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Purification of reduced upgraded titania slag by iron removal using mild acids

Jaehun Cho, Syamantak Roy, Amarchand Sathyapalan, Michael L. Free *, Z. Zak Fang, Weizhi Zeng

Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah 84112, United States

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ABSTRACT

In this study, we focused on removal of iron from upgraded titania slag (UGS) that has been reduced by hydrogen gas, magnesium powder and salts at 750 °C for 5 h. Reduced UGS is mainly composed of titanium hydride and oxide impurities that include iron, silicon, aluminum, and magnesium. Mild concentrations of hydrochloric and boric acids were used in this investigation to remove iron from reduced UGS. The concentration of hydrochloric and boric acids and the leaching temperature have been chosen as the prime variables to identify the optimum conditions and leaching characteristics for purification of reduced UGS. Both ambient pressure leaching and elevated pressure leaching were performed to assess the rate of iron removal from reduced UGS without titanium loss. It was observed that under the constraint that 1% (*w*/*w*) of titanium hydride loss is the maximum amount tolerable, 0.1 M hydrochloric acid at 140 °C was found to be the most effective conditions for iron removal (87.63%). A factorial design of experiment for equation modeling with three main factors (temperature, concentration of hydrochloric and boric acids) was performed and associated modeling results were in good agreement with experimental data. The overall rate of reaction seems to follow interfacial reaction controlled kinetics. The calculated activation energy of the reaction is 73.9 kJ/mol.

1. Introduction

Pure metallic titanium is of great industrial importance because of its use in various applications such as aviation (Zhou et al., 2005), aerospace (Boyer, 1996), biomedical (Niinomi, 2003), marine (Gorynin, 1999), and nuclear waste storage (Hua et al., 2005) due to its corrosion resistance, high specific strength, light weight, relatively high melting point, and chemical/heat stability. Moreover, it has great optical, mechanical, and electronic properties, as well as biocompatibility (Amarchand et al., 2000). Although it is predominantly found as rutile (TiO_2) and ilmenite ($FeTiO_3$), which are abundant in the earth's crust, the production cost is relatively high compared to competing metals such as steel and aluminum (Froes and Eylon, 1990). In general, titanium can be extracted from its ore by sulfate or chloride processes. Even though low grade ilmenite feed stock can be used, the major drawback of sulfate processes is the generation of a large quantity of waste iron sulfates. In the case of chloride processes, greenhouse gas is generated and it requires an upgraded starting material, which increases the cost of production (Middlemas et al., 2013).

The current commercial method for production of metallic titanium is the Kroll process in which metallic titanium is obtained by magnesiothermic reduction of titanium tetrachloride ($TiCl_4$) (Park et al., 2005), which is produced from the chlorination of titanium dioxide (TiO_2) or synthetic rutile. After that, additional leaching or heated vacuum distillation is carried out on the porous titanium sponge resulting from the reduction process as a further purification step (Kroll, 1940). Although the Kroll process allows industry to produce high-purity metallic titanium with low oxygen level, there are several challenges. Firstly, developing a continuous reduction process is difficult due to the high vacuum, long-term processing, and the generation of titanium deposits on the inner wall of the reactor. Secondly, batch-type processing for long periods of time results in high labor power and low productivity (Takeda and Okabe, 2006). Furthermore, environmental issues such as generation of greenhouse gas and corrosive intermediate products like titanium tetrachloride are involved (Amarchand et al., 2000; Middlemas et al., 2013).

To mitigate the challenges of the Kroll process, several new alternative techniques with low cost and high purity and productivity have been suggested. Recently, titanium subchlorides such as titanium dichloride ($TiCl_2$) and titanium trichloride ($TiCl_3$) have been investigated as potential replacements for titanium tetrachloride ($TiCl_4$) feed. This process keeps the advantages of the Kroll process such as an oxygen-free environment and easy impurity-control and may increase the process speed (Takeda and Okabe, 2006). However, concerns such as handling volatile titanium tetrachloride require further technical and practical studies before industrial application. Another alternative technique is direct reduction from titanium dioxide by electrodeposition of titanium from ionic solutions, but this approach has several problems like difficulties in handling the redox cycle of multivalent titanium

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* Corresponding author.
E-mail address: michael.free@utah.edu (M.L. Free).

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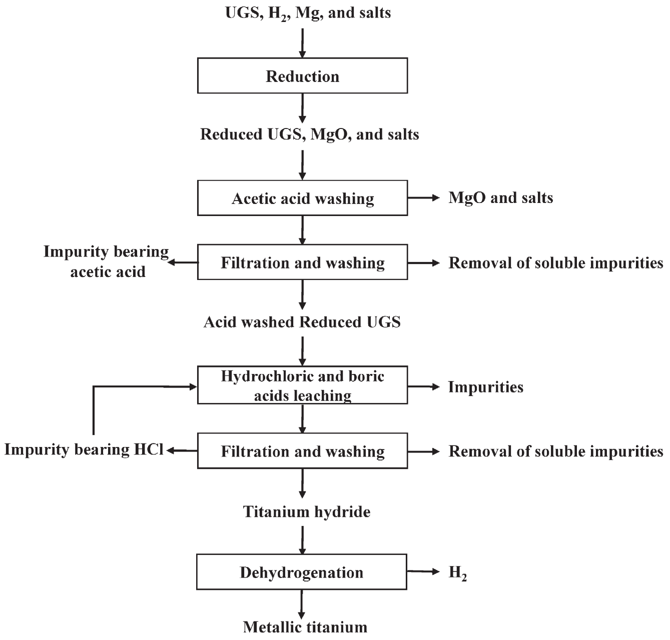

Fig. 1. Flow sheet of new route for production of metallic titanium.

ions and reactive dendritic products (Chen et al., 2000). Recently, Fang et al. (2013) suggested titanium production from titanium hydride (TiH_2), which can be obtained by reduction of upgraded titania slag (UGS) or synthetic rutile under a controlled environment in the presence of magnesium and salts. After making titanium hydride, metallic titanium is produced by dehydrogenation of titanium hydride at about 500 °C (Fang et al., 2013). In this new route, production costs and environmental problems can be significantly reduced and productivity can be improved compared to the Kroll process. The feed material, UGS is obtained by reduction of ilmenite ore in a blast furnace followed by roasting and acid leaching. However, one of the concerns in this process is the level of residual impurities such as iron oxide.

