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A new method to improve the corrosion resistance of titanium for hydrometallurgical applications

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ABSTRACT

The main objective of the present work was to develop a method to fabricate titanium oxide films with high corrosion resistance by controlled chemical oxidation with H_2O_2 solutions at 90 °C. The prepared chemically oxidized films (COFs) were characterized by X-ray diffraction (XRD) measurements and found to be a mixture of anatase and rutile or pure rutile, depending mainly on the presence of Cl^- and $SO_4{}^{2-}$ in H_2O_2 solutions. XRD results indicated that the addition of $SO_4{}^{2-}$ ions promoted the formation of anatase; while the addition of Cl^- ions favored the formation of rutile. Linear polarization resistance and electrochemical impedance spectroscopy measurements were used to evaluate the corrosion resistance of the as grown COFs for hydrometallurgical applications. Results verified that chemical oxidation with H_2O_2 solutions is capable of improving the corrosion resistance of Ti for hydrometallurgical applications. Chemical oxidation with 2 M H_2O_2/0.1 M HCl solution led to the best improvement of the corrosion resistance of Ti.

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1. Introduction

With its good fabricability and excellent resistance to corrosion in many environments, titanium is often selected for many internal autoclave parts, where they are subjected to very corrosive environments, such as those prevalent in hydrometallurgical pressure leaching [1–4]. The excellent corrosion resistance of Ti is due to the chemically unreactive and mechanically strong oxide film formed on its surface [5,6]. Titanium oxide forms instantly when a freshly polished titanium surface is exposed to air [7]. The native oxide is normally thin (~10 nm), amorphous, and stoichiometrically defective [8]. As a result, the leaching lixiviants in the 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 [6,7]. 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 [9–14]. Thermal oxidation is simple, but its reproducibility is poor and should be preceded by acid pickling to remove embedded surface contaminants, such as iron [15]. Also, the temperature of oxidation should be at least 500 °C to build a film with good corrosion resistance, usually blue in color [9,14,16]. It is not practical to heat a large vessel at 500 °C to rebuild the oxide films, especially when no source of heat is readily available. 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 [16]. 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 [15,16]. In our previous work, anodic oxide films (AOFs) were potentiostatically formed on commercially pure titanium in 0.5 M sulfuric acid (H_2SO_4) solutions at various anodizing voltages (up to 80 V) at room temperature [6]. Even though a suitable corrosion resistance can be accomplished by anodizing, it remains difficult to apply anodizing to a large autoclave with complex internals [15]. Furthermore, according to Cotton [16] and McMaster [15], constant voltage power sets for 25–80 V are usually utilized and anodizing times must be on the order of 10–72 h for very large vessels. Anodizing (80 V) may be applied to autoclaves after installation, but it is a time consuming and laborious operation with potential safety problems. These vessels are very large and applying current to such surfaces is not practical.

On the other hand, controlled chemical oxidation is an attractive technique for growing oxide layers on titanium substrates. Hydrogen peroxide (H_2O_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_2O_2

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Table 1
Correlation of color and thickness of titanium oxide films to conditions for different oxidation methods.

Solutions/COFs No.	Solutions composition for chemical oxidation	Color	Thickness (nm)[a]	Voltage (DC) for anodic oxidation[a]	T (°C) for thermal oxidation[a]
1	2 M H_2O_2	Golden brown	49	10	385
2	2 M H_2O_2 + 0.1 M H_2SO_4	Purple	110	60	523
3	2 M H_2O_2 + 0.1 M H_2SO_4 + 0.1 M HCl	Bronze	150	80	579
4	2 M H_2O_2 + 0.1 M HCl	Grey	190	100	635
5	2 M H_2O_2 + 0.05 M HCl	Rose	170	90	607
6	2 M H_2O_2 + 0.2 M HCl	Gold purple	160	85	593

[a] Previous published results [9,28–30]. The values for thickness, anodic oxidation voltage, and thermal oxidation temperature are all published results related to colors of the obtained COFs.

solutions. Nanci et al. treated titanium with a H_2O_2/H_2SO_4 mixture at room temperature to eliminate surface contaminants and to produce a consistent and reproducible titanium oxide surface layer [7,17,18]. Wang et al. reported the formation of an amorphous titanium oxide layer after the titanium specimen was treated with an 8.8 M H_2O_2/0.1 M HCl solution at 80 °C for various times up to 1 h [19]. 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 [19]. Wu et al. later used 30 wt.% H_2O_2 solutions to oxidize metallic titanium at 80 °C for 72 h to prepare crystalline TiO_2 nanorods [20–22]. They found that the crystal phases could be controlled by adding F^- (5 mM NaF), Cl^- (5 mM NaCl) and $SO_4{}^{2-}$ (5 mM Na_2SO_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 [22]. Most recently, Wu et al. oxidized titanium with a 5 wt.% (1.5 M) H_2O_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 [23]. The above methods were mainly aimed at modifying Ti surfaces for the improvement of bioactivity or photocatalytic activity. To the authors' 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.

The present work aims to develop a new method to fabricate oxide films on Ti substrates with high corrosion resistance by controlled chemical oxidation with H_2O_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). Scanning electron microscopy (SEM) and X-ray diffraction (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 the COFs for hydrometallurgical applications.

2. Experimental

2.1. Controlled chemical oxidation of Ti

The substrate material investigated was commercially 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. Deionized (DI) water, H_2O_2 (30 wt.%, Fisher Scientific), H_2SO_4 (95.0–98.0%, Fisher Scientific), HCl (37%, Fisher Scientific) and sodium chloride (NaCl, Cryst./Certified ACS) were used to prepare the solutions employed for controlled chemical oxidation of Ti. There are 6 solutions (listed in Table 1) used in this work, they will be referred-to by their associated number throughout the remainder of this work (denoted as COFs 1–6). The solutions were not sparged with gases prior to or during the chemical oxidation.

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 h. 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 h. 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 ($\lambda = 1.5405$ Å) to determine the crystal structures of the as grown COFs.

In order to assess 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 h after abrasion using successive grades of SiC papers down to 1200 grit followed by ultrasonication for 5 min in DI water.

2.2. 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 simulate copper sulfide concentrate leaching) containing 30 g L^{-1} H_2SO_4 + 12 g L^{-1} Cl^- + 15 g L^{-1} Cu^{2+} + 1 g L^{-1} Fe^{3+}. DI water, H_2SO_4 (95.0–98.0%, Fisher Scientific), NaCl (Cryst./Certified ACS), cupric sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, Cryst./Certified ACS), and iron(III) sulfate pentahydrate ($Fe_2(SO_4)_3{\cdot}5H_2O$, 97%, Acros) were used to prepare the leaching solution. This solution was de-aerated using high-purity N_2 for at least 30 min 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. Open circuit potential (OCP), linear polarization resistance (LPR) and electrochemical impedance spectroscopy (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

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