TiOSO$_4$.H$_2$O and Ti$_2$O(SO$_4$)$_3$.5H$_2$O (Dugdale & Cotton, 1964). Dugdale and Cotton found that no pitting was observed on anodically polarized Ti in mixed halide/SO$_4^{2-}$ solutions above a critical concentration of SO$_4^{2-}$, and the Ti anode behaved as if it were in contact with a pure SO$_4^{2-}$ solution. However, no similar work has been reported on the pitting corrosion of Ti in SO$_4^{2-}$/ Cl$^-$ solutions at high temperatures, and the inhibition effect of SO$_4^{2-}$ ions on the pitting corrosion is not well understood.

\textbf{2.2.5 Characterization of a solution-filled external pressure balanced reference electrode}

Any reliable electrochemical measurement is dependent on the utilization of a reference electrode having a stable, reproducible, and durable potential which is well defined in terms of thermodynamics. The room temperature reference electrodes possess these features while many factors should be considered to have such a reference electrode suitable for high-temperature, high-pressure experiments. Recent interest in the electrochemistry and corrosion behavior of metals and alloys in high temperature aqueous systems has stimulated research into the construction and characterization of external reference electrodes for use in this hostile environment. External reference electrodes are housed in separate compartments that are maintained at ambient temperature and system pressure via solution bridges. Thus external electrodes are not exposed to solution contamination at high temperatures, and can provide good
stability and durability. However, the temperature gradient between the high temperature system and the reference electrode at ambient temperature gives rise to a thermal liquid junction potential. Therefore, many studies have focused on experimental and theoretical determination of the magnitude of thermal liquid junction potential. The measured potential using an external pressure balanced reference electrode (EPBRE) consists of a thermodynamics component as well as components resulting from irreversibility of the cell, and should be converted to the SHE scale at 25 °C. The experimental and theoretical aspects of $E_{\text{measured}}$ using an EPBRE have previously been studied in detail by Macdonald et al. (Engelhardt et al., 1997; Lvov & Macdonald, 1996; Macdonald et al., 1979a, 1979b), and Nickchi and Alfantazi (Nickchi & Alfantazi, 2012). The EPBRE used in this work is the same design as that of Nickchi and Alfantazi (Nickchi & Alfantazi, 2012), as shown in Figure 2-7.
The method used to convert the $E_{\text{measured}}$ to the SHE scale at 25 °C is described in this section. Generally, the approach developed by Macdonald for Cl$^-$ solutions and later used by Nickchi for SO$_4^{2-}$ solutions was used here (Macdonald et al., 1979a, 1979b; Nickchi & Alfantazi, 2012). The SHE potential is zero at all temperatures by definition; however, between two SHEs at different temperatures there exists a definite and measurable potential difference (Bosch et al., 2003). According to Bosch et al.’s work, $\Delta E_{\text{SHE}}$ is the potential difference of the SHE thermal cell at T and 25 °C, with the values being 57.2 mV at 100 °C, 71.7 mV at 125 °C, 83.9 mV at 150 °C, 93.7 mV at 175 °C, and 101.2 mV at 200 °C (Bosch et al., 2003). Thus, $E_{\text{measured}}$ can be converted to the SHE scale at 25 °C by Eq. (2-1) in the present work. In Eq. (2-1), $E_{\text{measured}}$ is the
potential of the WE measured against the RE, \( E_{\text{vs.SHE}} \) is the potential of the WE reported against the SHE at 25 °C, \( E_{\text{Ag/AgCl}} \) is the potential of the RE measured against the SHE at 25 °C, \( E_{\text{TLJ}} \) is the magnitude of the thermal liquid junction potential, \( E_{\text{LJP}} \) is the isothermal liquid junction potential at room temperature, and \( iR \) is the Ohmic loss.

\[
E_{\text{vs.SHE}} = E_{\text{measured}} + E_{\text{Ag/AgCl}} - E_{\text{TLJ}} - E_{\text{LJP}} - iR + \Delta E_{\text{SHE}} \quad (2-1)
\]

Since the portion of the EPBRE subjected to the temperature gradient was filled with the experimental solution, \( E_{\text{TLJ}} \) and \( E_{\text{IR}} \) originated from this solution. Equations (2-2)–(2-7) were used to calculate \( E_{\text{TLJ}} \) and \( R \) (Nickchi & Alfantazi, 2012), where \( S_i^* \) is the entropy of transport (J mol\(^{-1}\) K\(^{-1}\)), \( t_i^* \) is the transport number, \( z_i \) is the charge on the ion, \( u_i \) is ion mobility (cm\(^2\) V\(^{-1}\) s\(^{-1}\)), \( C_i \) is ion concentration (mol cm\(^{-3}\)), \( \lambda_i \) is the individual ionic conductivity (cm\(^2\) Ω\(^{-1}\) equiv\(^{-1}\)), \( F \) is Faraday’s constant (coulombs mol\(^{-1}\)), \( \varepsilon \) is the dielectric constant of water (= \( \varepsilon_r \varepsilon_0 \), F m\(^{-1}\)), \( \varepsilon_0 \) is the vacuum permittivity (=8.85×10\(^{-12}\) F m\(^{-1}\)), \( \varepsilon_r \) is the relative permittivity of water and the constants are equal to: \( A \), 5321 K; \( B \), 233.76; \( C \), −0.9297 K\(^{-1}\); \( D \), 0.001417 K\(^{-2}\); \( E \), 0.0000008291 K\(^{-3}\) (Akerlof & Oshry, 1950).

\[
E_{\text{TLJ}} = \frac{-1}{F} \int_{T_1}^{T_2} \left( \sum \frac{t_i^* S_i^*}{z_i} \right) dT \quad (2-2)
\]

\[
R = \int_0^L \frac{dt}{A \sum |z_i| \lambda_i C_i} \quad (2-3)
\]

\[
\lambda_i = F u_i \quad (2-4)
\]

\[
t_i^* = \frac{|z_i| \lambda_i C_i}{\sum |z_j| \lambda_j C_j} \quad (2-5)
\]

25
\[
\frac{S_i^*(T)}{S_i^*(T_0)} = \frac{\varepsilon(T_0)^2}{\varepsilon(T)^2} \left( \frac{\partial \varepsilon}{\partial T} \right)_{p} |T| \left( \frac{\partial \varepsilon}{\partial T} \right)_{p} |T_0|
\]

(2-6)

\[
e_r = \frac{A}{T} + B + CT + DT^2 + E
\]

(2-7)

There were four unknowns in the above equations, \(T, u_i, C_i\) and \(S_i^*\). Since the EPBRE used in this work was the same design as that of Nickchi and Alfantazi (Nickchi & Alfantazi, 2012), their temperature profiles were also used in this study, as shown in Figure 2-8. Both concentration and temperature can affect the individual ionic \(\lambda_i\) (= \(F u_i\)). For ions involved in the calculation of \(E_{TLJ}\) and \(R\), the concentration dependence of individual ionic \(\lambda_i\) at higher temperatures was, to the authors’ knowledge, not available. Quist and Marshal reported the temperature–dependent \(\lambda_i\) data for some of the ions involved in this work (Table 2–3) (Quist & Marshall, 1965).
Figure 2-8 The longitudinal temperature profile along the tubing axis at various initial temperatures (Nickchi & Alfantazi, 2012).

Table 2-3 Ionic conductance (cm² Ω⁻¹ equiv⁻¹) for several ions at temperatures up to 200 °C.

<table>
<thead>
<tr>
<th></th>
<th>λ(H⁺)</th>
<th>λ(HSO₄⁻)</th>
<th>λ(SO₄²⁻)</th>
<th>λ(Na⁺)</th>
<th>λ(Cl⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C</td>
<td>349</td>
<td>51</td>
<td>80</td>
<td>50</td>
<td>76</td>
</tr>
<tr>
<td>100 °C</td>
<td>634</td>
<td>140</td>
<td>246</td>
<td>151</td>
<td>211</td>
</tr>
<tr>
<td>200 °C</td>
<td>824</td>
<td>290</td>
<td>525</td>
<td>304</td>
<td>391</td>
</tr>
</tbody>
</table>
The values of \( S_i^* \) at 25 °C can be extracted from published data, 8.1 J mol\(^{-1}\) K\(^{-1}\) for Na\(^+\), 41.1 J mol\(^{-1}\) K\(^{-1}\) for H\(^+\), −2.5 J mol\(^{-1}\) K\(^{-1}\) for SO\(_4^{2-}\), and 136.3 J mol\(^{-1}\) K\(^{-1}\) for Cu\(^{2+}\) (deBethune et al., 1959; Lvov & Macdonald, 1996; Nickchi & Alfantazi, 2012). Then, using the relationship \( S_{HSO_4^-}^* = S_{H^+}^* + S_{SO_4^{2-}}^* \) and \( S_{CuCl^+}^* = S_{Cu^{2+}}^* + S_{Cl^-}^* \) (Engelhardt et al., 1997; Nickchi & Alfantazi, 2012), the values of \( S_i^* \) for HSO\(_4^-\) and CuCl\(^+\) were calculated to be 38.6 and 141.5 J mol\(^{-1}\) K\(^{-1}\), respectively. After the four unknowns were determined, the \( E_{TLJ} \) and \( R \) were calculated for different initial temperatures. The \( E_{LJP} \) is caused by a chemical or concentration difference between the experimental solution (\( \alpha \) phase) and reference electrode solution (1 mol L\(^{-1}\) KCl, \( \beta \) phase). The Henderson equation, \textit{i.e.} Eq. (2-8), was applied to calculate the \( E_{LJP} \) (Bard & Faulkner, 2001). The \( u_i \) values for K\(^+\) and Cl\(^-\) were extracted from Bard and Faulkner's work (Bard & Faulkner, 2001).

\[
E_{LJP} = \frac{\sum |z_i|u_i[C_i(\beta) - C_i(\alpha)]}{\sum |z_i|u_i[C_i(\beta)]} \frac{RT}{F} \ln \frac{\sum |z_i|u_iC_i(\alpha)}{\sum |z_i|u_iC_i(\beta)} \tag{2-8}
\]

### 2.3 Improving the corrosion resistance of Ti

The excellent corrosion resistance of Ti is due to the chemically unreactive and mechanically strong oxide film formed on its surface (Donachie, 2000). Titanium oxide forms instantly when a freshly polished titanium surface is exposed to air (Variola et al., 2008). The native oxide is normally thin (~10 nm), amorphous, and stoichiometrically defective (Zhu et al., 2004). As a result, the lixiviants used during leaching in an autoclave are in contact with the surface oxide film instead of the metal itself. The properties of the film, such as the film structure, composition,
and thickness, determine the corrosion behavior of the metal (Variola et al., 2008). Thus, it is of interest to know the chemical and physical properties of the oxide layers on titanium and to prepare titanium oxide layers with a known structure and thickness.

The protective titanium oxide can be enhanced by three methods: thermal oxidation, anodic oxidation and chemical oxidation (Birch & Burleigh, 2000; Gaul, 1993; Kumar et al., 2010a; Kumar et al., 2009, 2010b; Schutz & Covington, 1981). Thermal oxidation is simple, but its reproducibility is poor and should be preceded by acid pickling to remove embedded surface contaminants, such as iron (McMaster, 2001). Also, the temperature of oxidation should be at least 500 °C to build a film with good corrosion resistance, usually blue in color (Cotton, 1970; Gaul, 1993; Kumar et al., 2010b). Given these requirements, it is very difficult to repair the Ti surface film using thermal oxidation, especially after parts have been installed and in service.

Anodic oxidation is more consistent and also can be effective as a single step if it is applied for a sufficiently long time to dissolve surface contamination (Cotton, 1970). Currently, it is industry practice to oxidize the Ti liner using sulfuric acid, ammonium phosphate or some other suitable solution to favor the formation of an artificially thick anodic oxide film at constant voltages of 25-80 V (Cotton, 1970; McMaster, 2001). A large number of papers and patents have dealt with Ti anodizing (Beck, 1960; Bernard, 1963; Chen et al., 2005; Cigada et al., 1992; Cotton, 1970; Delplancke et al., 1982; Delplancke et al., 1994; Delplancke & Winand, 1988a, 1988b; Gaul, 1993; Karambakhsh et al., 2011; Marino & Mascaro, 2011; Marino et al., 2004; Schutz & Covington, 1981; Sharma, 1992; Shibata & Zhu, 1995; Sibert, 1963; Sul et al., 2001; Yan et al., 2002). It has been found that the anodic oxide films (AOFs) formed on Ti depend on the substrate surface character, electrolyte type, applied potential and temperature (Critchlow & Brewis, 1995; Marino & Mascaro, 2011; Marino et al., 2004; Sibert, 1963; Sul et al., 2001).
Sibert pointed out that it is difficult to distinguish between purity and surface preparation effects, therefore an effort should be made to determine surface effects by anodizing the same type of Ti substrate with varying surface preparations (Sibert, 1963). A large variety of acidic, basic and neutral electrolytes have been used to produce Ti based anodic films, and sulfuric acid and phosphoric acid were used most frequently and produced by far the best AOFs (Critchlow & Brewis, 1995; Marino & Mascaro, 2011; Marino et al., 2004; Sibert, 1963; Sul et al., 2001). Sul et al. have found that an increase of electrolyte concentration and electrolyte temperature decreased the anodic forming rate and the current efficiency (Sul et al., 2001). As a general trend, anodic film growth on Ti was carried out at room temperature. It has been found that AOFs can be formed with the incorporation of species from the electrolyte, affecting the structure and properties of the final oxide (Habazaki et al., 2002; Leach & Pearson, 1988; Marino et al., 2004; Oliveira et al., 2000). AOFs of Ti show a wide range of structural and electrochemical properties, depending on the electrolyte and the applied potential (Diamanti & Pedeferri, 2007). Diamanti et al. suggested that the optimum concentration of sulfuric acid solutions for Ti anodization was 0.5 M which promoted the oxidation conversion to anatase instead of an amorphous oxide (Diamanti & Pedeferri, 2007). Based on the above discussion, AOFs will be produced on Ti in 0.5 M sulfuric acid solutions at room temperature in this work.

Electrochemical characterizations of AOFs formed on Ti have previously been reported (Cotton, 1970; Diamanti & Pedeferri, 2007; Fadl-allah & Mohsen, 2010; Karambakhsh et al., 2011; Ma & Peres, 1951; Sharma, 1992; Souza et al., 2007). However, there is a lack of publicly available information as to the corrosion of anodized Ti in strong, chloride containing, reducing acid such as that of interest here i.e. de-aerated 30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\) solutions. Even though a suitable corrosion resistance to this copper leaching environment can be accomplished by
anodizing, it is still very difficult to apply anodizing on a large autoclave with complex internals (McMaster, 2001). Furthermore, according to Cotton (Cotton, 1970) and McMaster (McMaster, 2001), constant voltage power sets delivering 25 to 80 volts are usually utilized and anodizing times must be on the order of 10 to 72 hours for very large vessels. Anodizing may be applied to autoclaves after installation, but it is a time consuming and laborious operation with potential safety problems.

On the other hand, controlled chemical oxidation is an attractive technique for growing oxide layers on titanium substrates. Hydrogen peroxide (H$_2$O$_2$) is an oxidant that brings no external contamination. Recently, a few publications have reported the formation of porous titanium oxide layers on Ti surfaces in H$_2$O$_2$ solutions. Nanci et al. first treated titanium with a H$_2$O$_2$ / H$_2$SO$_4$ mixture at room temperature to eliminate surface contaminants and to produce a consistent and reproducible titanium oxide surface layer (Nanci et al., 1998; Variola et al., 2008; Yi et al., 2006). Wang et al. reported the formation of an amorphous titanium oxide layer after the titanium specimen was treated with an 8.8 M H$_2$O$_2$ / 0.1 M HCl solution at 80 °C for various times up to 1 hour (Wang et al., 2002b). They also noticed that oxide thickness increased almost linearly with the period of the treatment, and a subsequent heat treatment above 300 °C resulted in a gradual transformation of the oxide to the anatase crystal structure (Wang et al., 2002b). Wu et al. later used 30 wt. % H$_2$O$_2$ solutions to oxidize metallic titanium at 80 °C for 72 hours to prepare crystalline TiO$_2$ nanorods (Wu et al., 2002a, 2002b; Wu, 2004). They found that the crystal phases could be controlled by adding F$^-$ (5mM NaF), Cl$^-$ (5mM NaCl) and SO$_4^{2-}$ (5mM Na$_2$SO$_4$) to the solutions. For example, the addition of F$^-$ and SO$_4^{2-}$ promoted the formation of pure anatase; while the addition of Cl$^-$ favored the formation of rutile (Wu, 2004). Most recently, Wu et al. oxidized titanium with a 5 wt. % (1.5 M) H$_2$O$_2$ solution at 80 °C and the as-prepared
films were hydrothermally treated in deionized (DI) water at 150 °C; it was reported that the hydrothermal step facilitated the crystallization of the amorphous titanium dioxide (Wu et al., 2010). The above methods were mainly aimed at modifying Ti surfaces for the improvement of bioactivity or photocatalytic activity. To the author’s knowledge, there is no chemical oxidation method that has been purposely developed for improving the corrosion resistance of titanium. Further, there is no public research on the electrochemical characterization of titanium oxide films prepared by controlled chemical oxidation methods. It may be possible, and very useful, to control the properties of Ti surfaces, including the thickness of the oxide layers, by varying the conditions of the chemical treatment. This may lead to the creation of both chemically and mechanically strong surfaces designed to resist the aggressive pressure leaching environments.

Meanwhile the color of oxide films has been explained by multiple−beam interference theory and it is well established that the thickness of the oxide formed dictates the film color (Chen et al., 2005; Cigada et al., 1992; Gaul, 1993; Karambakhsh et al., 2011; Sharma, 1992; Yan et al., 2002). In the case of thermal oxidation and anodic oxidation, the film thickness depends on the temperature and anodizing voltage, respectively. Thus, the correlation of color and thickness to chemical oxidation conditions, anodizing voltage and the heating temperature can be used to compare titanium oxide films obtained by different oxidation methods. The correlation of color and thickness to anodizing voltage from published results (Chen et al., 2005; Gaul, 1993; Karambakhsh et al., 2011; Sharma, 1992) is listed in Table 2–4.
Table 2-4 Correlation of color and thickness to Ti anodization voltage.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Colors</th>
<th>Thickness (µm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>golden brown (Sharma, 1992)</td>
<td>0.049 (Sharma, 1992)</td>
<td>385</td>
</tr>
<tr>
<td>20</td>
<td>violet blue (Gaul, 1993)</td>
<td>0.046 (Gaul, 1993)</td>
<td>412</td>
</tr>
<tr>
<td></td>
<td>dark blue (Sharma, 1992)</td>
<td>0.058 (Sharma, 1992)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>dark blue (Chen et al., 2005)</td>
<td>0.063 (Kambakhsh et al., 2011)</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>pale aqua (Gaul, 1993)</td>
<td>0.066 (Gaul, 1993)</td>
<td>468</td>
</tr>
<tr>
<td></td>
<td>light olive (Sharma, 1992)</td>
<td>0.103 (Sharma, 1992)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>light olive (Chen et al., 2005)</td>
<td>0.09 (Kambakhsh et al., 2011)</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>purple (Gaul, 1993)</td>
<td>0.11 (Gaul, 1993)</td>
<td>523</td>
</tr>
<tr>
<td></td>
<td>pink (Sharma, 1992)</td>
<td>0.141 (Sharma, 1992)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pink (Chen et al., 2005)</td>
<td>0.141 (Kambakhsh et al., 2011)</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>bronze (Gaul, 1993)</td>
<td>0.15 (Gaul, 1993)</td>
<td>579</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.19 (Kambakhsh et al., 2011)</td>
<td></td>
</tr>
</tbody>
</table>
3 Objectives

In view of the preceding discussion, the following objectives were set-out.

A. To determine the influence of Cu$^{2+}$, Fe$^{3+}$ and Cl$^{-}$ ions on the corrosion of Ti in sulfuric acid solutions below 100 °C.

B. To evaluate the uniform corrosion rates of Ti under simulated pressure leaching conditions by both mass loss and electrochemical measurements.

C. To construct iso-corrosion diagrams for Ti in sulfuric acid solutions from room temperature to 175 °C to guide materials selection.

D. To study the effects of both temperature (100-230 °C) and SO$_4^{2-}$ (0-0.5 mol L$^{-1}$) on the pitting corrosion of Ti in Cl$^{-}$ containing solutions.

E. To investigate the corrosion behavior of anodized oxide film (AOFs) in sulfuric acid solutions in the presence of 12 g L$^{-1}$ Cl$^{-}$, 15 g L$^{-1}$ Cu$^{2+}$ and 1 g L$^{-1}$ Fe$^{3+}$, which are their typical tenors in copper sulfide leaching solutions. AOFs are produced on commercially pure titanium in 0.5 M sulfuric acid solutions at room temperature and in the potential range of 20 to 80 V.

F. To develop a novel and improved method to fabricate oxide films on Ti substrates with high corrosion resistance by controlled chemical oxidation with H$_2$O$_2$ solutions, and to study the effects of Cl$^{-}$ and SO$_4^{2-}$ ions on the growth of chemically oxidized films (COFs).

G. To characterize the as grown AOFs and COFs in leaching solutions to generate a best practices guide for the hydrometallurgical industry.
4 Influence of cupric, ferric and chloride ions on the corrosion of Ti in H$_2$SO$_4$ solutions below 100 °C

The aim of this work is to evaluate the corrosion behavior of Ti in synthetic copper sulfide leaching solutions containing 30 g L$^{-1}$ H$_2$SO$_4$ (=S) as well as 12 g L$^{-1}$ Cl$^-$ (=Cl), 15 g L$^{-1}$ Cu$^{2+}$ (=Cu) and 1 g L$^{-1}$ Fe$^{3+}$ (=Fe). As a first step, it is necessary to have a fundamental understanding of the effects of Cu$^{2+}$, Fe$^{3+}$ and Cl$^-$ ions on the corrosion of Ti in H$_2$SO$_4$ solutions. Therefore, we started with experiments at low temperatures, particularly below 100 °C. This, considering the ease of setup and experimentation, provides a baseline and a fundamental understanding of Ti corrosion in leaching solutions. The present chapter focuses on temperatures below 100 °C.

4.1 Experimental

The material investigated was pure Ti (Goodfellow Corporation, USA) and its chemical composition is listed in Table 4-1. The working electrode was 3 mm thick with a circular surface area of 0.71 cm$^2$. DI water, H$_2$SO$_4$ (95.0-98.0%, Fisher Scientific), NaCl (Cryst./Certified ACS), cupric sulfate pentahydrate (CuSO$_4$·5H$_2$O, Cryst./Certified ACS), and iron(III) sulfate pentahydrate (Fe$_2$(SO$_4$)$_3$·5H$_2$O, 97%, Acros) were used to prepare the leaching solution. Solutions (listed in Table 4-2) used in this section will be referred-to by their associated symbols throughout the remainder of Chapter 4.
Table 4-1 Chemical compositions of Ti (ppm, by weight).

|   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|
| Al | Sb | As | C  | Cr | Cu | Fe | Ni | Rb | Si | Zr | Ti |
| 31 | 1.7 | 0.86 | 76 | 0.41 | 0.48 | 8.9 | 2.3 | <5 | 1.1 | 0.93 | Bal. |

Table 4-2 Solution Compositions.

<table>
<thead>
<tr>
<th>Solution symbol</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>30 g L⁻¹H₂SO₄</td>
</tr>
<tr>
<td>SCl</td>
<td>30 g L⁻¹H₂SO₄ + 12 g L⁻¹Cl⁻</td>
</tr>
<tr>
<td>SCl1Fe</td>
<td>30 g L⁻¹H₂SO₄ + 12 g L⁻¹Cl⁻ + 1 g L⁻¹Fe³⁺</td>
</tr>
<tr>
<td>SClCu1Fe</td>
<td>30 g L⁻¹H₂SO₄ + 12 g L⁻¹Cl⁻ + 15 g L⁻¹Cu²⁺ + 1 g L⁻¹Fe³⁺</td>
</tr>
<tr>
<td>SClCu</td>
<td>30 g L⁻¹H₂SO₄ + 12 g L⁻¹Cl⁻ + 15 g L⁻¹Cu²⁺</td>
</tr>
</tbody>
</table>
The experimental setup for the electrochemical measurements consisted of a conventional three-electrode jacketed cell, with a graphite rod as the counter electrode and with a Ag/AgCl ([KCl] =4 M) reference electrode introduced to the cell through a Luggin probe. The potentiostat used was a Princeton Applied Research Versastat 4 potentiostat/galvanostat. After solutions were made, they were introduced into the cell, heated to the desired temperature and de-aerated using argon for at least 30 minutes prior to introducing the Ti working electrode. Argon sparging was maintained during the entire experimental process. Titanium samples were ground with 320, 600, 800, and 1200 grit silicon carbide papers in series. These samples were then cleaned by rinsing with deionized water, rinsed a second time and ultrasonically cleaned in deionized water for 3 minutes. The sample preparation procedure was always finished within 15 min before starting a given test to ensure a freshly polished surface.

Open circuit potential (OCP), potentiodynamic polarization (PDP), potentiostatic polarization (PS), electrochemical impedance spectroscopy (EIS) and Mott–Schottky analysis experiments were conducted to study the influence of different additions on the corrosion behaviors of Ti at 25-85 °C. All potential values are quoted with respect to the Ag/AgCl reference electrode (0.197 V vs. SHE). Open circuit potential measurements were carried out for 1 hour in order to monitor the potential-time behavior of the electrodes in sulfuric acid solutions with various additions. The PDP tests were performed from −0.25 V vs. OCP up to 1.0 V vs. Ag/AgCl with a scan rate of 0.167 mV s⁻¹. The corrosion mechanism at the oxide film/electrolyte interface was investigated by EIS. To stabilize the potential, each sample was immersed in the solution for 1 h before starting an EIS test. The EIS perturbation voltage amplitude was 10 mV (peak to peak). The frequency range for all experiments was 0.1 Hz to 100 kHz with sampling at 10 points per decade. All EIS measurements were taken at the OCP.
The passive films on Ti were formed by potentiostatic anodization of the WE at different potentials for 12 h until the passive current reached a steady state value \( (i_{ss}) \). After the steady state was reached at a given film formation potential \( (E_f) \), Mott–Schottky analysis was carried out immediately by sweeping the voltage in the negative direction from \( E_f \) to \(-1.0 \) V vs. Ag/AgCl with a scan rate of 50 mV s\(^{-1}\). The excitation voltage was 10 mV (peak-to-peak) and the frequency was 5 kHz.