In this work, we are investigating the hydrometallurgical leaching characteristics using hydrochloric and boric acids associated with the removal of iron from UGS which has been reduced using hydrogen gas, magnesium powder and salts at 750 °C for 5 h (Fang et al., 2013). Reduced UGS is predominantly composed of titanium hydride and oxide impurities involving iron, silicon, aluminum, and/or magnesium. In fact, extraction of titanium using hydrochloric acid has been investigated extensively due to its low cost, reduced environmental issues, and potential for recycling compared to competing lixiviants such as sulfuric acid. However, most of the work has focused on extraction of titanium from ilmenite ore (El-Hazek et al., 2007; Ogasawara and Veloso de Araujo, 2000; Van Dyk et al., 2002). Thus, this study, the goal of which is iron removal from reduced UGS, can be differentiated from other research. The flow chart shown in Fig. 1 illustrates the overall production of pure titanium from UGS. In this investigation, modest concentrations of hydrochloric and boric acids were used to reduce product loss. Boric acid was used to accelerate iron removal kinetics, because boric acid and borate tend to form complexes with hydrous iron oxides as shown in Eq. (1) (Peak et al., 2013).

$$Fe^{3+} + H_3BO_3 + H_2O = FeB(OH)_4^{2+} + H^+ \tag{1}$$

Table 1
Chemical composition of reduced UGS before and after acetic acid washing.

Component (%)	Mg compounds and salts	Ti	Fe	Al	Si
Before washing	79.79	19.52	0.22	0.07	0.41
After washing	0.36	96.20	1.07	0.35	2.02

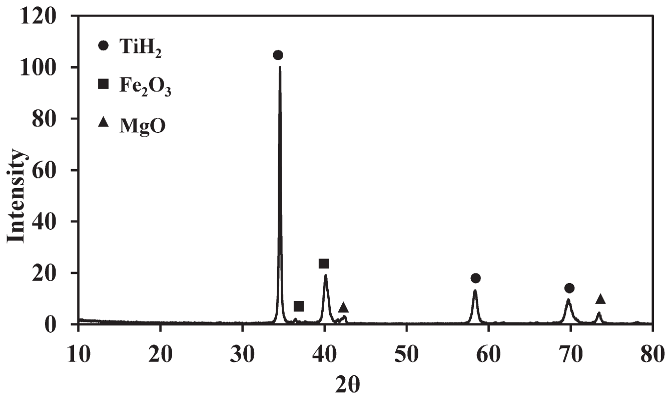

Fig. 2. XRD pattern of the reduced UGS after acetic acid washing.

The stability constant of iron borate complexes is $1.0 \pm 0.2 \times 10^{-2}$ 25 °C for an ionic strength of 0.68 (Elrod and Kester, 1980).

Important factors such as leaching temperature and concentrations were considered to identify the optimum condition and leaching characteristics for iron removal.

2. Materials & methods

2.1. Preparation of reduced UGS by reduction and acetic acid leaching

UGS is composed of about 96% titanium dioxide and 4% impurities. A mixture of UGS (less than 40 μm), magnesium powder and salts, such as magnesium chloride ($MgCl_2$) and potassium chloride (KCl), with a ratio of 1:1:1 by weight were placed in a furnace under hydrogen atmosphere and reduced for 5 h at 750 °C. Excess magnesium and salts are used to help increase kinetics (Fang et al., 2013). The product resulting from the reduction is washed using 4.3 M acetic acid (CH_3COOH) with a solid to liquid ratio of 1 g to 40 ml for 2 h at 70 °C to remove magnesium compounds and salts from reduced UGS. After acetic acid washing and filtration, the residue was washed with deionized water and 0.05 M hydrochloric acid. The sample so obtained is used as the feed in this study.

2.2. Experimental procedures

A solution of 200 ml which contained 0.05 or 0.1 M hydrochloric acids with or without 1 M boric acid was prepared in a flask made of semi-clear polymethylpentene. A chemical and temperature resistant plug with a hole that allows for a thermometer insertion was applied

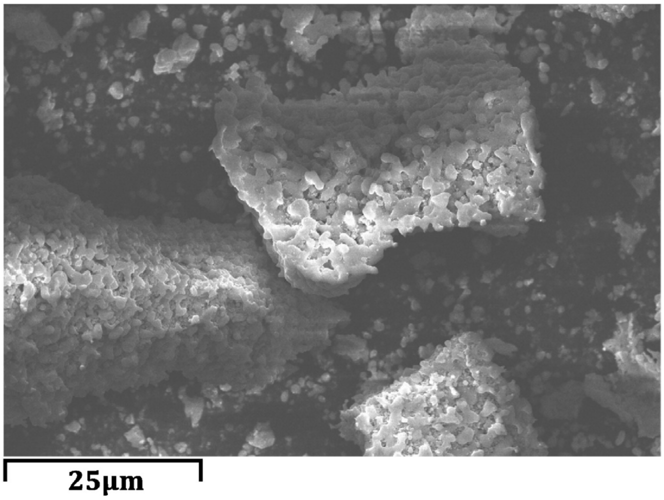

Fig. 3. SEM image of reduced UGS after acetic acid washing.