Titanium samples, 10×10×10 mm, were further studied by XPS analysis to clarify the chemical composition of the oxide films formed at 85 °C. Each sample was immersed in one of five 500 mL beakers, each containing 200 mL of a solution from solutions 1-5. The beakers were subsequently sealed with rubber stoppers and placed in an oven to keep the temperature of the solution at 85 ± 2 °C. The immersion tests lasted for 1 week. After the tests, all the samples were ultrasonically washed in deionized water for 3 min, dried in warm air and sent for the subsequent characterization. Surface morphology of the samples was observed using a Hitachi S-3000N SEM. The surface chemical composition of the samples was analyzed by a Leybold MAX2000 XPS spectrometer, using a monochromatic Mg Kα X-ray source and pass energies of 192 and 48 eV for wide and high resolution scans, respectively, was employed for these measurements. XPS tests were carried out at the take-off angle of 90 ° with no sputtering and no charge neutralization.

4.2 Results and discussion

4.2.1 The effect of chloride ions on the passive films of titanium in H\(_2\)SO\(_4\) solutions

Many investigations in the area of Ti corrosion and its electrochemistry in chloride solutions have been reported, and they all find that Cl\(^-\) ions facilitate the anodic passivity of Ti in sulfuric acid solutions (Greene & Judd, 1965; Thomas & Nobe, 1973; Thomas & Nobe, 1969; Vaughan
Nevertheless, there is still no explanation for the enhancing effect that Cl$^-$ ions have on Ti passivity.

It is well known that the electronic properties of passive films are crucially important in understanding their protective mechanism (Ahn & Kwon, 2005; Jiang et al., 2011a; Kong et al., 2009; Macdonald, 1992). Many studies have shown that the anodic oxide film formed on Ti surface is an n-type semiconductor. For the n-type semiconductive oxide film, two types of point defect, the metal interstitials and oxygen vacancies, act as donors. According to the point defect model (PDM) developed by Macdonald et al., the passive film on a reactive metal surface is a highly defective oxide film with point defects resulting from metal and oxygen vacancies and metal interstitials. When at steady state, the passive film is grown on the metal by migration of the point defects. These oxygen vacancies or metal interstitials must transport from the metal/film surface to the film/solution interface, and the point defect (metal vacancy) must transport from the film/solution interface to the metal/film interface. The key parameters for passive film growth are the diffusivity ($D_0$) and density ($N_D$) of the defects within the film (Bojinov, 1997; Macdonald, 1992). The transport behavior of the point defects within the passive film is of great interest for describing the growth of the passive film.

The PDP behavior of Ti in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ solutions with different Cl$^-$ additions at 50 °C is shown in Figure 4-1. In Figure 4-1 (a), the polarization curves of Ti in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ solutions with or without Cl$^-$ additions were almost identical at potentials below 0 V; the passive current density ($i_{\text{passive}}$) of Ti decreased with increasing Cl$^-$ additions, confirming, as expected, that Cl$^-$ ions facilitate the anodic passivity of Ti in H$_2$SO$_4$ solutions. According to Figure 4-1, applied potentials for film formation ($E_f$) were chosen in the range of 0 to 1.5 V, i.e., the passive region.
Figure 4-1 Polarization results of Ti in de-aerated 30 g L\(^{-1}\) H\(_2\)SO\(_4\) with different Cl\(^-\) additions at 50 °C. (a) PDP results; (b) 12 h-potentiostatic polarization results.
The values of $i_{ss}$ were read at the end of each 12 h-potentiostatic polarization measurement, and the results are presented in Figure 4-1 (b). In Figure 4-1 (b), a linear relationship is revealed between log $i_{ss}$ and $E_f$, which is in agreement with the predictions of the PDM (Kong et al., 2009; Macdonald, 1992). The slope of each log $i_{ss}$ vs. $E_f$ line was estimated and presented in Figure 4-1 (b), and the values are close to the reported value of 0.49 for Ti in 1.0 M HClO$_4$ solution (Kong et al., 2009). The Mott–Schottky relationship expresses the potential dependence of the space charge capacitance ($C$) of a semiconductor electrode under the depletion condition (Ahn et al., 2005). For an n-type semiconductor, the relation can be written as (Jiang et al., 2011a; Kong et al., 2009):

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 e N_D} (E - E_{FB} - \frac{kT}{e}) \ . \ (4-1)$$

where $\varepsilon_o (=8.854\times10^{-14} \text{ F cm}^{-1})$ is the vacuum permittivity; $\varepsilon$ ($\approx$80 of bulk rutile) is the dielectric constant of an oxide (Jiang et al., 2011a); $e (=1.602\times10^{-19} \text{ C})$ is the electron charge; $k (=1.38\times10^{-23} \text{ J K}^{-1})$ is the Boltzmann constant and $T (=323 \text{ K})$ is the absolute temperature. The $N_D$ value of the passive film can be determined from the slopes in the Mott–Schottky plots.

The plots of $C^{-2}$ vs. the applied potential for the passive films formed on Ti at various $E_f$ are presented in Figure 4-2. Figure 4-2 shows that regardless of the different $E_f$, all plots converge to approximately the same potential of ca. −0.5 V, i.e., the value of the flatband potential ($E_{FB}$), which is in good accordance with previously reported data (Cooper et al., 1982). The positive slopes of the Mott-Schottky plots in Figure 4-2 indicate that the passive film formed on Ti behaves as an n-type semiconductor.
Figure 4-2 Mott–Schottky plots of the passive films formed on Ti for 12 h at various $E_f$ in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ with different Cl$^-$ additions at 50 °C.
The values of $N_D$ estimated by Eq. (4-2) are shown in Figure 4-3 (a), indicating that $N_D$ decreases exponentially with increasing $E_f$. According to the PDM, the dependence of $N_D$ on $E_f$ can be expressed by Eq. (4-2), and the fitting results are presented in Figure 4-3 (a). Bojinov (Bojinov, 1997) demonstrated that $w_2$ in Eq. (4-2) was related to $D_o$ by Eq. (4-3).

$$N_D = w_1 \exp(-bE_f) + w_2 \tag{4-2}$$

$$D_o = \frac{2ai_{ss}}{zew_2 \exp(zFaE_o/RT)} \tag{4-3}$$

where $b$ is the decay constant; $w_1$ and $w_2$ are two unknown constants, which were obtained by fitting of the $N_D \sim E_f$ data shown in Fig.3(a); $a$ ($0.25$ nm) is the half-jump distance (Kong et al., 2009); $E_o$ ($\approx 4 \times 10^6$ V cm$^{-1}$) is the mean electric field strength for the anodic films on Ti (Armstrong & Quinn, 1977; Kong & Wu, 2008; Ohtsuka et al., 1985); $z$ is the charge number of the mobile point defects in the film. As it is not possible to separate the contribution of these two point defects (i.e., Ti$^{4+}$ and O$^{2-}$ vacancies) in the passive film, the average value of $z = 3$ for O$^{2-}$ and Ti$^{4+}$ vacancies was used in this work as the charge number of the migrating point defects (Ahn & Kwon, 2005; Kong et al., 2009; Macdonald, 1992).
Figure 4-3 (a) Donor density, $N_D$, and (b) diffusivity, $D_o$ of the defects in the film formed on Ti for 12 h at various $E_f$ in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ with different Cl$^-$ additions at 50 °C.
In Figure 4-3 (a), the donor level is slightly higher than that of bulk rutile (~$10^{20}$ cm$^{-3}$) (Kong et al., 2009), suggesting that the passive films are nonstoichiometric and deficient in oxygen. Figure 4-3 (a) also shows that $N_D$ decreased with the increasing concentration of Cl$^-$ ions at the same $E_f$. The lower defect density means that the oxide layer (TiO$_x$) is closer to TiO$_2$ as Cl$^-$ concentration is increased, and subsequently higher resistance to corrosion should be expected (Jiang et al., 2011a). Figure 4-3 (b) presents the estimated values of $D_o$ for the passive films formed at various $E_f$. The values of $D_o$ increased from $10^{-20}$ to $10^{-19}$ cm$^2$ s$^{-1}$ with the $E_f$ increasing from 0 to 1.5 V, which is comparable to reported data for passive films formed on Ti in 1.0 M HClO$_4$ solution (Kong et al., 2009). Figure 4-3 (b) also reveals that $D_o$ increased with increasing Cl$^-$ additions, which could be explained by the thermodynamic E$_h$-pH diagram for the Ti-Cl-H$_2$O system (Vaughan & Alfantazi, 2006). As suggested by the E$_h$-pH diagram, Cl$^-$ ions would complex with Ti$^{4+}$ to form TiOCl$_4^{2-}$ (Vaughan & Alfantazi, 2006). It is possible that Ti$^{4+}$ vacancies in the oxide films diffuse to the oxide film/electrolyte interface and tend to form TiOCl$_4^{2-}$ dissolving into the electrolyte. This dissolution process behaves as a driving force for the diffusion of Ti$^{4+}$ vacancies in the oxide films, leading to a higher diffusivity of Ti$^{4+}$ vacancies and the renewal of the passive film.

**4.2.2 Effects of cupric, ferric and chloride ions on Ti corrosion behavior in H$_2$SO$_4$ solutions**

According to Kelly et al. (Kelly et al., 2002), a reasonable criterion for steady state would be a change of 5 mV in OCP over a 10 minute period. The change of OCP over the last 10 minutes of each OCP measurement in Figure 4-1 was less than 5 mV. Therefore, all potentials in Figure 4-1 reached a steady state according to this criterion within 1 hour at all temperatures.
Figure 4-4 OCP recorded on Ti in Solutions S (=30 g L\(^{-1}\) H\(_2\)SO\(_4\)) and SCl (=30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\)) as a function of time, T=25, 55 and 85 °C.
Figure 4-5 (a) Nyquist and (b) Bode plots for Ti in S (=30 g L\(^{-1}\) H\(_2\)SO\(_4\)) and SCl (=30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^{-}\)) after 1 hour OCP measurements, T=25, 55 and 85 °C. The inset shows details of Nyquist plots for Ti at 55 and 85 °C.
EIS plots of Ti in sulfuric acid solutions with different additions after 1 hour OCP measurements are shown in Figure 4-5. It is also shown that the impedance magnitude of the Ti electrode in these two solutions was less than 1000 Ω cm² at 25 °C and even smaller at a higher temperature. The above discussion suggests that the mixed chloride-sulfuric acid solution is very corrosive for Ti with a freshly polished surface. It is shown that the impedance magnitude of the Ti working electrode in Solution S is essentially the same as that in Solution SCl for the studied temperature range. Figure 4-5 shows that the second time constant is observed at lower frequencies (<10⁰ Hz) for experiments at 55 and 85 °C. The details of the obtained EIS data are explained together with the effect of Cu²⁺ and Fe³⁺ ions later, on page 56.

The effect of Cl⁻ ions on the corrosion behavior of Ti in 30 g L⁻¹ H₂SO₄ is shown in Figure 4-6. The cathodic behavior, corrosion potential ($E_{corr}$) and primary passive potentials ($E_{pp}$) of Ti were not appreciably affected by the presence of Cl⁻ ions. When the potential was above 0.3 V, which was well within the passive region, the passive currents registered in the presence of Cl⁻ ions were lower than those obtained in the absence of Cl⁻ ions at all temperatures tested here. This result is consistent with a previous study presenting the effects of Cl⁻ ions on the anodic behavior of Ti in 1 N H₂SO₄ with different concentrations of NaCl at 24 ± 1 °C, where it was also found that the passive current density decreased with an increase in Cl⁻ ion concentration (Thomas & Nobe, 1969). It can thus be concluded that Cl⁻ ions facilitated the anodic passivity of Ti in sulfuric acid solutions.
Figure 4-6 Potentiodynamic polarization plots for Ti in Solutions S (=30 g L$^{-1}$ H$_2$SO$_4$) and SCl (=30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-)$.
Generally for Ti, oxidizing species such as cupric and ferric ions, are known to be corrosion-inhibiting cations (Cobb & Uhlig, 1952). It is shown in Figure 4-7 and Figure 4-8 that the presence of Cu$^{2+}$ and Fe$^{3+}$ ions shifted the open circuit potential of Ti to the passive region, enforcing the passivity. Figure 4-9 shows the passive current densities ($i_{\text{passive}}$) at 1.0 V obtained by potentiodynamic polarization tests with a scan rate of 0.167 mV s$^{-1}$ in all five solutions at 25, 55 and 85 °C. The passive current density, $i_{\text{passive}}$, increased with increasing temperature. The addition of cupric and ferric ions decreased $i_{\text{passive}}$ except in Solution SCICu at 85 °C, which indicates a negative effect of cupric on improving corrosion resistance for Ti in this mixed chloride–sulfuric acid environment. Solution SC1Fe gave the lowest $i_{\text{passive}}$ at all temperatures. Both Figure 4-7 and Figure 4-8 show that the presence of Fe$^{3+}$ had the most significant beneficial effect on increasing corrosion resistance of Ti at all temperatures, even though the added amount of Fe$^{3+}$ was only 1.0 g L$^{-1}$ compared to 15 g L$^{-1}$ Cu$^{2+}$. 
Figure 4-7 OCP recorded on Ti in Solutions SCl1Fe (=30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\) + 1 g L\(^{-1}\) Fe\(^{3+}\)), SClCu1Fe (=30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\) + 15 g L\(^{-1}\) Cu\(^{2+}\) + 1 g L\(^{-1}\) Fe\(^{3+}\)), and SClCu (=30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\) + 15 g L\(^{-1}\) Cu\(^{2+}\)) as a function of time, T=25, 55 and 85 °C.
Figure 4-8 Potentiodynamic polarization plots for Ti in Solution SClCu1Fe (=30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$ + 15 g L$^{-1}$ Cu$^{2+}$ + 1 g L$^{-1}$ Fe$^{3+}$), T=25, 55 and 85 °C.
Figure 4-9 Passive current densities at 1.0 V from potentiodynamic polarization tests for Ti in 30 g L\(^{-1}\) H\(_2\)SO\(_4\) solutions with different additions.
EIS plots of titanium in sulfuric acid solutions with different additions after 1 hour OCP measurements are shown in Figure 4-10. To investigate the oxide film properties as a function of temperature in sulfuric acids with Cu\(^{2+}\), Fe\(^{3+}\) and Cl\(^-\) additions, it is necessary to model the datasets with electrical equivalent circuits (EECs). Many papers have been published in the field of Ti corrosion related to chloride-sulfate solutions (Assis et al., 2006; Aziz-Kerrzo et al., 2001; de Souza & Robin, 2007; Delgado-Alvarado & Sundaram, 2007; González & Mirza-Rosca, 1999; He et al., 2002; He et al., 2007; Mogoda et al., 2004; Pan et al., 1996; Shibata & Zhu, 1995). Among them, \(R_{\text{sol}}(R_{\text{ct}}Q_{\text{dl}})\) and \(R_{\text{sol}}(Q_{\text{film}}(R_{\text{ct}}Q_{\text{dl}}))\) were the two equivalent circuits used most frequently. The single time constant circuit includes solution resistance \(R_{\text{sol}}\), double layer capacitance behavior \(Q_{\text{dl}}\) and charge transfer resistance \(R_{\text{ct}}\). The two time constant circuit includes solution resistance \(R_{\text{sol}}\), oxide film capacitance behavior \(Q_{\text{film}}\), oxide film resistance \(R_{\text{f}}\), double layer capacitance behavior \(Q_{\text{dl}}\), and charge transfer resistance \(R_{\text{ct}}\). The Constant Phase Element (symbolized here by \(Q\)) was used to compensate for the non-ideal behavior of the capacitor (Hsu & Mansfeld, 2001).
Figure 4-10 (a, b, c) Nyquist and (d, e, f) Bode plots for Ti in Solutions SCl1Fe (≈30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ + 1 g L⁻¹ Fe³⁺), SClCu1Fe (≈30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ + 15 g L⁻¹ Cu²⁺ + 1 g L⁻¹ Fe³⁺), and SClCu (≈30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ + 15 g L⁻¹ Cu²⁺) after 1 hour OCP measurements.
He et al. (He et al., 2002) showed that the two time constant circuit fits EIS data with better precision than the single time constant circuit at 55 °C, and their testing condition was 0.27 mol L\(^{-1}\) deaerated NaCl solution with freshly polished sample immersed in solution for 24 hours. Shibata et al. (Shibata & Zhu, 1995) found no evidence for a two–time constant circuit up to 80 °C in 0.5 M deaerated sulfuric acid solution after polarization at 1.0 V for 1 hour. It is well known that more than one EEC may fit a specified set of experimental data. The chosen EEC should give the best possible fit between the simulated and measured results while remaining as simple as possible to represent the system. The Pearson correlation coefficient is an effective measurement of the strength of linear dependence among all parameters in the EEC model and a correlation value greater than 0.8 is considered as a strong correlation (Eghbalnia & Dixon, 2012). In this study, EIS data were analyzed using the Z\(_{\text{Simp}}\)Win program. In order to choose a proper EEC for each system, Pearson correlation coefficient matrices were used to determine whether it was necessary to use a two–time constant model. Table 4-3 shows the correlation matrix of elements of the equivalent circuit \(R_{\text{sol}}(Q_{\text{film}}(R_{\text{ct}}(Q_{\text{dl}})))\) of Ti in Solution SCl at 55 °C. The weak correlation of \(R_{\text{film}}\) and \(R_{\text{ct}}\) made it necessary to use a two–time constant model at 55 °C.

It turns out that the equivalent circuit \(R_{\text{sol}}(R_{\text{ct}}Q_{\text{dl}})\) provided a good fit to the EIS data of Solution S and Solution SCl at 25 °C while \(R_{\text{sol}}(Q_{\text{film}}(R_{\text{ct}}Q_{\text{dl}})))\) provided a better fit to all other data sets. The typical error for each parameter is: \(R_{\text{sol}}, 0.5\%; Q_{\text{film}}-Y_0, 1.3\%; Q_{\text{film}}-n, 0.2\%; R_{\text{film}}, 0.8\%; R_{\text{ct}}, 0.3\%; Q_{\text{dl}}-Y_0, 1.5\%; Q_{\text{dl}}, 1.3\%\). Figure 4-11 shows the equivalent circuit diagrams and the corresponding data are presented in Table 4-4. Film resistances of solutions without ferric ions decreased with increasing temperature. As shown in Table 4-4, the film resistance of cupric-containing solutions was very low (less than 10 Ω cm\(^2\)) at 85 °C. This is consistent with
results shown in Figure 4-9, which demonstrate that $i_{\text{passive}}$ obtained in Solution SCICu was even higher than that obtained in Solution S and Solution SCI at 85°C. Therefore, there is a possibility that cupric ions can affect the chemistry of passive films formed on Ti, and this idea was further examined by XPS analyses, as shown in the next section.

Figure 4-11 The equivalent circuits (a) $R_{\text{sol}}(R_{\text{ct}}Q_{\text{dl}})$ and (b) $R_{\text{sol}}(Q_{\text{film}}(R_{\text{film}}(R_{\text{ct}}Q_{\text{dl}})))$ used to fit the EIS data.
Table 4-3 Correlation matrices of elements of equivalent circuit $R_{sol}(Q_{film}(R_{film}(R_{ct}Q_{dl})))$ of Ti in $30 \text{ g L}^{-1} \text{H}_2\text{SO}_4 + 12 \text{ g L}^{-1} \text{Cl}^{-}, \text{T}=55 ^\circ \text{C}$.

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
 & R_{sol} & Q_{film} - Y_0 & Q_{film} - n & R_{film} & R_{ct} & Q_{dl} - Y_0 & Q_{dl} - n \\
\hline
R_{sol} & 1.00 & -0.27 & 0.32 & -0.19 & -0.09 & -0.13 & -0.12 \\
Q_{film} - Y_0 & -0.27 & 1.00 & -0.94 & 0.71 & 0.40 & 0.53 & 0.53 \\
Q_{film} - n & 0.32 & -0.94 & 1.00 & -0.67 & -0.34 & -0.48 & -0.48 \\
R_{film} & -0.19 & 0.71 & -0.67 & 1.00 & 0.50 & 0.62 & 0.75 \\
R_{ct} & -0.09 & 0.40 & -0.34 & 0.50 & 1.00 & 0.35 & 0.79 \\
Q_{dl} - Y_0 & -0.13 & 0.53 & -0.48 & 0.62 & 0.35 & 1.00 & 0.49 \\
Q_{dl} - n & -0.12 & 0.53 & -0.48 & 0.75 & 0.79 & 0.49 & 1.00 \\
\hline
\end{array}
\]
Table 4-4 Values of elements of equivalent circuits for all situations.

<table>
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<tr>
<th>Solution</th>
<th>$T$ (°C)</th>
<th>$R_{sol}$ (Ω cm$^2$)</th>
<th>$Q_{film-Y_0}$ (μF cm$^{-2}$ s$^{-1}$)</th>
<th>$Q_{film}$ $-n$ (Ω cm$^2$)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$Q_{dl-Y_0}$ (μF cm$^{-2}$ s$^{-1}$)</th>
<th>$Q_{dl}$ $-n$</th>
<th>$X^2$ $\times 10^5$</th>
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<td>3.1</td>
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<td>121.3</td>
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<td>0.9</td>
<td>5.6</td>
</tr>
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<td>1005</td>
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<td>155.8</td>
<td>182</td>
<td>4252</td>
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<td>0.9</td>
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<td>3995</td>
<td>75</td>
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<td>42</td>
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</tr>
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<td></td>
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<td>0.9</td>
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<td>0.6</td>
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<td>1.0</td>
<td>5.4</td>
<td>1217</td>
<td>94</td>
<td>0.7</td>
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Note: The typical error for each parameter is: $R_{sol}, 0.5\%$; $Q_{film-Y_0}, 1.3\%$; $Q_{film}^{-n}, 0.2\%$; $R_{film}$, 0.8\%; $R_{ct}, 0.3\%$; $Q_{dl-Y_0}, 1.5\%$; $Q_{dl}, 1.3\%$. 

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4.2.3 Effect of cupric ions on Ti oxide films

To further investigate the oxide film properties, Ti samples were immersed for one week as described above. Ti 2p spectra of these five samples were taken and are shown in Figure 4-12. All five samples had two peaks in the same locations, the peak at 458.7 eV is attributed to Ti$^{4+}2p_{3/2}$ and that at 464.2 eV is attributed to Ti$^{4+}2p_{1/2}$, both for TiO$_2$. All these results were consistent with those observed for TiO$_2$ reference spectra (Ernsberger et al., 1986; Hopfengärtner et al., 1993) and by He and Noël (He et al., 2002; Noël, 1999). There was no evidence of Ti$^0$ on the surfaces after one week of immersion. The Cu 2p peaks from the Ti samples are shown in Figure 4-12. The peak at 932 eV is attributed to Cu 2p$_{3/2}$ (Marcus & Bussell, 1992; Rochefort et al., 1993) and that at 952 eV is attributed to Cu 2p$_{1/2}$ (Jolley et al., 1989; Rochefort et al., 1993); both refer to Cu$^0$. The XPS signals of Cu$^0$ and Cu$^+$ are basically the same, but they are different from Cu$^{2+}$ signals (Chadwick & Hashemi, 1978; Jolley et al., 1989; Marcus & Bussell, 1992; Rochefort et al., 1993). This result provided evidence that cupric ions were reduced to Cu$^0$ or Cu$^+$ in the Ti oxide films. In view of the results from the EIS measurements and XPS analyses, it is possible that cupric ions could migrate into the Ti oxide films (originating from immersion in cupric-containing solution), and could be reduced to cuprous oxide or copper metal within the film. The reduction reaction of cupric ions in Ti oxide films was further investigated by thermodynamic calculations and electrochemical tests, both presented in the following section.
Figure 4-12 Ti 2p and Cu 2p spectra of Ti after one-week of immersion in five solutions, $T=85^\circ C$. 
Table 4-5 Thermodynamic data at 25 °C for the Cu–Cl system.

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>$\Delta_f G^\circ$ (kJ mol$^{-1}$)</th>
<th>$S^\circ$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$C_j$ (mol L$^{-1}$)</th>
<th>$f_{m,j}$#</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>s</td>
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<td>33.15</td>
<td>—</td>
<td>1*</td>
</tr>
<tr>
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<td>0.001</td>
<td>1.134</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>l</td>
<td>$-237.18$</td>
<td>69.95</td>
<td>—</td>
<td>1*</td>
</tr>
<tr>
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<td>0.71</td>
</tr>
<tr>
<td>HCl</td>
<td>aq</td>
<td>$-131.25$</td>
<td>56.5</td>
<td>$2.54 \times 10^{-7}$</td>
<td>1.13</td>
</tr>
<tr>
<td>Ti</td>
<td>s</td>
<td>0</td>
<td>30.72</td>
<td>—</td>
<td>1*</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>s</td>
<td>$-888.8$</td>
<td>50.62</td>
<td>—</td>
<td>1*</td>
</tr>
</tbody>
</table>

Note: * from OLI Electrolyte Simulation Software, and $f_{m,j}$ is the activity coefficient on the mole fraction scale; * is activity not activity coefficient.

The values of the equilibrium potential, $E$, of reactions (4-4) and (4-5) were calculated with the Nernst and Maxwell equations for Solution SClCu at 85 °C. The standard Gibb's free energy and entropies are listed in Table 4-5 (Beverskog et al.; Dean; Tromans & Silva, 1997). The required molar concentration and activity coefficients of species in Solution SClCu at 85 °C are from the OLI Electrolyte Simulation Software. The activity coefficient model of OLI is based upon an extended Debye-Huckel term, a Uniquac term, and a middle-range electrolyte term, and with this model, very good accuracy has been obtained in reproducing experimental data for various systems (Anderko et al., 2002; Kosinski et al., 2007; Wang et al., 2006; Wang et al., 2002a; Wang et al., 2004).
\[ CuCl_2 + 2H^+ + 2e \rightarrow Cu + 2HCl, \quad E = 0.44 \text{ V vs. } Ag/AgCl, T = 85 \degree C \] (4-4)

\[ TiO_2 + 4H^+ + 4e \rightarrow Ti + 2H_2O, \quad E = -0.80 \text{ V vs. } Ag/AgCl, T = 85 \degree C \] (4-5)

OCP was approximately 0.40 V in Solution SCICu at 85°C and was thus between the equilibrium potentials of reaction (4-3) and reaction (4-4). Therefore, elemental Cu\(^0\) can be formed as described in reaction (4-3). As hypothesized above, it is thus thermodynamically possible that the low film resistance obtained in this study may be due to Cu\(^0\) formed in the Ti oxide films. If a higher potential (>0.44 V vs. Ag/AgCl) is applied on the Ti working electrode, this Cu\(^0\) may be oxidized to cupric ions.

4.3 Summary

Based on electrochemical measurements, sulfuric acid solution is very corrosive for Ti with freshly polished surface at higher temperatures. Potentiodynamic polarization tests demonstrated that the presence of Cl\(^-\) promoted the anodic passivity of Ti while Cu\(^2+\) and Fe\(^3+\) ions enforced the anodic passivity of Ti in sulfuric acid solutions. EIS tests showed that the presence of ferric ions (1.0 g L\(^{-1}\)) had the most significantly beneficial effect on increasing polarization resistance of Ti at all temperatures. It was also shown in EIS results that the film resistance of cupric-containing solutions was very low (less than 10 \(\Omega \text{ cm}^2\)) at 85 °C. The effect of cupric ions on Ti oxide films was further investigated by thermodynamic calculations and electrochemical tests. This lower film resistance of cupric-containing solutions could be due to Cu\(^0\) formed in the Ti oxide films when immersed in cupric-containing solutions.

The polarization results indicate that Cl\(^-\) ions facilitate the anodic passivity of Ti in sulfuric acid solutions. This facilitating effect of Cl\(^-\) ions on the passivity of Ti was explained in this work
through study of point defects in the passive film. Based on the PDM and Mott-Schottky analysis, the values of $N_D$ within the film formed on Ti in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ were estimated to be $\sim 10^{20}$ cm$^{-3}$, and decreased with increasing Cl$^-$ concentrations at the same $E_f$; while the values of $D_o$ were estimated to be $\sim 10^{-20}$ cm$^2$ s$^{-1}$, and increased with increasing Cl$^-$ concentrations at the same $E_f$. 
5 Corrosion rates of Ti in H\textsubscript{2}SO\textsubscript{4} solutions obtained by mass loss

Measuring the corrosion rates of Ti under severe conditions of acidity, temperature and pressure is useful to predict and design against disastrous failures during the service of Ti liners. In the present chapter, in order to determine if Ti is a durable material for pressure leaching processes, the corrosion rates of Ti under simulated pressure leaching conditions were determined by both mass loss measurements. Iso-corrosion diagrams, with 0.1 mm yr\textsuperscript{-1}, 0.5 mm yr\textsuperscript{-1}, and 1 mm yr\textsuperscript{-1} lines for Ti in 3-50 wt.% H\textsubscript{2}SO\textsubscript{4} solutions with no addition, with the addition of 15 g L\textsuperscript{-1} Cu\textsuperscript{2+} and with the addition of 1 g L\textsuperscript{-1} Fe\textsuperscript{3+} from room temperature to 175 °C were constructed from mass loss data.

5.1 Experimental

The material investigated was pure Ti, ASTM Grade 2 (0.14 wt.% Fe, 0.005 wt.% C, 0.005 wt.% Al, 0.008 wt.% Ni, 0.01 wt.% H, Bal. Ti; Timet, Henderson NV). DI water, H\textsubscript{2}SO\textsubscript{4}, NaCl, CuSO\textsubscript{4}\cdot5H\textsubscript{2}O and Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}\cdot5H\textsubscript{2}O were used to prepare the electrolytes. The solutions were not sparged with gases prior to- or during experiments. The simulated leaching solutions always contain 30 g L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} + 12 g L\textsuperscript{-1} Cl\textsuperscript{-} + 15 g L\textsuperscript{-1} Cu\textsuperscript{2+} (=SCICu).

For all immersion experiments, the samples had a dimension of 12.7 mm × 12.7 mm × 3 mm with a 3 mm-diameter hole drilled in the center. Prior to immersion, the samples were abraded using successive grades of SiC papers down to 600 grit, ultrasonically washed for 5 min in DI water, dried in air, and weighed with a 0.1 mg precision scale (SCIENTECH ZSA 120). After the samples were removed from the experimental solution, they were ultrasonically cleaned for 5 min in DI water, dried in air and then the final mass was measured using the scale.
5.1.1. Immersion experiments at 150 °C

In order to carry out immersion experiments in hot, pressurized acid solutions, six carbon steel pressure vessels with polytetrafluoroethylene (PTFE) liners were designed to allow for the performance of experiments according to the ASTM G31-72 standard. (Standard, 2006) The dimensions of the pressure vessels and the PTFE sample-tree are shown in Figure 5-1. Each sample was attached to the sample-tree by a PTFE screw. The screw was loose enough to avoid crevice corrosion. A sample-tree was placed in a pressure vessel and then 200 mL of a given solution was added to the vessel. For each pressure vessel, there were two samples immersed in the experimental solution. The ratio between solution volume and surface area of the immersed specimens was 0.21 mL mm\(^{-2}\). Each vessel was sealed with a PTFE cover to prevent interaction with the steel cap, which was secured to the vessel body with six bolts. The vessels were then put in a high temperature furnace (DZF-6050, MTI Corporation) with temperature controlled to 150±2 °C. Due to the very aggressive nature of the 30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\) (=SCl) solution, the samples exposed to this solution were kept in the furnace for only one week. For solutions with Cu\(^{2+}\) and Fe\(^{3+}\) additions, the samples were kept in the furnace for 4, 8 and 16 weeks for each solution composition. In order to address reproducibility, the set of 8 week-immersion experiments was carried out twice.
Figure 5-1 Schematic overview of the pressure vessel and sample holder. (a) Pressure vessel with PTFE liner and sealing lid; (b) The PTFE sample-tree (the black pieces are samples).
5.1.2. Iso-corrosion experiments

Since 60 wt.% H$_2$SO$_4$ solution cannot dissolve 1 g L$^{-1}$ Fe$^{3+}$ ions at room temperature, the upper limit of H$_2$SO$_4$ concentration in this study was 50 wt.% and the lower limit was 3 wt.% as this is the typical acid concentration in medium temperature copper sulphide leaching, i.e., 3 wt.% H$_2$SO$_4$ ≈ 30 g L$^{-1}$ H$_2$SO$_4$. The samples were exposed to 3-50 wt.% H$_2$SO$_4$ solutions, 3-50 wt.% H$_2$SO$_4$ + 15 g L$^{-1}$ Cu$^{2+}$ solutions, and 3-50 wt.% H$_2$SO$_4$ + 1 g L$^{-1}$ Fe$^{3+}$ solutions at different temperatures (from 25 to 175 °C). For each solution, the iso-corrosion experiment was performed with three sequential periods of 24, 48, and 72 hours, respectively, and a fresh experimental solution was used for each period. For each experiment, the samples were only polished before the first period. Before and after each period the samples were cleaned and weighed using the same procedure as the long-term immersion experiments. The corrosion rates (in mm yr$^{-1}$) were calculated from the mean value of the mass losses of the second and third periods. The temperature was increased at intervals of 10 °C until corrosion rates of 0.1, 0.5 and 1.0 mm yr$^{-1}$ were obtained. To increase the accuracy of the measurements, some additional experiments at other temperatures and acid concentrations were necessary and the corresponding results are also presented below.

5.1.3. Corrosion rate calculation

When localized corrosion is not present, according to ASTM standard G31-72 the average corrosion rate for mass loss coupons can be calculated by Eq. (5-1) (Standard, 2006).

$$\text{Corrosion Rate (mm yr}^{-1}) = \frac{K \times W}{A \times t \times D}$$

(5-1)

Where $K$ is a unit conversion parameter ($=8.763 \times 10^4$ hour mm yr$^{-1}$ cm$^{-1}$); $t$ is the time of exposure in hours; $A$ is the sample area in cm$^2$; $D$ is density in g cm$^{-3}$; and $W$ is the average mass
loss in g of the two immersed samples in each immersion experiment. As will be discussed later, the contribution of the corroded Ti that went to oxide formation is negligible compared to that which dissolved in solution. Thus the total corrosion rate of Ti is essentially equal to that obtained through mass loss.

5.1.4. Characterization techniques

Lead acetate paper (Fisherbrand™ Special Experiment Papers, Fisher Scientific Canada) was used to test for the presence of hydrogen sulphide (H$_2$S). At the end of the immersion experiment in 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$ solution at 150 °C, lead acetate paper was placed in the headspace inside the pressure vessel as quickly as possible and without completely displacing the vessel lid. The vessel lid was then replaced so as to maintain the lead acetate paper in the vessel headspace. The lead acetate paper was left inside the vessel for 5 minutes. Lead acetate paper turns black if H$_2$S is present. The chemical reaction associated with this color change is characteristic of the presence of H$_2$S and is as follows (Buckley & Woods, 1996):

$$\text{Pb(C}_2\text{H}_3\text{COO)}_2 + \text{H}_2\text{S} \rightarrow \text{PbS} + 2\text{C}_2\text{H}_3\text{COOH}$$  \hspace{1cm} (5-2)

The presence of hydrogen (H$_2$) was confirmed by a combustion experiment. Both H$_2$ and H$_2$S are combustible. However, for the pressure vessel experiments, it was difficult to separate H$_2$S from H$_2$ to perform a combustion experiment. Thus to confirm the presence of H$_2$ without the interference of H$_2$S, a Ti sample was immersed in a sealed glass cell containing 200 mL 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$ solution at 95 °C. The generated gas was first passed through a 1 M NaOH solution, and then a combustion experiment was performed.

The corrosion products were studied by X-Ray Diffraction (XRD), using Ni filtered Cu Kα ($\lambda$Cu Kα = 0.154186 nm, radiation at 40 kV and 20 mA) over the 2θ range of 20–80° (scan speed: 2°
per minute, and step size: 0.04°). XRD was used to characterize the precipitate corrosion product only, i.e., the powdered oxide found at the bottom of the pressure vessels after immersion experiments. The surface morphology of samples was observed using a Zeiss Sigma field emission SEM.

5.2 Results and discussion

5.2.1 Effect of chloride ions on the corrosion behavior of Ti in H₂SO₄

The corrosion rates for Ti in 30 g L⁻¹ H₂SO₄ (=S) solutions with and without 12 g L⁻¹ Cl⁻ from 25 to 95 °C were obtained using the iso-corrosion test procedure described above, and the results are shown in Figure 5-2. In Figure 5-2, corrosion rates for Ti in S solutions are, for most the part, the same as those in 30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ (=SCl) solutions. This result is consistent with previous studies. As shown in Figure 4-3 the cathodic behavior, corrosion potential (E_{corr}) and primary passive potentials (E_{pp}) of Ti were not appreciably affected by the presence of Cl⁻ ions. It was also found by Greene and Judd that the dissolution current density of Ti in 0.5 mol L⁻¹ H₂SO₄ was equal to that in 0.5 mol L⁻¹ H₂SO₄ + 1 mol L⁻¹ NaCl solution at 25 °C (Greene & Judd, 1965). It could be concluded here that the corrosion rate of Ti may be unaffected by the presence of Cl⁻ in sulfuric acid alone.
Figure 5-2 Corrosion rates of Ti in 30 g L$^{-1}$ H$_2$SO$_4$ solution with and without 12 g L$^{-1}$ Cl$^-$ addition in temperature range from 25 to 95 °C.
According to the standards for relative corrosion resistance (Jones, 1996), corrosion rates below 0.5 and 5 mm y<sup>-1</sup> are defined as good and fair, respectively; corrosion rates above 5 mm y<sup>-1</sup> are defined as unacceptable. Then there are three regions of corrosion resistance in Figure 5-2, good (<45 °C), fair (<75 °C) and unacceptable (>75 °C). The corrosion rate of Ti in 30 g L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution at 95 °C is slightly smaller than published values, 20.1 mm y<sup>-1</sup> compared with 23.4 mm y<sup>-1</sup> (920 mpy) (Golden <i>et al.</i>, 1952). 23.4 mm y<sup>-1</sup> was for titanium in air-saturated 3 wt.% H<sub>2</sub>SO<sub>4</sub> at 100 °C (Golden <i>et al.</i>, 1952).

As a point of interest, there was visible hydrogen evolution occurring on the Ti surface during immersion at temperatures from 75 to 95 °C. Also, hydrogen evolution was more severe at higher temperatures. Since Ti has a standard potential of −1.63 V vs. SHE, hydrogen evolution would be expected when metallic Ti (rather than the oxide) is exposed to acidic solutions. It is shown in Figure 5-2 that the corrosion rate of Ti in S solution at 95 °C was 20.1 mm y<sup>-1</sup> and only slightly lower than the previously published value of 23.4 mm y<sup>-1</sup> (920 mpy) for Ti in air-saturated 3 wt.% H<sub>2</sub>SO<sub>4</sub> solution at 100 °C (Golden <i>et al.</i>, 1952). Based on the above results, it can be assumed that the mixed chloride–sulfuric acid solution is very corrosive for Ti, and that Ti would have an extremely high corrosion rate in SCI solution at temperatures above 100 °C.

5.2.2 The corrosion behavior of Ti in the mixed chloride-sulfuric acid solution at 150 °C

After one week immersion in SCI solution at 150 °C, the Ti samples were completely corroded. Assuming that the entire Ti sample dissolved over a period of 7 days, the corrosion rate of Ti estimated by Eq. (5-1) was at least 62 mm y<sup>-1</sup> in SCI solution at 150 °C. According to the E<sub>H</sub>–pH diagrams for the Ti–H<sub>2</sub>O system (Lee, 1981) the standard electrode potential for the Ti/Ti<sup>2+</sup> couple is −1.63 V vs. SHE at 25 °C and this potential becomes more negative with increasing temperature to a value of −1.66 V vs. SHE at 150 °C, which confirms that Ti is a very
reactive material and the corrosion rate of 62 mm yr$^{-1}$ under this specific condition is not unexpected, provided that the surface oxide was not protective. When the pressure vessel was opened, the gas released had the characteristic smell of H$_2$S and it reacted with lead acetate paper to produce a black product, which proved that H$_2$S was produced. A combustion experiment was performed as described in the experimental section. The generated gas was first passed through an NaOH solution, and the remaining gas was confirmed to be combustible, indicating the presence of H$_2$. Even though the operating temperature (95 °C) was lower than 150 °C here, together with the standard equilibrium potentials of reactions (5−4)−(5−6), it is still possible that H$_2$ was generated when Ti samples were immersed in the SCl solution at 150 °C. A control test was also performed to exclude the possibility that H$_2$ or H$_2$S is generated from the experimental solution. The test was performed in 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$. The precipitated corrosion product was analyzed by XRD and the XRD spectrum is shown in Figure 5-3. The XRD spectrum presented in Figure 5-3 presents very sharp peaks and indicates that the corrosion products are mainly TiO$_2$, which is in good agreement with already published work. (Chuang & Chen, 2008; Guo et al., 2012) Given the presence of H$_2$S, H$_2$ and the formation of TiO$_2$, it is likely that reactions (5−4)-(5−8) took place in the sealed vessel. The standard equilibrium potentials, $E^o$, of reactions (5−5)-(5−7) at 150 °C were calculated and are also presented. The required standard Gibb's free energies at 150 °C are available in the literature (Lee, 1981; Murray & Cubicciotti, 1983; Vaughan & Alfantazi, 2004).
Figure 5-3 XRD spectrum for the TiO$_2$ precipitate obtained after one week of Ti immersion in 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$ solution at 150 °C.
$T = 150 \, ^{\circ}\text{C}$,

\[ 2H^+ + 2e^- \rightarrow H_2, E^\circ = 0 \text{ V vs. SHE} \quad (5-4) \]

\[ 10H^+ + SO_4^{2-} + 8e^- \rightarrow H_2S + 4H_2O, E^\circ = 0.38 \text{ V vs. SHE} \quad (5-5) \]

\[ TiO^{2+} + 2H^+ + 4e^- \rightarrow Ti + H_2O, E^\circ = -0.75 \text{ V vs. SHE} \quad (5-6) \]

\[ 5Ti + 2SO_4^{2-} + 14H^+ \rightarrow 2H_2 + 2H_2S + 5TiO^{2+} + 3H_2O, \ E^\circ = 1.06 \text{ V vs. SHE} \quad (5-7) \]

\[ TiO^{2+} + 4Cl^- \rightarrow TiOCl_4^{2-} \quad (5-8) \]

\[ T = 25 \, ^{\circ}\text{C and pH} > 1.5, \]

\[ TiOCl_4^{2-} + H_2O \rightarrow TiO_2 + 4Cl^- + 2H^+ \quad (5-9) \]

Reaction (5–7) is the overall reaction obtained by combining reactions (5–4)–(5–6) and is a H$^+$ consuming reaction, which would increase the pH of the experimental solution. It was confirmed that the pH of the experimental solution was ~0 before the immersion experiment, and the pH of the experimental solution was ~2 after the immersion experiment. According to the E$_h$–pH diagrams for Ti–SO$_4$–H$_2$O and Ti–Cl–H$_2$O systems, SO$_4^{2-}$ ions can complex with TiO$^{2+}$ to form TiO(SO$_4$)$_2^{2-}$; while Cl$^-$ ions can complex with TiO$^{2+}$ by reaction (5–8) to form TiOCl$_4^{2-}$, and extend the stability range of TiO$_2$ (pH>~1.5) (Vaughan & Alfantazi, 2006). In view of the pH value (~2) of the final solution, TiO$_2$ may have been formed by reaction (5–9) as the reactor cooled to room temperature, as suggested by the E$_h$–pH diagram for Ti–Cl–H$_2$O system at 25 °C (Vaughan & Alfantazi, 2006). As shown by reactions (5–7)–(5–9), the overall reaction occurring in the sealed vessel was a net H$^+$ consuming reaction, that is, to form 2.5 moles of TiO$_2$, 2 moles of H$^+$ would be consumed. The pH of the experimental solution would increase as observed.
5.2.3 Long-term corrosion behavior of Ti in simulated copper leaching solutions at 150 °C

Cu\(^{2+}\) and Fe\(^{3+}\) ions are known to be corrosion inhibitors for Ti in acidic solutions (Cobb & Uhlig, 1952). Considering the extremely high corrosion rate of Ti in SCl solution at 150 °C (as documented above), it was deemed necessary to perform long-term immersion experiments in the same SCl solution but also in the presence of Cu\(^{2+}\) or Fe\(^{3+}\) ions. For each solution composition, SCl solution with various Fe\(^{3+}\) additions, samples were immersed for 4, 8 and 16 weeks.

For experiments in the presence of Fe\(^{3+}\) ions, there was a yellow precipitate formed after immersion. Umetsu et al. have reported a set of empirical formulas for Fe\(^{3+}\) solubility in H\(_2\)SO\(_4\) solutions at high temperatures (Umetsu et al., 1977). According to these formulas, the Fe\(^{3+}\) solubility in S solutions should be around 0.37 g L\(^{-1}\) at 150 °C, which is lower than the Fe\(^{3+}\) concentrations used in this work, i.e. 1 and 5 g L\(^{-1}\). Later, Sasaki et al. also reported that, at the same H\(_2\)SO\(_4\) concentration, the concentration of Fe\(^{3+}\) ions decreased considerably with an increase in the addition of Na\(^{+}\) ions, and the Fe\(^{3+}\) ions precipitated as sodium jarosite (Sasaki et al., 1994). Based on the above discussion and the presence of NaCl (Cl\(^{-}\)) in the system, the yellow precipitate formed in our work is most likely sodium jarosite.

The mass changes of Ti after up to 16 weeks of immersion in the SClCu solution with various Fe\(^{3+}\) additions at 150 °C are presented in Figure 5-4. The points refer to the mean mass changes of the two immersed samples for each experimental condition. The error bars of the data obtained after 8 weeks immersion (8 week-results) proved that the mass loss data were repeatable. This mass gain phenomenon has also been observed elsewhere (He et al., 2005; Koike & Fujii, 2001; Yan et al., 2011). Koike and Fujii reported that the mass gain of pure Ti, when it was immersed in physiological saline solution, was due to Ti ion dissolution followed by
the formation of a TiO$_2$ scale on the surface of the samples (Koike & Fujii, 2001). Mass gain has also been observed in a crevice corrosion study for Ti-2, wherein the authors suggested that the mass gain was due to the precipitation of the highly insoluble corrosion products (TiO$_2$) (He et al., 2005; Yan et al., 2011). Thus, the observed mass gain could be related to the growth of the Ti oxide layer or precipitation of previously dissolved ions once their saturation point had been reached in a given environment. Considering mass changes vs. immersion time, the highest mass loss was observed for samples immersed for 8 weeks in all three solutions, and a small mass gain was generally observed on the 16 week-results compared to the 8 week-results for all samples; considering mass changes vs. solution composition, the highest mass loss for Ti was observed on samples immersed in the SCICu solution, while the mass changes of samples in solutions with Fe$^{3+}$ additions were negligible. The mass changes presented in Figure 5-4 suggest that Cu$^{2+}$ and Fe$^{3+}$ ions are good corrosion-inhibiting cations for Ti.
Figure 5-4 The average mass losses of Ti specimens after 4, 8 and 16 weeks immersion in the SCICu with different Fe$^{3+}$ additions at 150 °C.
After immersion, all samples exhibited a light brown surface color. As it is well established that the thickness of Ti oxide films dictates their color, the brown color corresponds to a thickness of approximately 0.036 µm. Given the redox potential of Fe$^{3+}$/Fe$^{2+}$ (~ +0.77 V) and Cu$^{2+}$/Cu (~ +0.34 V) in conjunction with the $E_{h^-pH}$ diagrams for the Ti-H$_2$O system (Lee, 1981), it is assumed here that the valence state of Ti, both in the oxide film and solutions, was 4+. Together with the published density value of 2.9 g cm$^{-3}$ for TiO$_2$ films (Anderson et al., 1997), it was calculated that there was $1.35 \times 10^{-9}$ mol mm$^{-2}$ of Ti$^{4+}$ associated with oxide film formation. According to the 8 week-results in Figure 5-4, we calculated that there were $520 \times 10^{-9}$, $50 \times 10^{-9}$, and $28 \times 10^{-9}$ mol mm$^{-2}$ of Ti$^{4+}$ ions dissolved in the SCICu solutions with no addition, with 1 g L$^{-1}$ Fe$^{3+}$ addition, and with 5 g L$^{-1}$ Fe$^{3+}$ addition, respectively. It is obvious that the amount of Ti$^{4+}$ associated with oxide formation is negligible compared to that which dissolved in SCICu solutions with no or 1 g L$^{-1}$ Fe$^{3+}$ addition; while there was 5% of Ti$^{4+}$ associated with oxide formation in the SCICu solution with 5 g L$^{-1}$ Fe$^{3+}$ addition. Since the total corrosion rate of Ti is equal to the metal dissolution plus passive film formation, it can be assumed here that the total corrosion rate of Ti is approximately equal to the dissolution rate of Ti$^{4+}$ under conditions with ≤ 1 g L$^{-1}$ Fe$^{3+}$ additions.

Figure 5-5 shows the surface morphology of samples after 8 weeks of immersion in the experimental solutions. Given that no sign of localized corrosion was observed on any of the specimens, Eq. (5–1) was used to calculate the corrosion rates from the 8 week-results (Figure 5-4). The calculated results are presented in Table 5-1. The corrosion rate decreased from more than 62 mm yr$^{-1}$ to less than 0.1 mm yr$^{-1}$ with the addition of either 15 g L$^{-1}$ Cu$^{2+}$ or 15 g L$^{-1}$ Cu$^{2+}$ + 1 g L$^{-1}$ Fe$^{3+}$ in SCICl solutions at 150 °C. Therefore, the oxidative conditions that prevail in the presence of either Cu$^{2+}$ or Fe$^{3+}$ ions should be maintained at all the times for the protection of
Ti-liners used in pressure leaching autoclaves. Moreover, the corrosion rate decreased by an order of magnitude with only 1 g L\(^{-1}\) Fe\(^{3+}\) addition in the SCICu solution, which indicates that Fe\(^{3+}\) ions are more effective than Cu\(^{2+}\) ions as a corrosion inhibitor. However, the corrosion rate did not decrease as dramatically when the Fe\(^{3+}\) concentration was increased from 1 g L\(^{-1}\) to 5 g L\(^{-1}\). Thus 1 g L\(^{-1}\) Fe\(^{3+}\) is sufficient to ensure adequate Ti performance in typical medium temperature sulphide leaching environments.

Table 5-1 Corrosion rates of Ti in the SCICu solutions with different Fe\(^{3+}\) additions at 150 and 175 °C.

<table>
<thead>
<tr>
<th>Fe(^{3+}) (g L(^{-1}))</th>
<th>Corrosion rate* by mass loss (mm yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.67\times10^{-2}</td>
</tr>
<tr>
<td>1</td>
<td>3.22\times10^{-3}</td>
</tr>
<tr>
<td>5</td>
<td>2.08\times10^{-3}</td>
</tr>
</tbody>
</table>

Note: Corrosion rate*, 8 week-results from mass loss measurements.
Figure 5-5 Sample morphology of Ti after 8-weeks of immersion in the SCICu solutions (a) with no addition, (b) with 1 g L$^{-1}$ Fe$^{3+}$ addition, and (c) with 5 g L$^{-1}$ Fe$^{3+}$ addition at 150 °C.
5.2.4 Iso-corrosion diagrams of Ti in H$_2$SO$_4$ solutions up to 175 °C

Iso-corrosion diagrams present a large amount of experimental data in a highly centralized but simple form, which can easily be used to predict the corrosion resistance of materials in specific environments. Iso-corrosion diagrams with 0.1, 0.5 and 1.0 mm yr$^{-1}$ Iso-corrosion lines for Ti in H$_2$SO$_4$ solutions are presented in Figures 5-6, 5-7 and 5-8. The Iso-corrosion line of 0.1 mm yr$^{-1}$ (Figure 5-6) for Ti in H$_2$SO$_4$ solutions with no added salts is close to the published value of 0.127 mm yr$^{-1}$ for Ti Grade 2 in H$_2$SO$_4$ solutions (Mountford Jr, 2002).

Iso-corrosion diagrams show that for any fixed corrosion rate, the operating temperature decreases with an increasing H$_2$SO$_4$ concentration in the range of 3–50 wt.%; the presence of 1 g L$^{-1}$ Fe$^{3+}$ or 15 g L$^{-1}$ Cu$^{2+}$ ions significantly extends the operating area below the Iso-corrosion line. It is known that Ti exhibits an active-to-passive transition in H$_2$SO$_4$ solutions when the potential is increased (Kelly, 1979; Kelly et al., 2002). According to our previous work, the presence of Cu$^{2+}$ and Fe$^{3+}$ ions can shift the OCP of Ti in H$_2$SO$_4$ solutions to the passive region (much higher than the primary passivation potential), leading Ti to exhibit spontaneous passivity, i.e., no primary passivation potential–critical anodic current density point is then visible. The oxidative environment (the presence of Cu$^{2+}$ and Fe$^{3+}$ ions) and consequently thicker passive film formed on the Ti surface provides an explanation for the expanded operating area below the Iso-corrosion line in the presence of 1 g L$^{-1}$ Fe$^{3+}$ or 15 g L$^{-1}$ Cu$^{2+}$ ions. This explanation will be proven by our electrochemical measurements in following sections.

In Iso-corrosion diagrams, the presence of 1 g L$^{-1}$ Fe$^{3+}$ is more effective as a corrosion inhibitor than 15 g L$^{-1}$ Cu$^{2+}$ for Ti in H$_2$SO$_4$ solutions and this result is consistent with the above–discussed long-term immersion results as well as our previous electrochemical experimental results. In Iso-corrosion diagrams, the position of the 3 wt.% H$_2$SO$_4$-150 °C point
is below the 0.1 mm yr⁻¹ Iso-corrosion line in the presence of 1 g L⁻¹ Fe³⁺ or 15 g L⁻¹ Cu²⁺, and is far away from the 1.0 mm yr⁻¹ Iso-corrosion line in the absence of oxidizers. These results corroborate the long-term immersion experiments in that the presence of either 15 g L⁻¹ Cu²⁺ or 15 g L⁻¹ Cu²⁺ + 1 g L⁻¹ Fe³⁺ addition can ensure the excellent corrosion resistance of Ti in SCl solution at 150 °C. Iso-corrosion diagrams in this work indicate that Ti is resistant to corrosion in H₂SO₄ solutions up to 15 wt.% at temperatures up to 175 °C when either 1 g L⁻¹ Fe³⁺ or 15 g L⁻¹ Cu²⁺ ions are present; Ti cannot be used in H₂SO₄ solutions in the absence of oxidants with a concentration higher than 3 wt.% at temperatures higher than 55 °C.
Figure 5-6 Iso-corrosion diagram at 0.1 mm yr$^{-1}$ for Ti in 3–50 wt.% H$_2$SO$_4$ solutions (with no addition; with the addition of 15 g L$^{-1}$ Cu$^{2+}$ and with the addition of 1 g L$^{-1}$ Fe$^{3+}$) for temperatures up to 175 °C.
Figure 5-7 Iso-corrosion diagrams at 0.5 mm yr$^{-1}$ for Ti in 3–50 wt.% H$_2$SO$_4$ solutions (with no addition; with the addition of 15 g L$^{-1}$ Cu$^{2+}$ and with the addition of 1 g L$^{-1}$ Fe$^{3+}$) for temperatures up to 175 °C.
Figure 5-8 Iso-corrosion diagrams at 1.0 mm yr$^{-1}$ for Ti in 3–50 wt.% H$_2$SO$_4$ solutions (with no addition; with the addition of 15 g L$^{-1}$ Cu$^{2+}$ and with the addition of 1 g L$^{-1}$ Fe$^{3+}$) for temperatures up to 175 °C.
5.3 Summary

The corrosion rates of Ti were studied using mass loss measurements in H₂SO₄ solutions with different additions of Cl⁻, Cu²⁺ and Fe³⁺ ions up to 175 °C. Based on the experimental results, the following conclusions were obtained:

1) The corrosion rate of Ti was unaffected by the presence of Cl⁻ in sulfuric acid alone.

2) The mixed chloride–sulfuric acid solution is very corrosive for Ti with a freshly polished surface. The corrosion rate of Ti in 30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ solution at 150 °C was estimated to be ≥ 62 mm yr⁻¹.

3) The mass changes of Ti were monitored in simulated pressure leaching solutions at 150 °C for 4, 8 and 16 weeks. The corrosion rate decreased from ≥ 62 mm yr⁻¹ to < 0.1 mm yr⁻¹ with either 15 g L⁻¹ Cu²⁺ addition or 15 g L⁻¹ Cu²⁺ + 1 g L⁻¹ Fe³⁺ addition in 30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ solution at 150 °C. The results from long-term immersion experiments indicated that Cu²⁺ and Fe³⁺ ions were good corrosion inhibitors for Ti.

4) The Iso-corrosion curves (0.1, 0.5, and 1 mm yr⁻¹) of Ti in 3–50 wt.% H₂SO₄ solutions (with no addition; with the addition of 15 g L⁻¹ Cu²⁺ and with the addition of 1 g L⁻¹ Fe³⁺) up to 175 °C were constructed from the mass loss data.
6 Corrosion rates of Ti in H₂SO₄ solutions measured by electrochemical experiments

Mass loss and electrochemical measurements are the two most common methods for the determination of corrosion rates of metals. With a proper experimental design, the corrosion rates of metals obtained by these two methods should be comparable to each other. In the present chapter, the corrosion rates of Ti under simulated pressure leaching conditions were determined polarization resistance measurements and compared with the mass loss results in Chapter 6. As reported in the above chapter, the corrosion rate of Ti in the 30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ (=SCl) solution at 150 °C was ≥ 62 mm yr⁻¹, which indicates that it is not practical to perform long-term electrochemical experiments for Ti in this solution at temperatures around 150 °C. However, the mass loss results also proved that the presence of either 1 g L⁻¹ Fe³⁺ or 15 g L⁻¹ Cu²⁺ ions is sufficient to ensure adequate Ti performance in typical medium temperature copper leaching environments. Therefore, the electrochemical behavior of Ti was studied in 30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ + 15 g L⁻¹ Cu²⁺ (=SClCu) with different Fe³⁺ additions at temperatures from 125 to 175 °C.

6.1 Experimental

Electrochemical experiments were carried out in a 1.8 L autoclave and a glass liner contained the solution. The autoclave was controlled with a PARR 4843 controller system, and the temperature accuracy was ±2 °C. The Ti working electrode (WE) was a cylindrical specimen and the holder was of the Stern-Makrides variation (Asselin et al., 2007; Kelly et al., 2002). The counter electrode (CE) was a Pt wire, and the area ratio CE: WE was around 3. An external pressure balanced reference electrode (EPBRE), Ag/AgCl ([Cl⁻]=1 M), was used as the reference electrode (RE) (Nickchi & Alfantazi, 2012). The RE bridge, subjected to a temperature gradient,
was designed to be filled with the experimental solution. The thermal junction and liquid
junction potential calculation is described in the following section. All the potentials reported in
this work are with respect to the standard hydrogen electrode (SHE) at 25 °C.

The potentiostat used was a Princeton Applied Research Versastat 4 potentiostat/galvanostat.
Prior to each experiment, the WE was abraded using successive grades of SiC papers down to
600 grit, ultrasonically washed for 5 min in DI water, and dried in air; the solution was introduced
to the glass liner. Afterwards, the autoclave was sealed and heated to the desirable
temperature. The PDP experiments were performed from −0.25 V vs. OCP up to 1.0 V vs. RE
(Ag/AgCl, [Cl\(^{-}\)] = 1 M) with a scan rate of 1 mV s\(^{-1}\) after 1 hour OCP measurement. For the
long-term electrochemical experiments, the OCP measurements were carried out for 10 hours.
The EIS experiments were performed at the OCP as a function of time along with the long-term
OCP measurement. The EIS perturbation voltage amplitude was 10 mV (peak to peak). The
frequency range for all experiments was 0.1 Hz to 100 kHz with sampling at 10 points per
decade. The LPR experiments were also performed within the OCP measurement as a function
of time from −20 mV to +20 mV vs. OCP with a scan rate of 0.167 mV s\(^{-1}\).

6.2 Results and discussion

6.2.1 Characterization of the measured potential

All the potentials reported in this chapter are with respect to the SHE at 25 °C. Equations
(2–1)-(2–8) were used to convert the \( E_{\text{measured}} \) to the SHE scale at 25 °C. The high temperature
electrochemical response of Ti was measured in the SCICu solution with different Fe\(^{3+}\) additions
(0-5 g L\(^{-1}\)) at temperatures around 150 °C. Since the portion of the EPBRE subjected to the
temperature gradient was filled with the experimental solution, \( E_{\text{TJ}} \) and \( E_{\text{IR}} \) originated from this
solution. Ions involved in the \( E_{\text{measured}} \) conversion are included in Table 6-1. The contribution of Fe\(^{3+}\) to the \( E_{\text{measured}} \) was not taken into account because the concentration of Fe\(^{3+}\) (in mol L\(^{-1}\)) was orders of magnitude lower than the other solution constituents. The required ion concentration \( C_i \) and ionic mobility \( u_i \) in the experimental solution from 25 to 115 °C were calculated using the OLI Electrolyte Simulation Software. A second order polynomial regression method was used to find the best correlation function of \( C_i = f(T) \), i.e., \( C_i = A_1(T-273)^2 + B_1(T-273) + C_1 \); while a linear regression method was used to find the best correlation function of \( u_i = f(T) \), i.e., \( u_i = A_2(T-273) + B_2 \). The fitting equations are listed in Table 6-1. Due to the limitation of the OLI Software, values of \( u_i \) and \( C_i \) from 115 to 175 °C were calculated by fitting equations (Table 6-1) based on data from 25 to 115 °C. The \( E_{\text{TLJ}} \) and \( R \) were calculated for three different initial temperatures. The values of \( E_{\text{TLJ}} \), \( R \) and \( E_{\text{LJP}} \) at various autoclave operating temperatures are presented in Table 6-2. In view of the small values of \( R \), \( iR \) was omitted in the potential characterization.
Table 6-1 Constants of the fitting equations, $C_i = A_1(T−273)^2 + B_1(T−273) + C_1$ and $u_i = A_2(T−273) + B_2$.

<table>
<thead>
<tr>
<th>Ions involved</th>
<th>$A_1$ (mol cm$^{-3}$ K$^{-2}$)</th>
<th>$B_1$ (mol cm$^{-3}$ K$^{-1}$)</th>
<th>$C_1$ (mol cm$^{-3}$)</th>
<th>$A_2$ (cm$^2$ V$^{-1}$ s$^{-1}$ K$^{-1}$)</th>
<th>$B_2$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
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</thead>
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<td>H$^+$</td>
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<td>-4.016×10$^{-3}$</td>
<td>0.358</td>
<td>1.961×10$^{-3}$</td>
<td>2.174×10$^{-3}$</td>
</tr>
<tr>
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<td>-1.598×10$^{-5}$</td>
<td>4.016×10$^{-3}$</td>
<td>0.254</td>
<td>7.021×10$^{-6}$</td>
<td>1.977×10$^{-4}$</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>1.075×10$^{-5}$</td>
<td>-2.932×10$^{-3}$</td>
<td>0.227</td>
<td>1.289×10$^{-3}$</td>
<td>2.327×10$^{-4}$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0</td>
<td>0</td>
<td>0.338</td>
<td>8.210×10$^{-6}$</td>
<td>1.388×10$^{-4}$</td>
</tr>
<tr>
<td>Cl$^-$</td>
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<td>-4.255×10$^{-4}$</td>
<td>0.306</td>
<td>1.075×10$^{-3}$</td>
<td>2.680×10$^{-4}$</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>-1.758×10$^{-6}$</td>
<td>-4.380×10$^{-4}$</td>
<td>0.204</td>
<td>9.911×10$^{-6}$</td>
<td>1.265×10$^{-4}$</td>
</tr>
<tr>
<td>CuCl$^+$</td>
<td>1.645×10$^{-6}$</td>
<td>4.505×10$^{-4}$</td>
<td>0.027</td>
<td>4.818×10$^{-5}$</td>
<td>6.438×10$^{-5}$</td>
</tr>
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Table 6-2 The values of $E_{TLJ}$, $R$ and $E_{LJP}$ at various autoclave operating temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$E_{TLJ}$ (V)</th>
<th>R (Ω)</th>
<th>$E_{LJP}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>-0.08</td>
<td>4.70</td>
<td>-0.02</td>
</tr>
<tr>
<td>150</td>
<td>-0.11</td>
<td>3.75</td>
<td>-0.02</td>
</tr>
<tr>
<td>175</td>
<td>-0.13</td>
<td>3.41</td>
<td>-0.02</td>
</tr>
</tbody>
</table>
6.2.2 Potentiodynamic polarization

Figure 6-1 Potentiodynamic polarization curves for Ti after 1 hour immersion in the (≈SCICu) solutions with different Fe\textsuperscript{3+} additions at 150 °C.
Figure 6-1 presents the PDP behavior of Ti in the SCICu solution with different Fe$^{3+}$ additions at 150 °C. In Figure 6-1, the corrosion potential ($E_{corr}$) was not remarkably affected by the addition of 1 g L$^{-1}$ Fe$^{3+}$ to the SCICu solution; while the presence of 5 g L$^{-1}$ Fe$^{3+}$ ions shifted the $E_{corr}$ of Ti to a much higher value compared to the results from the other two solutions. As shown in Figure 6-1, Ti exhibited spontaneous passivity in H$_2$SO$_4$ solutions with Cu$^{2+}$ and Fe$^{3+}$ additions, suggesting either a thicker or more protective passive film formed on the Ti surface. (Kelly et al., 2002) The presence of Fe$^{3+}$ ions remarkably decreased the passive current density ($i_{passive}$). This conclusion is consistent with previous electrochemical results in that the presence of Fe$^{3+}$ had the most significant beneficial effect on decreasing the $i_{passive}$ of Ti in H$_2$SO$_4$ solutions at temperatures below 100 °C. Thus, Fe$^{3+}$ ions can enhance the passivity of the Ti in the SCICu solution in certain potential ranges (from OCP to 1.2 V vs. SHE).

Figure 6-2 shows the $i_{passive}$ of Ti at 1.2 V vs. SHE obtained by PDP measurements in the SCICu solution with different Fe$^{3+}$ additions at temperatures from 125 to 175 °C. In Figure 6-2, for each electrolyte, the $i_{passive}$ of Ti increased with an increasing temperature; at 125 and 150 °C, the measured $i_{passive}$ of Ti in the SCICu solution decreased significantly when increasing the Fe$^{3+}$ concentration from 0 to 1 g L$^{-1}$, but did not decrease remarkably when increasing the Fe$^{3+}$ concentration from 1 g L$^{-1}$ to 5 g L$^{-1}$, which is in complete agreement with the above long-term immersion results; on the contrary, at 175 °C, the measured $i_{passive}$ of Ti in the SCICu solution decreased almost linearly with increasing Fe$^{3+}$ concentration up to 5 g L$^{-1}$. In order to investigate the effect of Fe$^{3+}$ ions on the electrochemical responses of Ti in the SCICu solution, long-term electrochemical experiments were carried out at 150 and 175 °C.
Figure 6-2 Passive current densities at 1.2 V obtained by PDP measurements for Ti after 1 hour immersion in the SCiCu solutions with different Fe$^{3+}$ additions at temperatures from 125 to 175 °C.
6.2.3 Electrochemical impedance spectroscopy

EIS experiments were performed to investigate the passive film properties as a function of exposure time. An EIS experiment was carried out after every hour of OCP measurement. The results from 10 hours of OCP measurement are presented in Figure 6-3. Figure 6-3 shows that for all experimental solutions, the OCP value was relatively stable within each 10−hour OCP experiment and was not obviously affected by increasing temperature from 150 °C to 175 °C; generally, the OCP value was not affected by the addition of 1 g L−1 Fe3+ to the ScCu solution, and the presence of 5 g L−1 Fe3+ ions shifted the OCP to a much higher value compared to the results from the other two solutions. This agrees with the $E_{corr}$ results in Figure 6-1. It is important to note that a yellow precipitate formed during the long term electrochemical experiments in the presence of Fe3+ at 150 °C and 175 °C, similar to that observed during immersion experiments. According to the formulas established (Umetsu et al., 1977), the Fe3+ solubility in 30 g L−1 H2SO4 solutions would be around 0.37 g L−1 and 0.23 g L−1 at 150 °C and 175 °C, respectively, which are lower concentrations than the Fe3+ concentrations used in this work, i.e. 1 and 5 g L−1. Thus, the presence of a ferric precipitate is expected.

Bode plots of Ti in the ScCu solution with different Fe3+ additions at 150 and 175 °C within the long-term OCP measurements are shown in Figure 6-4. Figure 6-4 (a) and (d) show that the Bode plots of Ti were relatively stable within the 10 hour−OCP measurements in the ScCu solutions at 150 and 175 °C. Figure 6-4 (b) and (c) show that at 150 °C, Bode plots changed as a function of the exposure time in the ScCu solutions with Fe3+ additions, and the development of a second time constant was probably due to the gradual precipitation of jarosite on the WE’s surface in the ScCu solutions with Fe3+ at 150 °C. Figure 6-4 (e) and (f) show that the Bode plots of Ti were stable within the 10 hour−OCP measurements in the ScCu solutions with Fe3+.
additions at 175 °C. In order to get more details of the ongoing processes at the interface, the EIS datasets were analyzed by EECs.

Figure 6-3 OCP vs. time for Ti in the SCICu solutions with different Fe$^{3+}$ additions at 150 and 175 °C.
Figure 6-4 Bode plots for Ti in the SClCu solutions with (a) no Fe$^{3+}$ at 150 °C, (b) 1 g L$^{-1}$ Fe$^{3+}$ at 150 °C, (c) 5 g L$^{-1}$ Fe$^{3+}$ at 150 °C, (d) no Fe$^{3+}$ at 175 °C, (e) 1 g L$^{-1}$ Fe$^{3+}$ at 175 °C, and (f) 5 g L$^{-1}$ Fe$^{3+}$ at 175 °C as a function of exposure time.
Many papers have been published in the field of Ti corrosion related to chloride/sulfate solutions (Assis et al., 2006; Aziz-Kerrzo et al., 2001; de Souza & Robin, 2007; Delgado-Alvarado & Sundaram, 2007; González & Mirza-Rosca, 1999; He et al., 2002; He et al., 2007; Mogoda et al., 2004; Pan et al., 1996; Shibata & Zhu, 1995). Considering the precipitation phenomenon mentioned above, the EECs of $R_{sol}(R_{film}Q_{film})$ and $R_{sol}(Q_{deposit}(R_{film}Q_{film}))$ were used, and also gave the best fitting results for our data. The typical error for each parameter is: $R_{sol}$, 0.75%; $Q_{film}-Y_0$, 0.2%; $Q_{film}-n$, 0.2%; $R_{film}$, 1.0%; $R_{deposit}$, 0.6%; $Q_{deposit}-Y_0$, 0.3%; $Q_{deposit}-n$, 0.3%.

These two EECs include solution resistance ($R_{sol}$), constant–phase element (CPE) behavior for oxide film ($Q_{film}$), oxide film resistance ($R_{film}$), CPE behavior for deposit layer ($Q_{deposit}$), and deposit layer resistance ($R_{deposit}$). Figure 6-5 shows the diagrams corresponding to these equivalent circuits. The fitting results for experiments in the presence of 1 g L$^{-1}$ and 5 g L$^{-1}$ Fe$^{3+}$ additions at 150 °C are presented in Tables 6-3 and 6-4, respectively. Since Bode plots did not change obviously as a function of exposure time under the other experimental conditions, as shown in Figure 6-4, only the fitting results for the EIS data obtained after 10 hours of exposure are presented in Table 6-5.
Figure 6-5 The equivalent circuits (a) $R_{sol}(Q_{film}R_{film})$ and (b) $R_{sol}(Q_{deposit}(R_{deposit}(R_{film}Q_{film})))$ used to fit the EIS data.
Tables 6-3 and 6-4 show that $R_{sol}$, $R_{deposit}$ and $R_{film}$ all increased during the exposure in the SCICu solution at any level of Fe$^{3+}$ addition at 150 °C. The value of the magnitude of impedance at high frequency corresponds to $R_{sol}$. As shown by the arrows of the Bode magnitude plots in Figure 6-4 (b) and (c), the value of $R_{sol}$ increased during the exposure in the SCICu solution with any level of Fe$^{3+}$ addition at 150 °C. The layer of precipitate is not compact. Due to diffusion, the solution concentration near the sample surface must be different from that of the bulk solution and change as a function of exposure time. This leads to an increase in $R_{sol}$. The increase of $R_{deposit}$ can be attributed to the gradual precipitation of jarosite on the WE’s surface. The increase of $R_{film}$ indicates that the presence of Fe$^{3+}$ ions improved the corrosion resistance of the passive films in the SCICu solution at 150 °C. According to Hsu and Mansfeld’s work, capacitance values can be extracted from CPE data using Eq. (6-1) (Hsu & Mansfeld, 2001).

$$C = Q^{1/n} R^{(1-n)/n}$$

(6-1)

After calculation, $C_{film}$ values of Ti were also listed in Tables 6-3 and 6-4, and suggest that $C_{film}$ values are relatively unchanged during the exposure in the SCICu solution at any level of Fe$^{3+}$ addition at 150 °C. Since $C_{film} \sim \delta_{film}^{-1}$ ($\delta_{film}$ is the film thickness) (Hirschorn et al., 2010), these $R_{film}$ and $C_{film}$ values indicate that the presence of Fe$^{3+}$ ions improved the corrosion resistance of the passive films without thickening in the SCICu solution at 150 °C.
Table 6-3 Summary of EIS equivalent circuit fitting data for Ti in 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$ + 15 g L$^{-1}$ Cu$^{2+}$ + 1 g L$^{-1}$ Fe$^{3+}$ (=SICu1Fe) solution at 150 °C.

<table>
<thead>
<tr>
<th>$t$ (h)</th>
<th>$R_{sol}$ (Ω cm$^2$)</th>
<th>$R_{deposit}$ (Ω cm$^2$)</th>
<th>$Q_{deposit-Y_0}$ (μF cm$^{-2}$ s$^{-1}$)</th>
<th>$Q_{deposit-n}$ (μF cm$^{-2}$ s$^{-1}$)</th>
<th>$R_{film}$ (Ω cm$^2$)</th>
<th>$Q_{film-Y_0}$ (μF cm$^{-2}$ s$^{-1}$)</th>
<th>$Q_{film-n}$ (μF cm$^{-2}$)</th>
<th>$C_{film}$ (μF cm$^{-2}$)</th>
<th>$X^2 \times 10^5$</th>
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</thead>
<tbody>
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<td>1030</td>
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<td>48</td>
<td>1.00</td>
<td>48</td>
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<tr>
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<td>3.8</td>
<td>577</td>
<td>0.81</td>
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Table 6-4 Summary of EIS equivalent circuit fitting data for Ti in 30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\) + 15 g L\(^{-1}\) Cu\(^{2+}\) + 5 g L\(^{-1}\) Fe\(^{3+}\) (=SCI\(_5\)Cu\(_5\)Fe) solution at 150 °C.

<table>
<thead>
<tr>
<th>(t) (h)</th>
<th>(R_{sol}) ((\Omega \text{ cm}^2))</th>
<th>(R_{deposit}) ((\Omega \text{ cm}^2))</th>
<th>(Q_{deposit-Y_0}) ((\mu\text{F cm}^{-2} s^{n-1}))</th>
<th>(Q_{deposit-n}) ((\mu\text{F cm}^{-2} s^{n-1}))</th>
<th>(R_{film}) ((\Omega \text{ cm}^2))</th>
<th>(Q_{film-Y_0}) ((\mu\text{F cm}^{-2} s^{n-1}))</th>
<th>(Q_{film-n}) ((\mu\text{F cm}^{-2} s^{n-1}))</th>
<th>(C_{film}) ((\mu\text{F cm}^{-2}))</th>
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<td>0.8</td>
<td>532</td>
<td>10.5</td>
</tr>
<tr>
<td>3</td>
<td>18.9</td>
<td>43.8</td>
<td>500</td>
<td>0.90</td>
<td>8.8 \times 10^4</td>
<td>219</td>
<td>0.8</td>
<td>547</td>
<td>9.4</td>
</tr>
<tr>
<td>4</td>
<td>23.1</td>
<td>51.5</td>
<td>383</td>
<td>0.85</td>
<td>9.0 \times 10^4</td>
<td>243</td>
<td>0.8</td>
<td>543</td>
<td>4.7</td>
</tr>
<tr>
<td>5</td>
<td>25.7</td>
<td>57.2</td>
<td>305</td>
<td>0.90</td>
<td>8.9 \times 10^4</td>
<td>269</td>
<td>0.8</td>
<td>530</td>
<td>6.3</td>
</tr>
<tr>
<td>6</td>
<td>28.5</td>
<td>70.6</td>
<td>268</td>
<td>0.92</td>
<td>9.0 \times 10^4</td>
<td>297</td>
<td>0.9</td>
<td>552</td>
<td>5.2</td>
</tr>
<tr>
<td>7</td>
<td>31.1</td>
<td>71.7</td>
<td>258</td>
<td>0.88</td>
<td>8.8 \times 10^4</td>
<td>315</td>
<td>0.9</td>
<td>510</td>
<td>7.6</td>
</tr>
<tr>
<td>8</td>
<td>33.4</td>
<td>77.1</td>
<td>253</td>
<td>0.88</td>
<td>9.0 \times 10^4</td>
<td>321</td>
<td>0.9</td>
<td>562</td>
<td>8.1</td>
</tr>
<tr>
<td>9</td>
<td>35.7</td>
<td>82.9</td>
<td>242</td>
<td>0.87</td>
<td>9.4 \times 10^4</td>
<td>331</td>
<td>0.9</td>
<td>545</td>
<td>9.3</td>
</tr>
<tr>
<td>10</td>
<td>38.3</td>
<td>101.9</td>
<td>231</td>
<td>0.84</td>
<td>9.6 \times 10^4</td>
<td>346</td>
<td>0.9</td>
<td>500</td>
<td>8.2</td>
</tr>
</tbody>
</table>
Table 6-5 The summary of EIS fitting data for Ti after 10-hour exposure in SCICu solutions with different Fe$^{3+}$ additions at 150 and 175 °C.

| T (°C) | Fe$^{3+}$ (g L$^{-1}$) | $R_{sol}$ (Ω cm$^2$) | $R_{deposit}$ (Ω cm$^2$) | $Q_{deposit} - Y_0$ (μF cm$^{-2}$ s$^{-1}$) | $Q_{deposit} - n$ | $R_{film}$ (Ω cm$^2$) | $Q_{film} - Y_0$ (μF cm$^{-2}$ s$^{-1}$) | $Q_{film} - n$ | $X^2 \times 10^5$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0</td>
<td>1.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4743</td>
<td>73</td>
<td>0.97</td>
<td>4.5</td>
</tr>
<tr>
<td>175</td>
<td>0</td>
<td>1.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>676</td>
<td>70</td>
<td>0.97</td>
<td>4.9</td>
</tr>
<tr>
<td>175</td>
<td>1</td>
<td>6.0</td>
<td>15.6</td>
<td>48</td>
<td>0.90</td>
<td>1506</td>
<td>47</td>
<td>0.96</td>
<td>3.1</td>
</tr>
<tr>
<td>175</td>
<td>5</td>
<td>29</td>
<td>37.1</td>
<td>173</td>
<td>0.89</td>
<td>15120</td>
<td>675</td>
<td>0.81</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 6-5 presents that $R_{sol}$, $R_{deposit}$ and $R_{film}$ of Ti all increased with increasing Fe$^{3+}$ concentration at 175 °C. Since the Fe$^{3+}$ solubility in the SCICu solution would be around 0.23 g L$^{-1}$ at 175 °C, there would be more precipitation on the sample surface from the solution with 5 g L$^{-1}$ Fe$^{3+}$ additions (as actually observed after the experiments), which makes the higher $R_{deposit}$ value reasonable. Table 6-5 also shows that at 175 °C, the $R_{film}$ of Ti in the SCICu solution increased significantly in the presence of 5 g L$^{-1}$ Fe$^{3+}$ ions, which is consistent with the $i_{passive}$ results in Figure 6-2. Thus, it can be concluded that the presence of Fe$^{3+}$ is the most important factor for the growth of Ti oxide films under pressure leaching conditions.
6.2.4 Polarization resistance and corrosion rate calculations

LPR experiments were also performed during the course of the long-term OCP measurements. As shown in Figure 6-6, LPR and EIS experiments gave similar polarization resistance ($R_p$) results for each condition; the $R_p$ value of Ti in the SClCu solution increased with an increasing amount of Fe$^{3+}$ at both 150 and 175 °C; also, the $R_p$ value of Ti gradually increases versus time in the SClCu solution with both 1 g L$^{-1}$ and 5 g L$^{-1}$ Fe$^{3+}$ additions at 150 °C. Figure 6-6 also shows that during the entire exposure time, the $R_p$ value remained nearly constant in the SClCu solution at 150 °C and in all solutions at 175 °C, which was consistent with the Bode plots.
Figure 6-6 $R_p$ vs. time for Ti in the SCICu solutions with different Fe$^{3+}$ additions at (a) 150 °C and (b) 175 °C.
In order to quantitatively compare with the results from immersion experiments, the corrosion rates of Ti in the various experimental solutions were estimated using Eq. (6-2)-(6-3) (Ahmad, 2006).

\[
Corrosion rates \ (mm \ yr^{-1}) = C \cdot \frac{M_{corr}}{n \rho} \tag{6-2}
\]

\[
i_{corr} = \frac{B}{R_p} \tag{6-3}
\]

\[
B = 2.3 \left( \frac{1}{\beta_{ox}} + \frac{1}{\beta_{red}} \right)^{-1} \tag{6-4}
\]

Where \(i_{corr}\) is the current density in \(\mu A \ cm^{-2}\); \(C\) is a constant which includes \(F\) and any other conversion factor for mm yr\(^{-1}\) (\(C = 3.27 \times 10^{-3}\) s mm mol yr\(^{-1}\) cm\(^{-1}\)); \(M\) is the atomic mass equal to 47.87 g mol\(^{-1}\); \(\rho\) is the density of 4.50 g cm\(^{-3}\); \(n\) is the valence state of Ti, and has been assumed to be 4+ for Ti in both the oxide film and solutions. According to the polarization curves in Figure 6-1, all the cathodic and anodic Tafel slope values, i.e., \(\beta_{ox}\) and \(\beta_{red}\), were estimated to be around 0.08 V and 0.70 V, respectively. Thus, \(B\) is the Stern–Geary constant, and is approximately 0.03 V in this work, which is very close to the common approximated value, \(B \approx 0.026\) V (Stansbury & Buchanan, 2000). Since the EIS and LPR experiments give similar \(R_p\) results, only the \(R_{p-LPR}\) value at the end of each 10-hour OCP measurement was used.

The values of \(R_{p-LPR}\), \(i_{corr}\), and the corrosion rate of Ti by LPR experiments are summarized in Table 6-6. The corrosion rates calculated from the electrochemical experiments represent the sum of the charge associated with Ti\(^{4+}\) dissolution and oxide film growth; whereas the corrosion rates calculated from the mass loss data only represent Ti\(^{4+}\) dissolution (albeit representing the
The vast majority of the charge passed as previously discussed. The corrosion rates obtained from both electrochemical and mass loss experiments are also compared in Table 6-6. From the data listed in Table 6-6, we can calculate that the contribution of the charge passed that is associated with Ti$^{4+}$ dissolution is 93.4%, 92.3%, and 82.9% for the no addition, 1 g L$^{-1}$ Fe$^{3+}$ addition, and 5 g L$^{-1}$ Fe$^{3+}$ addition conditions, respectively. Therefore, it can be confirmed that it is reasonable to use mass loss to determine the corrosion rate of Ti in solutions with $\leq$ 1 g L$^{-1}$ Fe$^{3+}$ addition. However, in the case of the solutions with $\geq$5 g L$^{-1}$ Fe$^{3+}$, the error is significant when applying only mass loss to determine the corrosion rate of Ti. The increased proportion of Ti$^{4+}$ ions associated with oxide film formation upon increase of solution Fe$^{3+}$ concentration provides further support for our conclusion that the presence of Fe$^{3+}$ ions enhances the growth of the passive film.
Table 6-6 Corrosion rates of Ti in the SCICu solutions with different Fe$^{3+}$ additions at 150 and 175 °C.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Fe$^{3+}$ (g L$^{-1}$)</th>
<th>$R_p$-LPR (kΩ)</th>
<th>$i_{corr}$ (µA cm$^{-2}$)</th>
<th>Corrosion rate by polarization resistance (mm yr$^{-1}$)</th>
<th>Corrosion rate* by mass loss (mm yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0</td>
<td>6.64</td>
<td>4.51</td>
<td>3.93×10$^{-2}$</td>
<td>3.67×10$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>75.9</td>
<td>0.39</td>
<td>3.49×10$^{-3}$</td>
<td>3.22×10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>103</td>
<td>0.28</td>
<td>2.51×10$^{-3}$</td>
<td>2.08×10$^{-3}$</td>
</tr>
<tr>
<td>175</td>
<td>0</td>
<td>0.78</td>
<td>38.4</td>
<td>0.33</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.61</td>
<td>18.5</td>
<td>0.16</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>17.3</td>
<td>1.73</td>
<td>0.01</td>
<td>–</td>
</tr>
</tbody>
</table>

Note: Corrosion rate*, 8 week-results from mass loss measurements.

Overall, the electrochemical results agree with immersion results in that, at 150 °C, the corrosion rate decreased by an order of magnitude with only 1 g L$^{-1}$ Fe$^{3+}$ addition in the SCICu solution. The corrosion rate did not decrease dramatically when the Fe$^{3+}$ concentration was increased from 1 g L$^{-1}$ to 5 g L$^{-1}$. The electrochemical results suggest that at 175 °C, increasing Fe$^{3+}$ concentration increases the inhibition of Ti corrosion. However, unlike the case at 150 °C, where after 1 g L$^{-1}$ Fe$^{3+}$ addition little improvement in corrosion resistance was observed, at 175 °C the corrosion resistance showed appreciable increase from 1 to 5 g L$^{-1}$ Fe$^{3+}$ addition, as shown in Figure 6-2 and Figure 6-4 (b).
6.3 Summary

The corrosion behavior of Ti was studied using mass loss and electrochemical measurements in $\text{H}_2\text{SO}_4$ solutions with different additions of $\text{Cl}^-$, $\text{Cu}^{2+}$ and $\text{Fe}^{3+}$ ions up to 175 °C. Based on the experimental results presented in Chapter 5 and Chapter 6, the following conclusions were obtained:

1) $\text{Cu}^{2+}$ and $\text{Fe}^{3+}$ ions were good corrosion inhibitors for Ti. Results from mass loss and electrochemical measurements suggest that temperature; acid concentration and the presence of $\text{Cu}^{2+}$ or $\text{Fe}^{3+}$ ions govern the position of each Iso-corrosion line.

2) The long-term OCP experiments along with LPR and EIS data show that the $R_p$ gradually increases as a function of the exposure time in the $\text{SClCu}$ solution with either 1 g L$^{-1}$ or 5 g L$^{-1}$ $\text{Fe}^{3+}$ additions at 150 °C.

3) Mass loss results generally agreed with corrosion rates calculated from LPR results. That is, the corrosion rate decreased by an order of magnitude with only 1 g L$^{-1}$ $\text{Fe}^{3+}$ addition in the $\text{SClCu}$ solution at 150 °C, and the corrosion rate did not decrease substantially when the $\text{Fe}^{3+}$ concentration was increased from 1 g L$^{-1}$ to 5 g L$^{-1}$. The difference observed in the corrosion rates estimated from mass loss and electrochemical experiments also suggested that the error is appreciable when applying mass loss to determine the corrosion rate of Ti in solutions with $\geq$ 5 g L$^{-1}$ $\text{Fe}^{3+}$ addition.
7 Effects of temperature and sulfate on the pitting corrosion of Ti in high-temperature chloride solutions

As mentioned in Chapter 5, the corrosion rate of Ti in an acidic mixed \( \text{SO}_4^{2-}/\text{Cl}^- \) solution at 150 °C was \( \geq 62 \text{ mm yr}^{-1} \), which indicates that it is not safe and practical to perform electrochemical experiments for Ti in this solution at elevated temperatures. Therefore in the present chapter, the effects of both temperature (100-230 °C) and \( \text{SO}_4^{2-} \) (0-0.5 mol L\(^{-1} \)) on the pitting corrosion of titanium were studied in neutral \( \text{Cl}^- \) containing solutions. One objective of the present work was to investigate the temperature dependence of the \( E_b \) and the repassivation potential (\( E_{rp} \)) of Ti in 1 mol L\(^{-1} \) NaCl solution. Another objective was to study the inhibition effect of \( \text{SO}_4^{2-} \) ions on the pitting corrosion of Ti in \( \text{Cl}^- \) containing solution. In the meantime, a metastable pitting temperature threshold (MPTT) was defined for Ti as a function of \( \text{SO}_4^{2-}/\text{Cl}^- \) mole ratio using linear-sweep thermammetry measurements.

7.1 Experimental

The neutral supporting electrolyte was 1 mol L\(^{-1} \) NaCl to which Na\(_2\)SO\(_4\) was added to yield different \( \text{SO}_4^{2-} \) concentrations (0-0.5 mol L\(^{-1} \)). Electrochemical experiments were carried out in a 1.8 L autoclave and a glass liner contained the experimental solutions. The autoclave was controlled with a PARR 4843 controller system, and the temperature accuracy was \( \pm 2 \) °C. The Ti working electrode (WE) was a cylindrical specimen with a surface area of 4 cm\(^2\) and the holder was of the Stern-Makrides variation (Asselin et al., 2007; Kelly et al., 2002). The counter electrode (CE) was a Pt mesh, and the area ratio CE: WE was around 3. An external pressure balanced reference electrode (EPBRE), Ag/AgCl ([Cl\(^-\)]\(=\)1 mol L\(^{-1} \), +0.235 V vs. the standard hydrogen electrode (SHE) at 25 °C), was used as the reference electrode (RE) (Nickchi &
The RE bridge, subjected to a temperature gradient, was designed to be filled with the experimental solution. The thermal junction and liquid junction potential calculation is described in the following section. The potentiostat used was a Princeton Applied Research Versastat 4 potentiostat/galvanostat. Prior to each experiment, the WE was abraded using successive grades of SiC papers down to 600 grit, ultrasonically washed for 5 min in DI water, and dried in air. The experiments were performed in an oxygen-free environment. The solution was sparged with N₂ for at least 30 minutes before beginning each experiment. The oxygen content of the solution was measured with a dissolved oxygen sensor (Omega DOB21 accuracy 12 ppb) to confirm that the solution was oxygen-free. The autoclave was then sealed and heated to the desired temperature.

The $E_b$ and $E_{rp}$ of Ti were determined by cyclic potentiodynamic polarization (CPP) experiments. As suggested by (Azumi & Seo, 2001), titanium will form a TiOOH layer during cathodic polarization at potentials lower than −0.5 V vs. SHE, and convert back to a TiO₂ layer during anodic polarization at potentials between + 0.5 V and 3 V vs. SHE in a neutral solution. For experiments in the autoclave, it is difficult to conduct the preparation procedure (including sealing the autoclave, safety inspection, and heating the autoclave to the desired temperature (~40 min for heating to 100 °C and ~ 90 min for heating to 200 °C)) such that it consistently takes the same amount of time. The different immersion time of the titanium sample in the solution will affect the accuracy and reproducibility of high temperature data. Before each CPP experiment, in order to ensure that each experiment started with a similar sample condition, the WE was cathodically polarized at −1 V vs. RE for 5 min and then allowed to stabilize at open circuit potential for 30 min at the desired temperature. Dugdale and Cotton reported that titanium did not go through visible breakdown before the anodic current density reached 1.67 mA cm⁻² in
1M KCl solution at room temperature; for 1M KCl + 0.1 M H_2SO_4, titanium did not go through breakdown until the anodic current density reached ~ 7.5 mA cm^{-2} at room temperature. Thus, CPP experiments for Ti in 1M NaCl solution with 0-0.5 M Na_2SO_4 additions were performed at a scan rate of 1 mV s^{-1} from open circuit potential to the potential corresponding to an anodic current of 10 mA, and then scanned back from this potential until the current density went below 10 μA (Ovarfort, 1989).

Optical microscopy (OM) was used to observe the morphology of the pits formed on the samples after the CPP experiments. There were 9 CPP conditions varying with the operating temperature and the concentration of Na_2SO_4. These 9 conditions were labeled from A to I (listed in Table 7-1) and they will be referred to by their associated letter throughout the remainder of this work. The linear-sweep thermammetry technique was based on recording the current density in the investigated system at an applied potential as a function of the operating temperature. (Deng et al., 2008; Mun et al., 2010) The applied potential in this work is 0.8 V vs. RE, and the reason for choosing this value is discussed in the section of “Effect of temperature and sulfate ions on metastable pitting”. After the autoclave was heated to 100 °C, the WE was first cathodically polarized at −1 V vs. RE for 5 min, and allowed to stabilize at open circuit potential for 10 min afterwards. An anodic potential of 0.8 V vs. RE was then applied. After 1 hour potentiostatic polarization at 0.8 V vs. RE at 100 °C, the solution temperature was increased at a rate of 0.5 °C min^{-1} from 100 to 230 °C.

To clarify the effect of SO_4^{2-} on the pitting corrosion of Ti in Cl^{-} containing solutions, immersion tests were performed in both 1 mol L^{-1} NaCl and 1 mol L^{-1} NaCl + 0.5 mol L^{-1} Na_2SO_4 solutions at 175 °C for 1 month. After immersion, the samples were washed by DI water, and then analyzed by XPS.
Table 7-1 CPP conditions and results for Ti in 1 mol L$^{-1}$ NaCl solution with different Na$_2$SO$_4$ additions at temperatures from 100 to 200 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature (°C)</th>
<th>Na$_2$SO$_4$ (mol L$^{-1}$)</th>
<th>Pitting/ No pitting</th>
<th>$E_{bd}$ (V vs. SHE)</th>
<th>$E_{rp}$ (V vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>0</td>
<td>No pitting</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>B</td>
<td>125</td>
<td>0</td>
<td>Pitting</td>
<td>3.6</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>150</td>
<td>0</td>
<td>Pitting</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>D</td>
<td>175</td>
<td>0</td>
<td>Pitting</td>
<td>1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>E</td>
<td>200</td>
<td>0</td>
<td>Pitting</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
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<td>Pitting</td>
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<td>1.1</td>
</tr>
<tr>
<td>G</td>
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<td>Pitting</td>
<td>4.4</td>
<td>2.6</td>
</tr>
<tr>
<td>H</td>
<td>175</td>
<td>0.5</td>
<td>No pitting</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>I</td>
<td>200</td>
<td>0.5</td>
<td>No pitting</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

7.2 Results and discussion

7.2.1 Characterization of the measured potential

All the potentials reported in this chapter are with respect to the SHE at 25 °C. The method used to convert the $E_{measured}$ to the SHE scale at 25 °C has been described above. After calculation, the temperature dependence of $E_{TIL}$ and $R$ for 1 mol L$^{-1}$ NaCl solution is shown in Figure 7-1; at 175 °C, the concentration dependence of $E_{TIL}$ and $R$ for 1 mol L$^{-1}$ NaCl solution with various
Na₂SO₄ additions are shown in Figure 7-2. In view of the small values of $R$, $iR$ was omitted in the potential characterization. The $E_{LJP}$ values are presented in Table 7-2.

Figure 7-1 The temperature dependence of $E_{TIL}$ and $R$ for 1 mol L$^{-1}$ NaCl solution.
Figure 7-2 The concentration dependence of $E_{TIL}$ and $R$ for 1 mol L$^{-1}$ NaCl solution with various Na$_2$SO$_4$ additions at 175 °C.
Table 7-2 The values of liquid junction potential for junction NaCl \([1 \text{ mol L}^{-1}] + \text{Na}_2\text{SO}_4 [x \text{ mol L}^{-1}]//\text{KCl [1 mol L}^{-1}\) at 25 °C.

<table>
<thead>
<tr>
<th>(\text{Na}_2\text{SO}_4 (\text{mol L}^{-1}))</th>
<th>0</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{\text{LJP}}(\text{mV}))</td>
<td>4.3</td>
<td>3.6</td>
<td>2.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

7.2.2 Effect of temperature

Figure 7-3 illustrates the anodic polarization curves in 1 mol L\(^{-1}\) NaCl solution at different temperatures. In Figure 7-3, the corrosion potential \((E_{\text{corr}})\) of Ti in 1 mol L\(^{-1}\) NaCl solution at temperatures from 100 to 200 °C is nearly \(-0.35\) V vs. SHE, which is slightly higher than the reported \(E_{\text{corr}} (\sim -0.50\) V vs. SHE\) of Ti in the same solution with \(\text{N}_2\) purging during the entire experimental process at 25 °C (Jiang \textit{et al.}, 2011b). No obvious active-passive transition below 1.0 V vs. SHE was observed in these polarization curves. This also agrees with the previous findings, which showed that Ti exhibited no obvious active-passive transition in neutral solutions (Jiang \textit{et al.}, 2011b; Thomas & Nobe, 1969). Titanium oxide forms instantly when a freshly polished titanium surface is exposed to air. Since the naturally air-formed titanium oxide film is thermodynamically stable in neutral solutions (Lee, 1981), Ti spontaneously exhibits passivity in neutral solutions. Thus there was no obvious active-passive transition.
Figure 7-3 CPP curves for Ti in 1 mol L$^{-1}$ NaCl solution at temperatures from 100 to 200 °C.
Figure 7-4 The $E_b$ and $E_{rp}$ obtained by CPP measurements for Ti 1 mol L$^{-1}$ NaCl solution at temperatures up to 200 °C. The $E_b^*$ line is from Posey and Bohlmann (1967).
As shown in Figure 7-3, Ti spontaneously passivates in 1 mol L\(^{-1}\) NaCl solution but pits upon anodic polarization at temperatures from 125 to 200 °C; a hysteresis loop appears during a reverse scan, which indicates the presence of stable pits, and the reverse line intersects the forward line at \(E_{rp}\) (Kelly et al., 2002). The \(E_b\) is defined as the potential where the current density continuously exceeds 4 mA. The reason for the selection of 4 mA rather than 100 µA, i.e., the typical value for stainless steels at temperatures below 100 °C, is that the passive current density of Ti can exceed the lower value when operating at higher temperatures (Ovarfort, 1989).

Figure 7-4 shows the \(E_b\) and \(E_{rp}\) of Ti in 1 mol L\(^{-1}\) NaCl solution as a function of temperature. Figure 7-4 also includes \(E_b\) of Ti in 1 mol L\(^{-1}\) NaCl solution determined previously by Posey and Bohlmann (1967), and their results are lower than the results obtained here. The main difference between the present work and Posey and Bohlmann's work is that their experimental solution was O\(_2\) saturated, while the experimental solution in this work is de-aerated using N\(_2\). The important features shown in Figure 7-4 are that \(E_b\) decreases dramatically up to 150 °C and the slope of the \(E_b\) vs. temperature plot becomes less steep from 150 to 200 °C; the \(E_b\) remains constant throughout the entire temperature range. This makes it convenient to estimate the \(E_b\) and \(E_{rp}\) of Ti for other similar conditions.

Figure 7-5 demonstrates the surface morphology of the samples after anodic polarization used to make Figure 7-3. As shown, there is no obvious pit formed on the sample surface at 100 °C (Figure 7-5 (a)); stable pits did form on the sample surface at 125-200 °C (Figure 7-5 (b)-(e)). These observations are in agreement with the CPP results shown in Figure 7-3, which demonstrate that Ti is pitted under Conditions B-F. Figure 7-5(b) shows that several pits were formed after the CPP experiment at 125 °C. Figure 7-5 also shows that the maximum diameter of the pits formed on each sample increases from ~16 to 130 µm as the operating temperature
increases from 125 to 200 °C. The $E_b$ and $E_{rp}$ values of Ti obtained by CPP experiments are listed in Table 7-1. Table 7-1 suggests that the passivity breakdown of Ti can occur at a potential of 1.2 V vs. SHE at 200 °C, which is not far away from the open circuit potential of Ti (~0.90 V vs. SHE) obtained under pressure leaching conditions, for example. As well, the pit formed at 200 °C is visible, and has a diameter of ~130 μm as shown in Figure 7-5 (e). Therefore, Ti is susceptible to pitting corrosion in NaCl solutions at high temperatures. Industry should monitor process conditions in these very aggressive environments that contain high Cl$^-$ concentrations at high temperature.
Figure 7-5 Optical microscopy morphology of pitting attack after anodic polarization for Ti in 1 mol L\(^{-1}\) NaCl solution at temperatures from 100 to 200 °C.
7.2.3 The inhibiting effect of sulfate ions

Figure 7-6 (a) shows the anodic polarization curves in 1 mol L$^{-1}$ NaCl solution with various SO$_4^{2-}$ additions at 175 °C. Firstly, it is noted that in the potential range of −1.0 to 1.0 V vs. SHE, the presence of only 0.1 mol L$^{-1}$ SO$_4^{2-}$ ions shifts the anodic polarization curve to higher current density values; increasing the concentration of SO$_4^{2-}$ ions from 0.1 to 0.5 mol L$^{-1}$ has an insignificant effect on the current density. This suggests that the uniform corrosion rate of Ti oxides was higher in the mixed Cl$^{-}$/SO$_4^{2-}$ media than that in pure Cl$^{-}$ media with the same Cl$^{-}$ concentration. Figure 7-6 (a) also demonstrates that the addition of 0.1-0.5 mol L$^{-1}$ SO$_4^{2-}$ ions to 1 mol L$^{-1}$ NaCl solution has a significant inhibitory effect on the pitting corrosion of Ti. This effect is more effective as the SO$_4^{2-}$ concentration increases, and the pitting corrosion of Ti in 1 mol L$^{-1}$ NaCl solution was totally inhibited by 0.5 mol L$^{-1}$ SO$_4^{2-}$ ions up to 9.0 V vs. SHE at 175 °C. The $E_b$ and $E_{rp}$ of Ti at different SO$_4^{2-}$ additions are summarized in Figure 7-6 (b). Both the $E_b$ and $E_{rp}$ of Ti in 1 mol L$^{-1}$ NaCl solution increase with the concentration of SO$_4^{2-}$ ions, which suggests an important beneficial effect of SO$_4^{2-}$ in reducing the tendency for pitting corrosion of Ti in Cl$^{-}$ containing solutions. In conclusion, the presence of SO$_4^{2-}$ ions in NaCl solutions increased the uniform corrosion rate of Ti; while the inhibiting effect of SO$_4^{2-}$ on the pitting corrosion of Ti in NaCl solutions was also confirmed.
Figure 7-6 (a) CPP curves and (b) the $E_b$ and $E_{rp}$ obtained by CPP measurements for Ti in 1 mol L$^{-1}$ NaCl solution with different Na$_2$SO$_4$ additions at 175 °C
It is well accepted that for metals covered by passive films, the first step in the pitting process is the adsorption of Cl\textsuperscript{−} ions on the oxide-covered surface (Frankel, 1998); also, the film won’t go through breakdown until the surface coverage with aggressive ions exceeds a critical value (Bockris & Minevski, 1993). Since Cl\textsuperscript{−} adsorption is significantly lower than that of sulfate, it has been suggested that the inhibiting effect of SO\textsubscript{4}\textsuperscript{2−} on the pitting corrosion of Ti in Cl\textsuperscript{−} solution can be explained in terms of adsorbed anions at the oxide/solution interface (Dugdale & Cotton, 1964). Jiang et al. demonstrated the existence of Cl\textsuperscript{−} ions in the outer oxide layer of Ti by XPS after immersion in artificially synthesized seawater (0.6 mol L\textsuperscript{−1} NaCl + 0.1 mol L\textsuperscript{−1} Na\textsubscript{2}SO\textsubscript{4}) for 2 months at 200 °C (Jiang et al., 2011b). However, Jiang et al. didn't mention if SO\textsubscript{4}\textsuperscript{2−} ions also existed on the sample surface (Jiang et al., 2011b). In order to clarify the inhibition effect of SO\textsubscript{4}\textsuperscript{2−} ions on the pitting corrosion of Ti in Cl\textsuperscript{−} solution relevant to the present work, samples were immersed in 1 mol L\textsuperscript{−1} NaCl (Sample 1) and 1 mol L\textsuperscript{−1} NaCl + 0.5 mol L\textsuperscript{−1} Na\textsubscript{2}SO\textsubscript{4} (Sample 2) solutions at 175 °C for 1 month. After immersion, XPS was performed to determine the oxidation states of Cl and S on the surface of these two samples. The Cl 2p spectra of these two samples are shown in Figure 7-7 (a). Sample 1 contains two peaks, the peak at 198.5 eV is attributed to Cl\textsuperscript{−} 2p\textsubscript{3/2} and that at 200.15 eV is attributed to Cl\textsuperscript{−} 2p\textsubscript{1/2}, both for Cl\textsuperscript{−} ions (Yu et al., 2000). Compared to Sample 1, the Cl\textsuperscript{−} signal obtained from Sample 2 is too weak to be distinguished from the background. The S 2p spectra of Sample 2 are shown in Figure 7-7 (b), and the peak at 169.2 eV can be attributed to SO\textsubscript{4}\textsuperscript{2−} ions (Peisert et al., 1994). Based on the above observations, the adsorption theory proposed by Dugdale and Cotton is reasonable to explain the inhibition effect of SO\textsubscript{4}\textsuperscript{2−} on the pitting of Ti (Dugdale & Cotton, 1964). That is, SO\textsubscript{4}\textsuperscript{2−} ions can compete with Cl\textsuperscript{−} ions for adsorption sites on Ti oxide surfaces, which leads to lower Cl\textsuperscript{−} ion
concentrations on the Ti oxide films and in turn inhibits the pitting corrosion of Ti in mixed $\text{SO}_4^{2-}$ / $\text{Cl}^-$ solutions.

Figure 7-7 XPS spectra of Cl and S of the samples after 1–month immersion in (1) 1 mol L$^{-1}$ NaCl and (2) 1 mol L$^{-1}$ NaCl + 0.5 mol L$^{-1}$ Na$_2$SO$_4$ solutions at 175 °C.
7.2.4 Effect of temperature and sulfate ions on the metastable pitting

Based on the above discussion, temperature and sulfate are two critical parameters in the pitting corrosion of Ti. Regarding temperature, the concept of CPT has been introduced and widely used as a criterion for the pitting susceptibility of stainless-steel alloys (Brigham & Tozer, 1973; Deng et al., 2008; Frankel, 1998). In addition, plots of $E_b$ vs. temperature are often used to define the CPT for stainless-steel alloys (Moayed & Newman, 2006; Ovarfort, 1989). It has been well accepted for stainless steels that the plot of $E_b$ vs. temperature typically presents as an “backwards S-shaped” curve and the position of the steep decrease in $E_b$ is referred to as the CPT for a given alloy (Moayed & Newman, 2006; Ovarfort, 1989). It has been proven here (Figure 7-4), and also by previous researchers, that Ti and its alloys do not exhibit this “backwards S-shaped” curve in halide solutions (Beck, 1973a; Posey & Bohlmann, 1967). Therefore, potentiodynamic polarization is likely not the best technique for determining the CPT of Ti. The CPT is related to stable pitting. Each instance of stable pitting is the result of nucleation and stable growth of metastable pits on the sample surface (Burstein et al., 2005; Pistorius & Burstein, 1992). It has been pointed out by Burstein et al. that metastable pitting has not been sufficiently examined in terms of its temperature dependence (Burstein et al., 2010). Metastable pitting can, and does, form at potentials between $E_b$ and $E_{rp}$ as the precursor for stable pitting (Burstein et al., 2010; Burstein et al., 2005; Frankel et al., 1987; Kelly et al., 2002). As well, metastable pitting can be observed as the transient fluctuations of current density before the onset of stable pitting under potentiostatic control at potentials between $E_b$ and $E_{rp}$ (Burstein et al., 2005; Kelly et al., 2002). According to the results presented in Table 7-1, 1.1 V vs. SHE is the approximate median value from $E_b$ and $E_{rp}$ for most of the pitting conditions. Therefore, potentiostatic polarization measurements at $E_{vs.SHE} = 1.1$ V were used to provide useful
information on the initiation of metastable pitting (Kelly et al., 2002). Rearranging Eq. (2-1), one can get Eq. (7-1), and the $E_{measured}$ is estimated to be around 0.8 V vs. RE in the studied temperature by Eq. (7-1).

$$E_{measured} = E_{vs.SHE} - \Delta E_{SHE} + E_{TLJ} + E_{LJP} - E_{Ag/AgCl}$$  \hspace{1cm} (7-1)

Figure 7-8 depicts the current density responses of Ti polarized at 0.8 V vs. RE (i.e., 1.1 V vs. SHE) in 1 mol L$^{-1}$ NaCl solution with various Na$_2$SO$_4$ additions as the system temperature increases at a rate of 0.5 °C min$^{-1}$ from 100 to ~230 °C. During the initial heating, the current density remains low suggesting that the WE was protected by the passive films on its surface. It can be seen that the current density in the initial stages of heating measured on Ti in 1 mol L$^{-1}$ NaCl solution (~40 µA, Figure 7-8 (a)) is much lower than in 1 mol L$^{-1}$ NaCl solution with any level of Na$_2$SO$_4$ additions (~120 µA, Figure 7-8 (b)-(d)). With increasing temperature, some current density transients were observed in Figure 7-8. It was suggested by previous published data that the current density transient due to metastable pitting has a magnitude of ca. 1 µA (Jiang et al., 2011b; Kelly et al., 2002; Neville & Xu, 2001). Since the current density transient refers to metastable pitting, the metastable pitting temperature threshold (MPTT) is defined in this work as the temperature, where the first current density transient ($> 4$ µA) occurs during heating.

In Figure 7-8 (a) and (b), the current density rose abruptly as the temperature reached the CPT, indicating the occurrence of stable pitting (Moayed & Newman, 2006). Clearly, the MPTT is lower than CPT, implying, as expected, that metastable pitting is the precursor to stable pitting.
In Figure 7-8 (c) and (d), no stable pitting was observed on Ti in 1 mol L$^{-1}$ NaCl solution with $\geq 0.3$ mol L$^{-1}$ Na$_2$SO$_4$ additions at temperatures from 100 to 230 °C. This agrees with the CPP results in Figure 7-6 (b) suggesting that Ti will not undergo passivity breakdown up to 4.4 V vs. SHE in 1 mol L$^{-1}$ NaCl solution with $\geq 0.3$ mol L$^{-1}$ Na$_2$SO$_4$ at 175 °C. In order to further prove the accuracy of the MPTT and CPT definition, a CPP experiment was performed on Ti in 1 mol L$^{-1}$ NaCl + 0.5 mol L$^{-1}$ Na$_2$SO$_4$ solution at 200 °C (Condition I). Figure 7-9 shows that there is no film breakdown on Ti up to 9 V under Condition I. Thus the CPP curve agrees with the thermammogram curve presented in Figure 7-8 (d), which confirms the accuracy of the MPTT and CPT definition in this study. Figure 7-8 also indicates the increase in both MPTT and CPT of Ti in NaCl solutions by addition of SO$_4^{2-}$ ions, and that SO$_4^{2-}$ ions are more effective as the concentration increases.
Figure 7-8 Thermamograms for Ti in 1 mol L$^{-1}$ NaCl solution with different Na$_2$SO$_4$ additions at a potential of 1.1 V.
Figure 7-9 CPP curves for Ti in 1 mol L\(^{-1}\) NaCl + 0.5 mol L\(^{-1}\) Na\(_2\)SO\(_4\) solution at 200 °C.
The mean and standard deviation for the MPTT are summarized in Figure 7-10. It could be concluded that the MPTT measurements were reproducible. In Figure 7-10, the MPTT is plotted as a function of the sulfate to chloride mole ratio. Figure 7-10 suggests that for experimental conditions at or below the MPTT line, metastable pitting is likely to occur on Ti. Thus, these operating conditions should be avoided for industry by increasing the sulfate to chloride mole ratio or by decreasing the operating temperature to move the operating condition into the safe region, i.e., above the MPTT line. The 9 CPP conditions studied in this work are also marked in Figure 7-10. According to the CPP results listed in Table 7-1, the $E_{rp}$ values of Ti under Conditions B-F are all lower than the applied potential ($E_{vs.SHE} = 1.1$ V), suggesting that metastable pitting can form on Ti during anodic polarization at $E_{vs.SHE} = 1.1$ V under Conditions B-F. The $E_{rp}$ value of Ti under Condition G is higher than the applied potential ($E_{vs.SHE} = 1.1$ V) and Ti did not undergo passivity breakdown under Conditions A, H and I in the studied potential range. This suggests that metastable pitting cannot form on Ti during anodic polarization at $E_{vs.SHE} = 1.1$ V under Conditions A and G-I. Therefore, the results presented in Figure 7-10 are consistent with the CPP results presented in Figure 7-3 and Figure 7-3. In conclusion, the correlation shown in Figure 7-10 appears to be a valid and a workable way of describing the metastable pitting susceptibility of Ti in terms of a parameter with process design significance.
Figure 7-10 The metastable pitting temperature threshold (MPTT) as a function of sulfate to 1 mol L$^{-1}$ NaCl mole ratio.
7.3 Summary

The susceptibility of Ti to pitting corrosion has been studied by CPP and thermammetry analysis in mixed SO$_4^{2-}$ / Cl$^-$ solutions at high temperatures. The main findings of this study can be summarized as follows:

1) In 1 mol L$^{-1}$ NaCl solution, the $E_b$ decreased, while the $E_{rp}$ remained constant as temperature increased from 125 to 200 °C. It was also noted that the dimension of the pits increased as the operating temperature increased.

2) Addition of SO$_4^{2-}$ ions inhibited the passivity breakdown of Ti in 1 mol L$^{-1}$ NaCl solution. Both the $E_b$ and $E_{rp}$ of Ti in 1 mol L$^{-1}$ NaCl solution increased with the concentration of SO$_4^{2-}$ ions. With 0.5 mol L$^{-1}$ SO$_4^{2-}$ addition, Ti did not undergo passivity breakdown at 200 °C even up to 9 V vs. SHE in 1 mol L$^{-1}$ NaCl solution.

3) XPS results confirmed that SO$_4^{2-}$ ions can compete with Cl$^-$ ions for adsorption sites on the Ti oxide surface, which leads to lower Cl$^-$ ion concentrations on the Ti oxide films and in turn inhibits the pitting corrosion of Ti.

4) As the precursor stage of stable pitting, metastable pitting was examined in terms of temperature dependence by thermammetry measurements. Metastable pitting was observed at temperatures much lower than those recorded for the CPT. The MPTT as a function of SO$_4^{2-}$ / Cl$^-$ mole ratio was defined for Ti in the temperature range of 100-230 °C. This is convenient to estimate the metastable pitting of Ti.
8 Characterization of anodized Ti for hydrometallurgical applications

In this chapter, AOFs were produced on commercially pure titanium in 0.5 M sulfuric acid solutions at room temperature and in the potential range of 20 to 80 V. The corrosion behavior of the AOFs was investigated in de-aerated sulfuric acid solutions in the presence of 12 g L\(^{-1}\) Cl\(^-\), 15 g L\(^{-1}\) Cu\(^{2+}\) and 1 g L\(^{-1}\) Fe\(^{3+}\), which are their typical tenors in copper sulfide leaching solutions.

8.1 Experimental

8.1.1. Anodizing and sealing

The titanium sample was 3 mm thick with a circular surface area of 2.0 cm\(^2\). Anodization was carried out in a 1 L jacketed cell with a graphite rod as a cathode and a 0.5 M sulfuric acid electrolyte. The temperature of the anodizing electrolyte was kept at 25 °C by a water circulator with an accuracy of ±1 °C. A magnetic stirrer was used to eliminate the bubbles generated during the anodic oxidation. Prior to anodization, the electrode was abraded using successive grades of SiC papers down to 1200 grit, washed with DI water and then washed with 0.5 M sulfuric acid solution. Constant voltages of 20, 40, 60 and 80 V were applied to the titanium sample using a DC power supply. The anodizing time at each specific voltage was 1 hour. After anodizing, samples were washed in DI water, sealed in boiling DI water for 30 min, and then dried in air.

8.1.2. Electrochemical experiments

Electrochemical experiments were carried out using a standard three-electrode cell with thermostated water jacket, a graphite rod as the counter electrode, the anodized titanium sample
as the working electrode and an Ag/AgCl ([KCl] =4 M) reference electrode. The potentiostat used was a Princeton Applied Research Versastat 4 potentiostat/galvanostat. The solutions were introduced into the cell, heated to the desired temperature and de-aerated using high-purity N\(_2\) for at least 30 minutes prior to introducing the working electrode. N\(_2\) sparging was maintained during the entire experimental process.

All potential values used in this work are quoted with respect to the Ag/AgCl reference electrode (0.197 V vs. SHE). Each sample was immersed in the solution for 1 h before starting an EIS or LPR test to stabilize the OCP. LPR tests were performed from −0.020 V vs. OCP up to +0.020 V vs. OCP with a scan rate of 0.167 mV s\(^{-1}\). The corrosion mechanism at the oxide film/electrolyte interface was investigated by EIS. The EIS perturbation voltage amplitude was 10 mV (peak to peak). The frequency range for all experiments was 10 kHz to 100 mHz with sampling rate of 10 points per decade. All EIS measurements were taken at OCP.

### 8.1.3. Surface examination

Two samples were prepared for each anodizing condition using the procedure previously described at 20 V, 40 V, 60 V and 80 V for a total of eight samples. One of each of these pairs was set aside with no further treatment, while the second was further immersed in 1L de-aerated 30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^-\) + 15 g L\(^{-1}\) Cu\(^{2+}\) (=SClCu) with 1 g L\(^{-1}\) Fe\(^{3+}\) addition for 12 hours at 85±1 °C. After immersion, samples were ultrasonically washed in DI water for 5 min and dried naturally. The surface morphology of all eight samples was observed using a Zeiss Sigma field emission SEM.

In order to investigate the surface chemistry of 80 V-AOFs in mixed Cu-Cl solutions, XPS analysis was carried-out on four 80 V-anodized titanium samples, each immersed in one of the
following four solutions at 85 °C for 12 hours, (1) N₂-de-aerated SCICu solution; (2) N₂-de-aerated SCICu1Fe solution; (3) N₂-de-aerated SCICu5Fe solution; (4) O₂-saturated SCICu solution. After the immersion, all samples were ultrasonically washed in DI water for 5 min and dried in an N₂ stream. The surface chemical composition of these samples was analyzed by XPS.

Time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiles and analysis were performed using a Trift V nanoToF-SIMS (Physical Electronics) instrument. For sputtering, the ion gun was operated at the accelerating voltage of 3 kV and with the raster area of 400 µm × 400 µm; the DC current of Ar⁺ primary ions delivered to the sample was 400 nA. Each sputter cycle was 20 seconds in duration. Analysis was carried out using Au LMIG operated with bunched mode using the Au⁺ primary ion. Each analytical cycle was 60 seconds in duration with the analysis area of 100 µm × 100 µm. Mass spectra were collected in the mass-to-charge (m/z) range of 0-1850 amu, in the positive polarity only.

8.2 Results and discussion

8.2.1 Potentiostatic formation of AOFs

Shibata and Zhu have reported that the growth of AOFs under potentiostatic conditions follows the logarithmic rate law (Shibata & Zhu, 1995). Figure 8-1 shows the plots of log i vs. log t obtained during 2 hours of potentiostatic formation of AOFs in 0.5 M sulfuric acid at 25 °C. A linear relationship can be seen in the early stage of anodization (up to t = 10³ s) followed by a wave-shaped curve. Shibata and Zhu point out that two processes are involved during anodization: a growth stage (linear section) and the balanced stage (non-linear part at t > 10³ s) (Shibata & Zhu, 1995). As it can be observed in Figure 8-1, the time scale for the growth stage decreased from 7200 s to 1000 s when the applied potential increased from 2 V to 8 V. This
indicates that the AOF grows to a steady thickness within 1 hour when the anodizing voltage is higher than 8 V. In the voltage range used in this work (20 to 80 V) it is therefore assumed that the 1 hour of applied anodization was easily sufficient to grow a film of steady thickness in 0.5 M sulfuric acid at 25 °C. A DC power supply was used to provide constant voltages of 20, 40, 60 and 80 V since the maximum applied voltage of most potentiostats is low (the Versastat 4 potentiostat used here has a maximum voltage of 10 V). Because the DC power supply used here did not have the capability to record current, no \( i \text{ vs. } t \) plots for the anodizing processes can be shown.
Figure 8-1 Variations in current density over 2 hours of potentiostatic film formation in 0.5 M sulfuric acid, T=25 °C.
As mentioned above, the AOF will grow to a specific thickness (related to color) at a given applied voltage. The colors of the anodized Ti samples at different potentials as determined by visual inspection are listed in Table 8-1. The correlation of color and thickness to anodization voltage as reported by other authors (Chen et al., 2005; Gaul, 1993; Karambakhsh et al., 2011; Sharma, 1992) are shown in Table 2-3. Our results are consistent with previous reports. From Table 2-3 we may conclude that the thickness of the AOFs obtained here at 80 V exceeds 100 nm.

Table 8-1 The colors of the anodized Ti samples at different potentials.

<table>
<thead>
<tr>
<th>Anodizing voltage (V)</th>
<th>8</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>brown</td>
<td>dark blue</td>
<td>light olive</td>
<td>pink</td>
<td>turquoise</td>
</tr>
</tbody>
</table>

8.2.2 Electrochemical behavior of Anodized Ti

The objective of this work is to investigate the corrosion response of AOFs in typical copper sulfide leaching solutions, *i.e.*, SClCu1Fe solution. To gauge the effect of cupric and ferric it is also important to study the stability of the AOFs in de-aerated SCl solutions. Electrochemical characterizations of AOFs formed on Ti have previously been reported (Cotton, 1970; Diamanti & Pedeferri, 2007; Fadl-allah & Mohsen, 2010; Karambakhsh et al., 2011; Ma & Peres, 1951; Sharma, 1992; Souza et al., 2007). However, there is a lack of publicly available information as to the corrosion of anodized Ti in strong, Cl⁻ containing, reducing acid such as that of interest
here *i.e.* de-aerated SCI solutions. The performance of AOFs in these solutions is first reported below. The OCP decay curves for anodized Ti in de-aerated SCI solutions at 25 and 85 °C are presented in Figure 8-2. Figure 8-2 (a) shows the OCP values of AOFs recorded over 12 hours at 25 °C. Both the 40 V−AOF and 80 V−AOF reached stable OCP values at 25 °C, which were maintained for the final 6 hours of immersion. The OCP values of the 20 V and 60 V−AOF kept decaying and did not reach a stable value over the 12 hours of immersion.
Figure 8-2 Open circuit potential decay curves for anodized Ti in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^{-}$ solutions, (a) T=25 °C and (b) T=85 °C.
Since the OCP of Ti with a freshly polished surface is around \(-0.60\) V in de-aerated SCl solution at 85 °C, Figure 8-2 (b) reveals that at 85 °C the AOFs retain virtually no increased passivation effect over freshly polished Ti within 2 hours of immersion (as the OCP shifts to \(-0.60\) V after 2 hours). This indicates that all AOFs were evidently completely reduced in the last phase of OCP breakdown at 85 °C. The above discussion suggests that the mixed chloride–sulfuric acid solution used in copper sulfide leaching is extremely corrosive, and that the protective oxide films formed on Ti at 20 to 80 V are not stable in this mixed chloride–sulfuric acid solution in the absence of an oxidant.

The change of OCP for anodized Ti in de-aerated SCl solutions with 15 g L\(^{-1}\) Cu\(^{2+}\) or 1 g L\(^{-1}\) Fe\(^{3+}\) additions at 85 °C is presented in Figure 8-3. The change of OCP over the last 10 minutes of each OCP measurement in Figure 8-3 is less than 5 mV. Therefore, AOFs formed on Ti at 20 to 80 V reach a steady state thickness (Kelly et al., 2002) within 1 hour in de-aerated SCl solutions with 15 g L\(^{-1}\) Cu\(^{2+}\) or 1 g L\(^{-1}\) Fe\(^{3+}\) additions at 85 °C. The passive region of Ti with a freshly polished surface starts at approximately \(-0.25\) V in de-aerated SCl solution at 85 °C. Figure 8-3 shows that the presence of Cu\(^{2+}\) and Fe\(^{3+}\) ions kept the OCP values of anodized Ti in the range of 0.3 to 0.5 V, which is well within the passive region of Ti at 85 °C.
Figure 8-3 Open circuit potential recorded on anodized Ti in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$ solutions with different additions, T=85 °C.
Figure 8-4 (a) and (b) present the LPR results of the AOFs after 1 hour immersion in de-aerated SClCu1Fe solutions at both 25 and 85 °C. The dashed lines in Figure 8-4 show the previously published $R_{p-LPR}$ results for Ti with a freshly polished surface under the same conditions. Figure 8-5 presents the Bode plots of freshly polished Ti after 1 hour immersion in de-aerated SClCu1Fe solutions at both 25 and 85 °C. It is shown that the impedance magnitude of the freshly polished Ti electrode in this solution was around 1000 $\Omega$ cm$^2$ at 25 °C and 10,000 $\Omega$ cm$^2$ at 85 °C, which agree with the previously published $R_{p-LPR}$ results under the same conditions.

It is evident that $R_{p-LPR}$ values for anodized Ti are much higher than those for freshly polished Ti at both 25 and 85 °C. Figure 8-4 also shows that the $R_{p-LPR}$ value of anodized Ti increased as the anodized voltage increased from 20 to 80 V. Thus, an 80 V anodization treatment lead to the best improvement of the corrosion resistance of Ti in this work.
Figure 8-4 $R_{p-LPR}$ of anodized Ti after 1 hour of OCP measurement in de-aerated SCICu1Fe solutions, (a) $T=25$ °C and (b) $T=85$ °C.
It has been proposed by many authors that equivalent electrical circuits (EECs) are a good method to characterize the structure of AOFs (Aziz-Kerrzo et al., 2001; Fadl-allah & Mohsen, 2010; Marsh & Gorse, 1997; Pan et al., 1996; Piazza et al., 1998; Souza et al., 2007). Among them, the equivalent circuit $R_s(Q_{pr}(R_{pr}(R_bQ_b)))$ is the one used most frequently for anodized Ti (Fadl-allah & Mohsen, 2010; Pan et al., 1996; Souza et al., 2007). In this EEC it is assumed that the AOF is a two−layer film, including an inner barrier layer and an outer porous layer. The parameters of this EEC are electrolyte resistance ($R_s$), outer porous film phase constant ($Q_{pr}$), outer porous film resistance ($R_{pr}$), inner barrier film resistance ($R_b$) and inner barrier film phase constant ($Q_{pr}$). Figure 8-5 shows the equivalent circuits used.

![Figure 8-5 The equivalent circuit $R_s(Q_{pr}(R_{pr}(R_bQ_b)))$ used to fit the EIS data.](image)
Figure 8-6 Nyquist and Bode plots for anodized Ti in de-aerated 30 g L\(^{-1}\) H\(_2\)SO\(_4\) + 12 g L\(^{-1}\) Cl\(^{-}\) solutions with different cupric and ferric additions after 1 hour OCP measurements, T=85 °C.
Figure 8-6 presents electrochemical impedance data for AOFs in SCl solutions with different additives at 85 °C in the form of Nyquist plots, Bode $|Z|$ and Bode Phase diagrams. The fitting curves obtained by using the EEC of $R_s(Q_{pr}(R_{pr}(R_bQ_b)))$ are also present in Figure 8-6. The typical error for each parameter is: $R_{sol}, 0.7\%$; $Q_{pr}-Y_0, 0.3\%$; $Q_{pr}-n, 0.2\%$; $R_{pr}, 0.8\%$; $R_b, 1.0\%$; $Q_b-Y_0, 0.5\%$; $Q_b, 0.3\%$. The corresponding analyzed data is presented in Table 8-2. As shown, very good agreement between experimental and simulated data is obtained. It could be concluded that the two–layer EEC model satisfactorily describes the AOFs in this work.

It can be observed in Figure 8-6 that the impedance magnitude of anodized Ti is increased with increasing applied anodization voltage at 85 °C. The influence of anodization voltage on the film resistance, $R_{pr}$ and $R_b$, is shown in Table 8-2. The $R_b$ values for the AOFs in all three solutions followed the same trend as the $R_{pr-LPR}$ values obtained in the LPR tests. That is, the $R_b$ value of anodized Ti increased as the applied potential increased from 20 V to 80 V. Regarding the values of $R_{pr}$, it is also observed that the 40 V–AOFs have the lowest value compared with the other AOFs in the same solution (Table 8-2). Based on these observations, it can be predicted that the thickness of the barrier layer of the AOFs increases as the anodization voltage increases, and that the 40 V–anodization produces a more porous outer layer than the others.
Table 8-2 EIS parameters of equivalent circuit $R_s(Q_{pr}(R_{pr}(R_bQ_b)))$ for anodized Ti in de-aerated 30 g L$^{-1}$ H$_2$SO$_4$ + 12 g L$^{-1}$ Cl$^-$ solutions with different additives, T=85 °C.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Anodizing voltage (V)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$Q_{pr} - Y_0$ (μF cm$^{-2}$ s$^{n-1}$)</th>
<th>$Q_{pr} - n$</th>
<th>$R_{pr}$ (Ω cm$^2$)</th>
<th>$R_b$ (Ω cm$^2$)</th>
<th>$Q_b - Y_0$ (μF cm$^{-2}$ s$^{n-1}$)</th>
<th>$Q_b - n$</th>
<th>$X^2 \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 g L$^{-1}$ Cu$^{2+}$</td>
<td>20</td>
<td>2.08</td>
<td>39.6</td>
<td>0.87</td>
<td>269</td>
<td>512</td>
<td>734</td>
<td>0.76</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.04</td>
<td>34.8</td>
<td>0.89</td>
<td>170</td>
<td>545</td>
<td>139</td>
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</tr>
<tr>
<td></td>
<td>60</td>
<td>2.34</td>
<td>35.8</td>
<td>0.91</td>
<td>240</td>
<td>966</td>
<td>89.7</td>
<td>0.70</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>2.46</td>
<td>40.9</td>
<td>0.92</td>
<td>482</td>
<td>1177</td>
<td>71.3</td>
<td>0.76</td>
<td>5.3</td>
</tr>
<tr>
<td>15 g L$^{-1}$ Cu$^{2+}$ + 1 g L$^{-1}$ Fe$^{3+}$</td>
<td>20</td>
<td>2.42</td>
<td>31.3</td>
<td>0.85</td>
<td>367</td>
<td>412</td>
<td>187</td>
<td>0.60</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>2.81</td>
<td>34.9</td>
<td>0.89</td>
<td>193</td>
<td>1313</td>
<td>92.2</td>
<td>0.67</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.62</td>
<td>35.6</td>
<td>0.90</td>
<td>282</td>
<td>1375</td>
<td>91.8</td>
<td>0.67</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.51</td>
<td>39.5</td>
<td>0.92</td>
<td>457</td>
<td>2042</td>
<td>79.1</td>
<td>0.70</td>
<td>6.6</td>
</tr>
<tr>
<td>1 g L$^{-1}$ Fe$^{3+}$</td>
<td>20</td>
<td>2.03</td>
<td>27.1</td>
<td>0.90</td>
<td>339</td>
<td>1086</td>
<td>96.9</td>
<td>0.70</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1.53</td>
<td>35.2</td>
<td>0.88</td>
<td>188</td>
<td>1612</td>
<td>102</td>
<td>0.66</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.61</td>
<td>32.0</td>
<td>0.86</td>
<td>308</td>
<td>1636</td>
<td>105</td>
<td>0.78</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1.37</td>
<td>40.6</td>
<td>0.84</td>
<td>352</td>
<td>2585</td>
<td>115</td>
<td>0.76</td>
<td>11.3</td>
</tr>
</tbody>
</table>
8.2.3 The morphology of surfaces

Figure 8-7a shows the surface morphology of AOFs produced on CP-Ti at different anodizing voltages in 0.5 M sulfuric acid for 1 hour. Figure 8-7a−20 V shows the fish scale–like anodized surface obtained at 20 V. When the anodization voltage was 40 V, the outer layer of the AOFs started peeling and generated oxide buds on the surface, as shown in Figure 8-7a−40 V. The detailed morphology of the 40 V−AOF is presented in Figure 8-8. Similar but much scarcer oxide buds were obtained also on the AOF obtained at 60 V, as shown in Figure 8-7a−60 V. These oxide buds have been reported by other authors under similar conditions (Fadlallah & Mohsen, 2010; Mohsen & Fadl–Allah, 2010). The 80 V condition gave a much smoother surface morphology, as shown in Figure 8-7a−80 V. The above discussion confirms the EIS results, where the 40 V−AOFs have the lowest $R_{pr}$ value compared with the other AOFs in the same solution at 85 °C (Table 8-3).

Figure 8-7b shows the surface morphology of the AOFs obtained at different anodizing voltages after 12 hours immersion in the de-aerated SClCu1Fe solution at 85 °C. Due to the coarse morphology of 20 V−AOFs and 40 V−AOFs, the active surface area was large and would lead to severe corrosion. As expected, the most severe corrosion (as judged by the smoothness of the surface) occurred on the AOFs obtained at 20 and 40 V as localized corrosion (black pits) was visible on these two samples. Figure 8-7b−60 V shows a much better surface with scarcer pitting compared with Figure 8-7b−20 V and Figure 8-7b−40 V. Uniform corrosion with little to no pitting is observed on the AOF obtained at 80 V due to its dense and smooth structure, as shown in Figure 8-7b−80 V. These SEM results corroborate the electrochemical results, that is, the 80 V anodization of Ti leads to the best improvement of its corrosion resistance in the de-aerated
SClCu1Fe solution. As shown in Figure 8-7, after 12 hours of immersion in de-aerated SClCu1Fe solution at 85 °C, only 80V–AOFs gave a uniform surface morphology. In order to reproduce the oxide films as much as possible, only 80V–AOFs were studied in the following section.
Figure 8-7 Surface morphology of anodized Ti, (a) samples anodized at different voltages and prior to immersion; (b) anodized samples after 12 hours of immersion in N$_2$–de-aerated SCICu1Fe solution, T=85 °C.
Figure 8-8 Surface morphology of the AOF formed in 0.5 M H₂SO₄ at 40 V for 1 hour on CP–Ti.
8.2.4. Effects of leaching oxidants on the 80 V−AOFs and the presence of reduced copper in the oxide film

It has been confirmed that AOFs on Ti obtained at 80 V (80 V−AOFs) show the best improvement in corrosion resistance in sulfuric acid solutions relevant to copper sulfide leaching. It has been proposed in Chapter 4 that the presence of Cu$^{2+}$ ions may affect the Ti oxide films in de-aerated SCICu solution at 85 °C, and the mechanism behind this effect can be described by reaction (4-3) and reaction (4-4). The OCP of the 80 V−AOF was around 0.37 V in de-aerated SCICu solution at 85 °C and was thus between the equilibrium potentials of reaction (4-3) and reaction (4-4). As discussed before, AOFs formed in this work have a porous outer layer. Therefore, Cu$^{0}$ may be formed as described in reaction (4-3) and be trapped in these pores when the Ti working electrode is immersed in de-aerated SCICu solution at 85 °C, provided that OCP is lower than 0.440 V vs. Ag/AgCl.

XPS spectra were gathered from the 80 V-AOFs after immersion in the de-aerated SCICu solutions for 5, 15, 30 and 720 minutes, respectively. The XPS spectra presented in Figure 8-9 show that these four samples had Cu 2p signals at the same binding energy. The peak at 932 eV is attributed to Cu 2p$_{3/2}$ and that at 952 eV is attributed to Cu 2p$_{1/2}$, both are associated with Cu$^{+}$/Cu$^{0}$ (Jolley et al., 1989; Rochefort et al., 1993). The XPS signals of Cu$^{0}$ and Cu$^{+}$ are basically the same, but they are different from Cu$^{2+}$ signals. This result provides evidence that Cu$^{2+}$ ions were reduced to Cu$^{+}$/Cu$^{0}$ on the titanium dioxide in the de-aerated SCICu solutions. Since XPS spectra only represent the signals from the top 0 to 10 nm of the material being analyzed, ToF-SIMS depth profiles were used to determine the distribution of Cu signals (either Cu$^{+}$ or Cu$^{0}$) as a function of depth for the same four samples. Depth profiles were obtained on at least two locations for each sample.
Figure 8-9 Cu 2p spectra for 80 V-anodized Ti samples after immersion in de-aerated SCiCu solution for 5, 15, 30 and 720 minutes, respectively, T=85 °C.
Figure 8-10 shows the representative Cu (Cu$^+/Cu^0$) and TiO$_x$ (Ti oxides) depth profiles of the AOFs after immersion in the de-aerated SCICu solutions for 5, 15, 30 and 720 minutes. As shown in Figure 8-10(a), Cu signals were no longer measurable beyond the depth of ca. 150 nm for the three samples immersed for ≤ 30 minutes. The maximum Cu depth observed for these three samples was almost the same. This indicates that Cu$^{2+}$ ions can diffuse deeply into the porous films within 5 minutes of immersion. As reported previously, an AOF will grow to a thickness of 150~190 nm after 80 V anodization (Gaul, 1993; Karambakhsh et al., 2011), which is consistent with the maximum TiO$_2$ depth value of the three samples immersed for ≤ 30 minutes. For the 720 min-sample, the maximum Cu depth values were around 60 nm. In order to verify that these 720 min depth profiles were credible, they were repeated. The dashed lines in Figure 8-10 confirm that the ToF-SIMS depth profiles for the 720 min-sample are reproducible. Figure 8-10(b) also shows that, for each sample, the TiO$_x$ signal was only measurable to the same depth as the Cu signal. In aggregate, Figure 8-10 suggests that Cu signals co-existed with TiO$_x$ signals in the AOFs.

It was observed that the interference color of the 720-min samples had disappeared, while the interference color remained purple for the other three samples (5, 15 and 30 min). Figure 8-11 shows three-dimensional plots of the AOF/Ti structures for the 720-min and 30-min samples. The images were reconstructed from a depth of 0 nm (the AOF surface) to about 248 nm (into the Ti metallic region). In Figure 8-11, the 720-min sample exhibits a much thinner titanium oxide layer on the surface compared with the 30-min sample with the same volume structure. These results suggest that the de-aerated cupric-chloride solution was very corrosive at 85 °C, and the AOFs get thinner as the sample is immersed for longer.
Figure 8-10 ToF-SIMS depth profiles of (a) Cu and (b) TiO$_x$ for the 80 V-anodized titanium samples after immersion in de-aerated SCICu solution for 5, 15, 30 and 720 minutes, respectively, T=85 °C.
Figure 8-11 Mass resolved 3D views of the AOF/Ti structure, (a) 720-min immersion sample and (b) 30-min immersion sample.
On the other hand, if a higher potential (>0.440 V vs. Ag/AgCl) is applied on the Ti working electrode, the Cu associated with the oxide film will be oxidized to cupric ions, or may not be formed in the first place. In order to examine this idea, OCP measurements and XPS analyses were carried out as detailed below. It is well known that both oxygen and ferric are extensively used as oxidants in copper leaching processes (Defreyne et al., 2006a; Hirato et al., 1986; Hirato et al., 1987b). To raise the corrosion potential of the Ti working electrode, ferric and oxygen were added respectively in the SCICu solution at 85 °C. The OCP was recorded on anodized Ti for 1 hour in SCICu solutions with different oxidants at 85 °C, as shown in Figure 8-12. The OCP value of the 80 V–AOFs was below 0.440 V in de-aerated SCICu solutions with or without 1 g L\(^{-1}\) Fe\(^{3+}\) solution at 85 °C. On the other hand, the OCP value of 80 V–AOFs was 0.445 V in O\(_2\)–saturated SCICu solution and 0.510 V in de-aerated SCICu solution with 5.0 g/L Fe\(^{3+}\) addition at 85 °C. Based on our thermodynamic calculation presented above, the OCP results from Figure 8-12 indicate that there would be no Cu formed in the AOFs in the latter two solutions. To confirm these results, XPS analyses were undertaken.
Figure 8-12 Open-circuit potential recorded on anodized Ti in SCICu solutions with different oxidants, T=85 °C.
In order to further investigate the surface chemistry of the 80 V−AOFs in mixed Cu−Cl solutions, four Ti samples were immersed for 12 hours. The wide−scan XPS spectra presented in Figure 8-13 show that the two samples from solutions (1) and (2) had Cu 2p signals in the same locations, and there was no Cu signal on the samples from solutions (3) and (4). Ti 2p spectra of these four samples are shown in Figure 8-14(a). All four samples had two peaks in the same locations, the peak at 458.7 eV is attributed to $\text{Ti}^{4+} 2p_{3/2}$ and that at 464.2 eV is attributed to $\text{Ti}^{4+} 2p_{1/2}$, both for $\text{TiO}_2$ (He et al., 2002; Hopfengärtner et al., 1993). The Cu 2p peaks of samples from solutions (1) and (2) are shown in Figure 8-14(b). The peak at 932 eV is attributed to Cu 2p$_{3/2}$ and that at 952 eV is attributed to Cu 2p$_{1/2}$, both refer to Cu$^0$ (Jolley et al., 1989; Rochefort et al., 1993). The XPS signals of Cu$^0$ and Cu$^+$ are basically the same, but they are different from Cu$^{2+}$ signals (Chadwick & Hashemi, 1978; Jolley et al., 1989; Rochefort et al., 1993). Since the OCP value of 80 V−AOFs in solution (3) is 0.510 (> 0.440 V), there should be no detectable Cu signal from the corresponding sample, as shown in Figure 8-14(b) line (3). A very weak Cu signal at 932 eV from the sample exposed to solution (4) is observed in Figure 8-14(b) line (4), which is probably due to the fact that the OCP value of the 80 V−AOFs in solution (4) (0.445V) was close to 0.440 V. In aggregate, these results provided evidence that cupric ions were reduced to Cu$^0$ (or perhaps Cu$^+$) on the AOFs in solutions (1) and (2). However, in keeping with thermodynamic predictions, under oxidative conditions this reduction was inhibited.
Figure 8-13 Wide−scan XPS spectra for 80 V−anodized Ti samples after 12 hours immersion in
(1) de-aerated SCI Cu solution; (2) de-aerated SCI Cu1Fe addition; (3) de-aerated SCI Cu5Fe
addition; (4) O₂-saturated SCI Cu solution, T=85 °C.
Figure 8-14 (a) Ti 2p spectra and (b) Cu 2p spectra for 80 V–anodized Ti samples after 12 hours immersion in (1) de-aerated SCICu solution; (2) de-aerated SCICu1Fe addition; (3) de-aerated SCICu5Fe addition; (4) O₂-saturated SCICu solution, T=85 °C.
The reduction of cupric ions may adversely affect the performance of both AOFs and naturally formed oxides on Ti in mixed Cu–Cl solutions. However, the presence of oxidants will inhibit this reduction, and 5 g L\(^{-1}\) Fe\(^{3+}\) is more effective than O\(_2\) saturation to this end. It is important to note that during operation at elevated temperatures it is difficult to maintain high ferric concentrations as this ion quickly hydrolyzes and precipitates as hematite or jarosite. On the other hand, high oxygen partial pressures are achievable during leaching at elevated temperatures and pressures. Nonetheless, the findings presented herein result in a practical suggestion for the protection of Ti liners used in pressure leaching autoclaves i.e. that oxidative conditions should be maintained at all times. The nature of sulfide pressure leaching is such that oxidative conditions are usually maintained, however, upset conditions and plant shutdowns can result in inadvertent contact with reducing or non-oxidative solutions. Furthermore, there is certainly also the possibility for localized and potentially reducing conditions under scale formed on reactor surfaces.

8.3 Summary

Based on the plots of log \(i\) vs. log \(t\) obtained in potentiostatic polarization tests, the growth of AOFs in this work is complete within 1 hour. OCP measurements demonstrated that the mixed chloride–sulfuric acid solution used in copper sulfide pressure leaching is extremely detrimental to AOFs even at relatively mild temperatures. The AOFs formed at 20 to 80 V failed within 2 hours in de-aerated 30 g L\(^{-1}\) \(\text{H}_2\text{SO}_4\) + 12 g L\(^{-1}\) \(\text{Cl}^-\) solutions without any oxidant at 85 °C. LPR and EIS results showed that 80 V–anodization of Ti lead to the best improvement of corrosion resistance of Ti in the de-aerated copper leaching solution. It was also shown from EIS results that the 40 V–AOFs had the lowest \(R_{pr}\) value, which indicated that the 40 V–anodization produced a more porous layer than the other conditions tested. SEM results confirmed the LPR
and EIS findings. XPS results confirmed that the reduction of cupric could spontaneously happen on titanium dioxide films in de-aerated mixed sulfate-chloride solutions at 85 °C. ToF-SIMS depth profiles of the immersed AOF samples indicate that Cu$^{2+}$ ions can diffuse deeply into the porous oxide films within 5 minutes of immersion. The depth profiles also reveal that Cu signals only exist in the oxide layer. The maintenance of oxidative conditions would inhibit the reduction of Cu$^{2+}$ on TiO$_2$ by shifting the OCP to a more positive value; 5 g L$^{-1}$ Fe$^{3+}$ is more effective than O$_2$ saturation to obtain this inhibiting effect at 85 °C.
9 A new method to improve the corrosion resistance of titanium for hydrometallurgical applications

The present chapter aims to develop a new method to fabricate oxide films on Ti substrates with high corrosion resistance by controlled chemical oxidation with H$_2$O$_2$ solutions. Since there are abundant Cl$^-$ and SO$_4^{2-}$ ions in autoclaves used in pressure leaching, it is important and necessary to study the effects of Cl$^-$ and SO$_4^{2-}$ ions on the growth of chemically oxidized films (COFs). SEM and XRD were performed to investigate the morphological and structural characteristics of the prepared COFs. Electrochemical and immersion experiments were performed to evaluate the corrosion resistance of COFs for hydrometallurgical applications.

9.1 Experimental

9.1.1. Controlled chemical oxidation of Ti

The substrate material investigated was pure Ti, ASTM Grade 2 (0.14 wt.% Fe, 0.005 wt.% C, 0.005 wt.% Al, 0.008 wt.% Ni, 0.01 wt.% H, Bal. Ti). The Ti sample was 3 mm thick with a circular surface area of 2.0 cm$^2$. DI water, H$_2$O$_2$ (30 wt.%, Fisher Scientific), H$_2$SO$_4$, HCl (37 %, Fisher Scientific) and NaCl were used to prepare the solutions used for controlled chemical oxidation of Ti. There are 6 solutions (listed in Table 9-1) used in this work, they will be referred-to by their associated number throughout the remainder of this chapter (denoted as COFs 1-6). The solutions were not sparged with gases prior to- or during the chemical oxidation.
Table 9-1 Correlation of color and thickness of titanium oxide films to conditions for different oxidation methods.

<table>
<thead>
<tr>
<th>Solutions / COFs No.</th>
<th>Solutions composition for chemical oxidation</th>
<th>Color</th>
<th>Thickness (nm)*</th>
<th>Voltage (DC) for anodic oxidation*</th>
<th>T (°C) for thermal oxidation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 M H₂O₂</td>
<td>Golden brown</td>
<td>49</td>
<td>10</td>
<td>385</td>
</tr>
<tr>
<td>2</td>
<td>2 M H₂O₂ + 0.1 M H₂SO₄</td>
<td>Purple</td>
<td>110</td>
<td>60</td>
<td>523</td>
</tr>
<tr>
<td>3</td>
<td>2 M H₂O₂ + 0.1 M H₂SO₄ + 0.1 M HCl</td>
<td>Bronze</td>
<td>150</td>
<td>80</td>
<td>579</td>
</tr>
<tr>
<td>4</td>
<td>2 M H₂O₂ + 0.1 M HCl</td>
<td>Grey</td>
<td>190</td>
<td>100</td>
<td>635</td>
</tr>
<tr>
<td>5</td>
<td>2 M H₂O₂ + 0.05 M HCl</td>
<td>Rose</td>
<td>170</td>
<td>90</td>
<td>607</td>
</tr>
<tr>
<td>6</td>
<td>2 M H₂O₂ + 0.2 M HCl</td>
<td>Gold purple</td>
<td>160</td>
<td>85</td>
<td>593</td>
</tr>
</tbody>
</table>

Note: * previous published results (Chen et al., 2005; Gaul, 1993; Karambakhsh et al., 2011; Sharma, 1992). The values for thickness, anodic oxidation voltage, and thermal oxidation temperature are all published results related to colors of the obtained COFs.
Prior to the oxidation, specimens were abraded using successive grades of SiC papers down to 1200 grit, ultrasonically washed for 5 min in DI water and dried in air. Each specimen was then soaked in 50 mL of oxidizing solution (solutions 1-6) at 90°C for 24 hours. The specimens were then removed, ultrasonically washed for 5 min in DI water and sealed in a PTFE-lined autoclave containing 300 mL DI water at 150 °C for 48 hours. Specimens were then removed and dried in air. After this oxidation procedure, the surface morphology of the as grown COFs was observed using a SEM. XRD was performed on a Bruker D8 diffractometer, using Cu Kα1 radiation (λ = 1.5405 Å) to determine the crystal structures of the as grown COFs.

In order to address the improvement of the corrosion resistance of Ti by chemical oxidation as described above, naturally air-formed oxide films (NOFs) were used as controls. NOFs were formed on Ti through contact with the atmosphere at room temperature for 72 hours after abrasion using successive grades of SiC papers down to 1200 grit followed by ultrasonication for 5 min in DI water.

9.1.2. Electrochemical measurements

The potentiostat used was a Princeton Applied Research Versastat 4 potentiostat/galvanostat. Electrochemical experiments were carried out using a standard three-electrode cell with thermostated water jacket, a graphite rod as the counter electrode, the chemically oxidized Ti sample as the working electrode and an Ag/AgCl ([KCl] =4 M) reference electrode. The electrolyte was the synthetic pressure leaching solution (in this case we used solutions that model copper sulfide concentrate leaching) containing 30g L^{-1} H_2SO_4 + 12 g L^{-1} Cl^- + 15 g L^{-1} Cu^{2+} + 1 g L^{-1} Fe^{3+} (=SCICu1Fe). The SCICu1Fe solution was de-aerated using high-purity N_2 for at least 30 minutes prior to introducing the working electrode. N_2 sparging was maintained during
the entire experimental process. All the electrochemical experiments were performed at 25 °C. OCP, LPR and EIS measurements were conducted to study the electrochemical behavior of the COFs formed on Ti. All potential values used in this work are with respect to the Ag/AgCl reference electrode (0.197 V vs. SHE). Each sample was immersed in the solution for 1 h before starting an EIS or LPR test to stabilize the OCP. LPR tests were performed from −0.020 V vs. OCP up to +0.020 V vs. OCP with a scan rate of 0.167 mV s⁻¹. EIS measurements were taken at OCP. The EIS perturbation voltage amplitude was 10 mV (peak to peak). The frequency range for all experiments was 10 kHz to 10 mHz with sampling rate of 10 points per decade.

9.1.3. Corrosion evaluation for pressure leaching

In order to evaluate the stability of the prepared COFs under simulated pressure leaching conditions, COFs were immersed in de-aerated SCICu1Fe solutions at 150 °C for 1 month. This high temperature (HT) immersion was performed in two PTFE-lined autoclaves. The ratio between solution volume and surface area of the immersed specimens was 0.21 mL mm⁻². The solution was purged with N₂ for at least 30 minutes in the autoclave before soaking the COFs while the oxygen content of the solution was monitored with a dissolved oxygen sensor (Omega DOB21 accuracy 12 ppb) to confirm the oxygen removal. Afterwards, the autoclave was sealed and placed in a high temperature furnace (DZF-6050, MTI Corporation) with temperature controlled to 150±2 °C. After 1 month immersion, samples were removed from the pressure vessel, ultrasonically washed for 5 min in DI water and dried in air. The surface morphology of the COFs after HT immersion was observed using a SEM. Then, the polarization resistance ($R_p$) of the COFs after HT immersion was also estimated by LPR measurements in de-aerated SCICu1Fe solutions at 25 °C, as described above.
9.2 Results and discussion

9.2.1. Controlled chemical oxidation

It is known that addition of H$_2$O$_2$ to an acidified Ti$^{4+}$ solution gives an intense yellow to orange color which is used as a sensitive analytical test for Ti$^{4+}$ and for H$_2$O$_2$ (Satterfield & Bonnell, 1955). The orange color is produced due to the formation of pertitanic acid (H$_2$TiO$_4$), as shown in Reaction 9-1 (Verma et al.). After soaking Ti samples in the solutions at 90 °C for 1 hour, the color of the 2 M H$_2$O$_2$ solution (Solution 1) changed to yellow, the color of the 2 M H$_2$O$_2$/0.1 M HCl solution (Solution 4) changed to intense yellow, and the color of the 2 M H$_2$O$_2$/0.1 M H$_2$SO$_4$ solution (Solution 2) and 2 M H$_2$O$_2$/0.1 M H$_2$SO$_4$/0.1 M HCl solution (Solution SC11Fe) changed to orange. This suggests that the presence of H$_2$SO$_4$ or HCl may facilitate the dissolution of Ti to Ti$^{4+}$. Solutions 1-4 changed to colorless after 24 hours, suggesting the consumption of all H$_2$O$_2$.

\[
\text{Ti}^{4+} + \text{H}_2\text{O}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{TiO}_4 \text{ (Orange)} + 4\text{H}^+ \quad (9-1)
\]

After chemical oxidation, the as grown oxide films present different colors. The color of titanium oxide films has been explained by multiple-beam interference theory, and it is well accepted that the color dictates the film thickness (Chen et al., 2005; Cigada et al., 1992; Gaul, 1993; Karambakhsh et al., 2011; Sharma, 1992; Yan et al., 2002). In the case of thermal oxidation and anodic oxidation, the film thickness also depends on the temperature used and anodizing voltage, respectively. Thus, the correlation of color and thickness to chemical oxidation conditions, anodizing voltage and the heating temperature can be used to compare titanium oxide films obtained by these three oxidation methods. The color of COFs 1-4 is listed in Table 9-1. The correlation of color and thickness to anodization voltage or the heating temperature reported by
other authors are also shown in Table 9-1 (Chen et al., 2005; Gaul, 1993; Karambakhsh et al., 2011; Sharma, 1992). Table 9-1 suggests that among Solutions 1-4, chemical oxidation with Solution 4 may produce the thickest COFs, ~ 190 nm.

In order to highlight the effect of 0.1 M HCl addition on the growth of COFs in 2 M H₂O₂ solutions, 2 M H₂O₂/0.05 M HCl solution (Solution 5) and 2 M H₂O₂/0.2 M HCl solution (Solution 6) were also used to oxidize Ti. After soaking Ti samples in the solutions at 90 °C for 1 hour, the color of Solution 5 changed to yellow while the color of Solution 6 was intense yellow. This color difference suggests that the Ti⁴⁺ concentration in Solution 6 is higher than that in Solution 5, which is reasonable since 0.2 M HCl is more corrosive for Ti than 0.05 M HCl. It is interesting to note that Solution 6 changed to colorless after soaking Ti samples in the solutions at 90 °C for 1 hour, again suggesting the consumption of all H₂O₂. It has been reported that Cl⁻ ions are very effective for accelerating the decomposition of H₂O₂ (Frasch & Mei, 1987). Thus, the decomposition of H₂O₂ in 2 M H₂O₂ with 0.2 M HCl addition may be too fast to effectively oxidize the Ti samples. The color of COFs 5 and 6 is also listed in Table 9-1. Table 9-1 suggests that among all 6 solutions used, chemical oxidation with Solution 5 produces the thinnest COFs, and chemical oxidation with Solution 4 produces the thickest COFs. For comparison purposes, it is interesting to note that similar thicknesses to those obtained for COF 4 (film colors) can be achieved using thermal oxidation at around 600 °C or by anodization at 100 V.

9.2.2. Morphological and structural characteristics of the COFs

Figure 9-1 presents the surface morphology of the as grown COFs. In Figure 9-1, COF 1 still reveals a surface scratch from abrasion, indicating only a very thin oxide film. COFs 5 and 6
clearly reveal the presence of the oxide film across the surface; it is also evident that COF 4 presents the smoothest and least porous surface.

Figure 9-1 Surface morphology of the as grown COFs 1-6.
Figure 9-2 XRD patterns of the as grown COFs 1-6 and the NOF.
The XRD patterns of naturally and chemically oxidized Ti samples are presented in Figure 9-2. Since the penetration depth of Cu-Kα radiation is in the range of 10-20 μm (Kumar et al., 2010a; Kumar et al., 2010b), which is much larger than the thickness of the oxide films, the presence of Ti peaks in the XRD patterns of oxidized Ti samples with thinner oxide films is quite evident. In Figure 9-2, the NOF and COF 1 samples are entirely comprised of hexagonal α-phase (denoted as ‘Ti’) (Kumar et al., 2010a; Kumar et al., 2010b). Thus the NOF and COF 1 are likely too thin to exhibit any oxide anatase or rutile peak due to the dominance of the Ti substrates. This agrees with the data listed in Table 9-1, where COF 1 is the thinnest, with an estimated thickness of only 49 nm. Broad bands around 25.3° and 27.4° in 2θ correspond to the (101) anatase reflection and (110) rutile reflection, respectively (Chang et al., 2009; Trotochaud & Boettcher, 2011). Thus, as indicated in Figure 9-2, the XRD patterns of COFs 2-6 exhibit the presence of a mixed anatase (denoted as ‘A’) and rutile or pure rutile (denoted as ‘R’) phases along with the predominant α-Ti peaks. Due to the dominance of metallic Ti, only the strongest diffraction peaks for the (101) anatase reflection and (110) rutile reflection were well resolved. It is noted that, the XRD patterns of COF 2 soaked in the 2 M H₂O₂ solution with 0.1 M H₂SO₄ addition exhibit a strong anatase peak compared to the rutile peak; the XRD patterns of COF 3 soaked in the 2 M H₂O₂ solution with both 0.1 M H₂SO₄ and 0.1 M HCl additions exhibit anatase and rutile peaks with comparable intensity; the XRD patterns of COFs 4-6 soaked in the 2 M H₂O₂ solution with only Cl⁻ additions exhibit rutile peaks. Therefore, the XRD patterns of COFs 2-6 suggest that SO₄²⁻ additions promoted the formation of the anatase phase; while the Cl⁻ additions favored the formation of pure rutile phase. This finding is consistent with previous studies (Wu, 2004; Xiao et al., 2014).
It is known that in the normal atmosphere, the thermodynamically stable Ti oxide is TiO$_2$ and it exists in three allotropic modifications, \textit{i.e.}, anatase, brookite and rutile (Velten \textit{et al.}, 2002). Among these TiO$_2$ modifications, rutile is thermodynamically the most stable modification, has the highest heat of formation ($\Delta H_{298}^{0} = 945$ kJ mol$^{-1}$) and dielectric constant ($\varepsilon = 110$) (Velten \textit{et al.}, 2002). Meanwhile, it has been reported that the heating temperature of thermal oxidation should be at least 650 °C for the formation of rutile as the dominant phase (Kumar \textit{et al.}, 2010a; Kumar \textit{et al.}, 2010b; Velten \textit{et al.}, 2002). According to the relationship of film thickness and color to voltage and heating temperature (Table 9-1), the voltage should be higher than 100 V for anodic oxidation, or the heating temperature should be above 650 °C for thermal oxidation, in order to produce Ti oxide films with similar thickness to COF 4. After the installation of hydrometallurgical autoclaves, it is clearly not practical to build oxide films via thermal oxidation at 650 °C, and it is not safe to grow oxide films by anodic oxidation at 100 V. The method proposed here for the preparation of COFs provides an alternative, which can also provide excellent corrosion resistance under pressure leaching conditions, as discussed below.

\textbf{9.2.3. Electrochemical impedance spectroscopy}

The objective of this section is to investigate the electrochemical response of these COFs in typical leaching solutions, \textit{i.e.}, SClCu1Fe. The OCP curves for COFs 1-6 and the NOF in de-aerated SClCu1Fe solutions at 25 °C are presented in Figure 9-3. According to Kelly \textit{et al.} (Kelly \textit{et al.}, 2002), a reasonable criterion for steady state would be a change of 5 mV in OCP over a 10 minute period. All potentials in Figure 9-3 reached a steady state according to this criterion within 1 hour.
Figure 9-3 Open circuit potential recorded on COFs 1-6 and the NOF in de-aerated SCICu1Fe solutions, T=25 °C.
EIS experiments were performed to investigate the passive film properties. EIS plots of COFs 1-6 and NOF in de-aerated copper sulfide SCICu1Fe solutions after 1 hour of OCP measurement are shown in Figure 9-4. The value of the magnitude of the impedance at high frequency corresponds to electrolyte resistance \( R_{\text{sol}} \), and the value of the magnitude of the impedance at low frequency corresponds to the sum of polarization resistances \( R_p \) and \( R_{\text{sol}} \). In Figure 9-4 (b) and (d), the value of \( R_{\text{sol}} \) did not vary for the different films; while COF 4 provides the maximum value of \( R_p + R_{\text{sol}} \), which indicates that chemical oxidation with 2 M H\(_2\)O\(_2\)/0.1 M HCl solution improves the corrosion resistance of Ti to the largest extent among all six solutions in Table 9-1.

In order to provide more details of the film properties, the EIS datasets were fitted with electrical equivalent circuits (EECs). The EEC of \( R_{\text{sol}}Q_{\text{pr}}(R_{\text{pr}}(Q_{b})) \) is the one used most frequently for Ti oxide films (Fadlallah & Mohsen, 2010; Pan et al., 1996; Souza et al., 2007). In this EEC it is assumed that the Ti oxide film is a two-layer film, including an inner barrier layer and an outer porous layer. The parameters of this EEC are electrolyte resistance \( R_{\text{sol}} \), outer porous film constant phase element \( Q_{\text{pr}} \), outer porous film resistance \( R_{\text{pr}} \), inner barrier film resistance \( R_b \) and inner barrier film constant phase element \( Q_b \). The fitting curves obtained by using this EEC are also shown in Figure 9-4. The corresponding fitting data are presented in Table 9-2. As shown in Figure 9-4, very good agreement between experimental and simulated data is obtained. The typical error for each parameter is: \( R_{\text{sol}} \), 1.0%; \( Q_{\text{pr}} - Y_0 \), 0.3%; \( Q_{\text{pr}}^\text{n} \), 0.2%; \( R_{\text{pr}} \), 0.8%; \( R_b \), 0.7%; \( Q_b - Y_0 \), 0.3%; \( Q_b \), 0.3%. It could be concluded that the two-layer EEC model satisfactorily describes the COFs in this work.
Figure 9-4 Nyquist (a, b) and Bode (c, d) plots for COFs 1-6 and the NOF in de-aerated SClCu1Fe solutions, T=25 °C.
Table 9-2 EIS parameters for equivalent circuit $R_{sol}(Q_{pr}(R_{pr}(R_{b}Q_{b})))$ for titanium oxide films in de-aerated SCICu1Fe solutions, $T=25$ °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$Q_{pr} - Y_0$ (μF cm$^{-2}$ s$^{-1}$)</th>
<th>$Q_{pr} - n$</th>
<th>$R_{pr}$ (kΩ cm$^2$)</th>
<th>$R_b$ (kΩ cm$^2$)</th>
<th>$Q_b - Y_0$ (μF cm$^{-2}$ s$^{-1}$)</th>
<th>$Q_b - n$</th>
<th>$X^2 \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOF</td>
<td>2.1</td>
<td>8.72</td>
<td>0.85</td>
<td>2.00</td>
<td>20.6</td>
<td>1.01</td>
<td>0.83</td>
<td>3.2</td>
</tr>
<tr>
<td>COF 1</td>
<td>2.1</td>
<td>8.35</td>
<td>0.70</td>
<td>2.80</td>
<td>28.9</td>
<td>3.69</td>
<td>0.81</td>
<td>2.7</td>
</tr>
<tr>
<td>COF 2</td>
<td>2.3</td>
<td>3.56</td>
<td>0.71</td>
<td>3.10</td>
<td>35.3</td>
<td>2.93</td>
<td>0.76</td>
<td>2.4</td>
</tr>
<tr>
<td>COF 3</td>
<td>2.2</td>
<td>4.24</td>
<td>0.70</td>
<td>3.86</td>
<td>68.5</td>
<td>2.69</td>
<td>0.75</td>
<td>3.6</td>
</tr>
<tr>
<td>COF 4</td>
<td>2.3</td>
<td>2.63</td>
<td>0.70</td>
<td>18.3</td>
<td>136</td>
<td>2.78</td>
<td>0.77</td>
<td>2.3</td>
</tr>
<tr>
<td>COF 5</td>
<td>2.2</td>
<td>3.07</td>
<td>0.73</td>
<td>9.50</td>
<td>101</td>
<td>2.80</td>
<td>0.81</td>
<td>3.0</td>
</tr>
<tr>
<td>COF 6</td>
<td>2.3</td>
<td>4.30</td>
<td>0.71</td>
<td>4.90</td>
<td>72.1</td>
<td>2.68</td>
<td>0.87</td>
<td>4.3</td>
</tr>
</tbody>
</table>
As shown in Table 9-2, the \( R_{pr} \) and \( R_b \) values of COFs 1-6 are higher than the \( R_{pr} \) and \( R_b \) values of the NOF, which proves that chemical oxidation with 2 M H\(_2\)O\(_2\) solutions successfully improves the corrosion resistance of Ti. It is also noted that the \( R_{pr} \) and \( R_b \) values of COFs increased from COF 1 to COF 4. This trend agrees with the estimated thickness increase shown in Table 9-1. Table 9-2 also shows that the \( R_{pr} \) and \( R_b \) values of COF 4 are higher than those for COF 5 and COF 6, which indicates that 0.1 M HCl is more effective than either 0.05 M HCl or 0.2 M HCl. The Constant Phase Element (symbolized here by \( Q \)) was used to compensate for the non-ideal behavior of the capacitor (Hsu & Mansfeld, 2001). According to Hsu and Mansfeld’s work, capacitance values can be extracted from CPE data using Eq. (9-2) (Hsu & Mansfeld, 2001). The thickness of a oxide film can be calculated by Eq. (9-3) (Hirschorn et al., 2010).

\[
C = Q^{1/n} R^{(1-n)/n} \tag{9-2}
\]

\[
\delta = \frac{\varepsilon \varepsilon_0}{C} \tag{9-3}
\]

In Eq. (9-4) and Eq. (9-5), \( C \) and \( R \) represent the capacitance and resistance of a film, respectively; \( \varepsilon_0 \) (=8.854×10\(^{-14}\) F cm\(^{-1}\)) is the vacuum permittivity (Bard & Faulkner, 2001); \( \varepsilon \) (= 48 for anatase and 110 for rutile; dimensionless) is the dielectric constant of an oxide (Velten et al., 2002). Since the NOF and COF 1 fail to exhibit either anatase or rutile peaks in Figure 9-2, their thickness values were not estimated here. The \( \varepsilon \) of COF 2 was assumed to be 48 due to its strong anatase peak compared to the rutile peak; the \( \varepsilon \) of COF 3 was assumed to be 79 (the average value of 48 and 110) because of its anatase and rutile peaks with comparable intensity. The calculated capacitance and thickness values for these films are presented in Table 9-3.
Table 9-3 Estimated capacitance and resistance values for titanium oxide films based on the corresponding EIS results (in Table 9-2).

<table>
<thead>
<tr>
<th>No.</th>
<th>ε</th>
<th>$C_{pr}$ (μF cm$^{-2}$)</th>
<th>$\delta_{pr}$ (nm)</th>
<th>$C_{film}$ (μF cm$^{-2}$)</th>
<th>$\delta_{b}$ (nm)</th>
<th>$\delta$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOF</td>
<td>-</td>
<td>4.26</td>
<td>-</td>
<td>7.34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COF 1</td>
<td>-</td>
<td>1.67</td>
<td>-</td>
<td>2.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>COF 2</td>
<td>48</td>
<td>0.564</td>
<td>75</td>
<td>1.43</td>
<td>29</td>
<td>104</td>
</tr>
<tr>
<td>COF 3</td>
<td>79</td>
<td>0.728</td>
<td>97</td>
<td>1.53</td>
<td>46</td>
<td>143</td>
</tr>
<tr>
<td>COF 4</td>
<td>110</td>
<td>0.716</td>
<td>135</td>
<td>2.08</td>
<td>46</td>
<td>181</td>
</tr>
<tr>
<td>COF 5</td>
<td>110</td>
<td>0.833</td>
<td>117</td>
<td>2.08</td>
<td>46</td>
<td>163</td>
</tr>
<tr>
<td>COF 6</td>
<td>110</td>
<td>0.889</td>
<td>109</td>
<td>2.09</td>
<td>46</td>
<td>154</td>
</tr>
</tbody>
</table>

Table 9-3 shows that the thickness value of each porous layer ($\delta_{pr}$) is larger than the thickness value of the corresponding barrier layer ($\delta_{b}$); COFs 3-6 give the same $\delta_{b}$ value, which is larger than the $\delta_{b}$ of COFs 2. Together with the difference of their treating solutions, it seems that chemical oxidation in the presence of Cl$^-$ ions can produce films with thicker barrier layers than films obtained by chemical oxidation without Cl$^-$ additions, and the total thickness of COFs mainly depends on the porous layers. Table 9-3 also presents that the total thickness values of these COFs ($\delta = \delta_{pr} + \delta_{b}$), which are close to those estimated by the surface colors (in Table 9-1). Therefore, it is reasonable to use the EEC of $R_{sol}(Q_{pr}(R_{pr}(R_{b}Q_{b})))$. The increasing sequence for the thickness of these COFs is: COFs 2 < COFs 3 < COFs 6 < COFs 5 < COFs 4.
9.2.4. Linear polarization resistance

LPR experiments were performed to evaluate the corrosion resistance of COFs and the NOF in de-aerated $30 \text{ g L}^{-1} \text{H}_2\text{SO}_4 + 12 \text{ g L}^{-1} \text{Cl}^- + 15 \text{ g L}^{-1} \text{Cu}^{2+} + 1 \text{ g L}^{-1} \text{Fe}^{3+}$ solutions at $25 \degree \text{C}$. In Figure 9-5, the solid line represents the $R_{\text{p-LPR}}$ values for the NOF, and the dashed line represents the previously published $R_{\text{p-LPR}}$ value for an 80 V-AOF. It is evident that $R_{\text{p-LPR}}$ values for the as grown COFs 1-6 are all higher than that for the NOF, and the $R_{\text{p-LPR}}$ value for the as grown COF 4 is even higher than that for the 80 V-AOF under the same conditions. As shown in Figure 9-5, the increasing sequence for the $R_{\text{p-LPR}}$ values of the as grown COFs is COF 1 < COF 2 < COF 3 < COF 6 < COF 5 < COF 4, which is consistent with the increasing sequence for the thickness of these COFs.

In order to evaluate the stability of the COFs under simulated pressure leaching conditions, the as grown COFs were immersed in de-aerated SCICu1Fe solutions at $150 \degree \text{C}$ for 1 month. Figure 9-6 presents the surface morphology of these COFs after this HT immersion. Figure 9-6 clearly reveals that COF 4 still presents the smoothest and least porous surface. The unfilled circles in Figure 9-5 represent the $R_{\text{p-LPR}}$ values for COFs 1-6 after the HT immersion, which are lower than the $R_{\text{p-LPR}}$ values for the as grown COFs 1-6, respectively. It is noted that after the HT immersion, the $R_{\text{p-LPR}}$ value for COF 4 is still higher than that for an 80 V-AOF under the same conditions. It can now be concluded that, chemical oxidation with $\text{H}_2\text{O}_2$ solutions improves the corrosion resistance of Ti for hydrometallurgical applications. Further, among the conditions tested here, chemical oxidation with 2 M $\text{H}_2\text{O}_2$/0.1 M HCl solution leads to the best improvement of the corrosion resistance of Ti.
Figure 9-5 $R_p$ values of COFs 1-6 after 1 hour OCP measurement in de-aerated SCICu1Fe solutions, T=25 °C. The solid line presents the $R_p$-LPR value for the NOF, and the dashed line shows the $R_p$-LPR value for an 80 V-AOF under otherwise identical conditions.
Figure 9-6 Surface morphology of COFs 1-6 after 1 month immersion in de-aerated SCICu1Fe solutions, T=150 °C.
9.3 Summary

A new method, comprising a 24-hours chemical oxidation with hydrogen peroxide solutions at 90 °C followed by 48-hours of hydrothermal treatment in DI water at 150 °C, was developed to produce titanium oxide films with high corrosion resistance for hydrometallurgical applications. Based on the experimental results, the following conclusions were obtained:

1) The as grown COFs were characterized by XRD measurements to be pure rutile, or a mixture of anatase and rutile, depending mainly on the presence of Cl\(^-\) and SO\(_4\)\(^{2-}\) ions. XRD results indicated that the addition of SO\(_4\)\(^{2-}\) ions promoted the formation of pure anatase; while the addition of Cl\(^-\) ions favored the formation of pure rutile.

2) According to the relationship of film thickness and color to voltage and heating temperature, the voltage should be higher than 100 V for anodic oxidation, or the heating temperature should be above 650 °C for thermal oxidation in order to produce Ti oxide films with similar thickness to the COF obtained in this work by chemical oxidation with 2 M H\(_2\)O\(_2\)/0.1 M HCl solution.

3) EIS results suggested that chemical oxidation in the presence of Cl\(^-\) ions can produce films with thicker barrier layers than films obtained by chemical oxidation without Cl\(^-\) additions. The thickest part of the COFs is the porous layer.

4) Surface morphology and electrochemical results indicated that chemical oxidation with H\(_2\)O\(_2\) solutions improves the corrosion resistance of Ti for hydrometallurgical applications, and chemical oxidation with 2 M H\(_2\)O\(_2\)/0.1 M HCl solution leads to the best improvement of the corrosion resistance of Ti in this work.
10 Conclusions and recommendations

The electrochemical, mass loss and characterization analyses performed in this study lead to the following conclusions, more tentative findings (requiring further work) and recommendations.

10.1 Conclusions

1) Both electrochemical and mass loss data have shown that H₂SO₄ solutions are very corrosive for Ti with a freshly polished surface, and Cu²⁺ and Fe³⁺ ions are good corrosion inhibitors for Ti. Potentiodynamic polarization experiments demonstrate that the presence of Cl⁻ ions promotes the anodic passivity of Ti while Cu²⁺ and Fe³⁺ ions enforce (maintain) the anodic passivity of Ti in H₂SO₄ solutions. Mass loss measurements have shown that the corrosion rates of Ti are unaffected by the presence of Cl⁻ in sulfuric acid alone.

2) The Iso-corrosion curves (0.1, 0.5, and 1 mm yr⁻¹) of Ti in 3–50 wt.% H₂SO₄ solutions (with no addition; with the addition of 15 g L⁻¹ Cu²⁺ and with the addition of 1 g L⁻¹ Fe³⁺) up to 175 °C were constructed from the mass loss data. Results from mass loss and electrochemical measurements suggest that temperature, acid concentration and the presence of Cu²⁺ or Fe³⁺ ions govern the position of each Iso-corrosion line.

3) Cyclic potentiodynamic polarization (CPP) results have shown that the breakdown potential $E_b$ of titanium decreases; while the repassivation potential $E_{rp}$ of titanium remains constant in 1 mol L⁻¹ NaCl solution with increasing temperature from 125 to 200 °C. CPP and XPS results have confirmed that the inhibition effect of sulfate on pitting may be attributed to the competition for adsorption sites on the oxide surface. A metastable pitting temperature threshold (MPTT) is defined for Ti as a function of sulfate to chloride mole ratio using linear-sweep thermammetry measurements. The MPTT results are consistent with those
obtained in CPP measurements. The results confirmed that the MPTT of titanium is elevated by the addition of sulfate ions.

4) AOFs are produced on Ti in 0.5 M sulfuric acid solutions at room temperature and in the potential range of 20 to 80 V. LPR and EIS results have shown that 80 V-anodization of Ti leads to the best improvement of the corrosion resistance of Ti in copper leaching solutions.

5) A new method, comprising a 24-hour chemical oxidation with hydrogen peroxide solutions at 90 °C followed by 48-hours of hydrothermal treatment in DI water at 150 °C, has been developed to produce Ti oxide films with high corrosion resistance for hydrometallurgical applications. Chemical oxidation with 2 M H₂O₂/0.1 M HCl solution leads to the best improvement of the corrosion resistance of Ti in this work.

10.2 Tentative findings

This work has also produced some results which require further investigation:

1) The process leading to the reduction of Cu²⁺ ions on TiO₂ films in de-aerated 30 g L⁻¹ H₂SO₄ + 12 g L⁻¹ Cl⁻ + 15 g L⁻¹ Cu²⁺ at 85 °C is not clear. The XPS signals of Cu⁰ and Cu⁺ are basically the same, but they are different from Cu²⁺ signals. XPS results provided evidence that Cu²⁺ ions were reduced to Cu⁰ or Cu⁺ in the Ti oxide films. Auger electron spectroscopy should be performed to characterize the exact valence state of Cu in the Ti oxide films.

2) The conversion of the \( E_{measured} \) at high temperatures to the SHE scale at 25 °C is not rigorous. Ions involved and the required \( C_i \) and \( u_i \) from 25 to 115 °C are calculated using the OLI Electrolyte Simulation Software. A second order polynomial regression method was used to find the best correlation function of \( C_i = f(T) \); while a linear regression method
was used to find the best correlation function of \( u_i = f(T) \). Due to the limitation of the OLI Software, values of \( u_i \) and \( C_i \) from 115 to 175 °C are calculated by fitting equations (Table 6-1) based on data from 25 to 115 °C. A thorough and more accurate set of \( C_i \) and \( u_i \) calculations at higher temperatures should be performed to correct the fitting equations.

10.3 Recommendations

The preceding discussions have also highlighted further areas of interest for future work:

1) **Leaching surfactants.** Surfactants are always added during medium temperature pressure leaching to disperse the insulating layer of elemental sulfur formed on mineral surfaces. The effect of leaching surfactants on the corrosion behavior of Ti should be investigated under pressure leaching conditions.

2) **O\(_2\).** Pressure leaching may be carried out under an oxygen partial pressure of 345-1725 kPa. The effect of oxygen partial pressure on the corrosion behavior of Ti should be investigated under pressure leaching conditions.

3) **pH.** The effects of both temperature and \( \text{SO}_4^{2-} \) on the pitting corrosion of titanium were studied in neutral \( \text{Cl}^- \) containing solutions. It is also of interest to determine the effect of pH on the pitting corrosion of Ti in high-temperature \( \text{Cl}^- \) solutions.

4) **AOFs and COFs.** The electrochemical responses of AOFs and COFs were not investigated in sulfate-chloride solutions at temperatures above 100 °C.
References


He, X., Noël, J. J., & Shoesmith, D. W. (2005). Crevice corrosion damage function for grade-2 titanium of iron content 0.078 wt% at 95 °C. *Corrosion Science, 47*(5), 1177-1195


Hsu, C., & Mansfeld, F. (2001). Technical note: concerning the conversion of the constant phase element parameter Y0 into a capacitance. *Corrosion, 57*(9), 747-748


Appendices

Appendix A – Low temperature electrochemical apparatus

Figure A-1 Three-electrode jacketed cell assembly.
Figure B-1 Autoclave assembly.
Figure B-2 Assembled autoclave at work.
Appendix C – High temperature immersion apparatus

Figure C-1 Immersion apparatus assembly.

Note: The schematic overview of the pressure vessel and sample holder is shown in Figure 5-1.
Appendix D – Controlled chemical oxidation

Figure D-1 Controlled chemical oxidation assembly.

Note: Each Ti sample was soaked in 50 mL of oxidizing solution at 90 °C for 24 hours. There were four samples in each glass container with 200 mL of oxidizing solution.