

A New, Energy-Efficient Chemical Pathway for Extracting Ti Metal from Ti Minerals

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S Supporting Information

ABSTRACT: Titanium is the ninth most abundant element, fourth among common metals, in the Earth's crust. Apart from some high-value applications in, e.g., the aerospace, biomedicine, and defense industries, the use of titanium in industrial or civilian applications has been extremely limited because of its high embodied energy and high cost. However, employing titanium would significantly reduce energy consumption of mechanical systems such as civilian transportation vehicles, which would have a profound impact on the sustainability of a global economy and the society of the future. The root cause of the high cost of titanium is its very strong affinity for oxygen. Conventional methods for Ti extraction involve several energy-intensive processes, including upgrading ilmenite ore to Ti-slag and then to synthetic rutile, high-temperature carbo-chlorination to produce TiCl_4 , and batch reduction of TiCl_4 using Mg or Na (Kroll or Hunter process). This Communication describes a novel chemical pathway for extracting titanium metal from the upgraded titanium minerals (Ti-slag) with 60% less energy consumption than conventional methods. The new method involves direct reduction of Ti-slag using magnesium hydride, forming titanium hydride, which is subsequently purified by a series of chemical leaching steps. By directly reducing Ti-slag in the first step, Ti is chemically separated from impurities without using high-temperature processes.

Titanium is the ninth most abundant element, fourth among common metals, in the Earth's crust. It has been used as a high-performance light metal in aerospace, defense, biomedical, petrochemical, and other high-value applications owing to its high specific strength, extreme corrosion resistance, and biocompatibility. However, the use of titanium in industrial or civilian applications has been extremely limited because of its high embodied energy and high cost, despite the fact that employing titanium would significantly reduce energy consumption of mechanical systems such as civilian transportation vehicles, which would have a profound impact on the sustainability of a global economy and the society of the future. Developing a technology to significantly reduce the energy consumption, and thus the cost, of extracting titanium has challenged scientists for nearly a century. In the work described herein, a novel method for extracting titanium metal from upgraded titanium minerals with 60% less energy consumption than conventional methods is discovered. This

Communication focuses on the fundamental principles of the new method and the experimental data that demonstrate its feasibility. The methods and data of the energy analysis are documented in the Supporting Information.

The root cause of the high cost of titanium is its very strong affinity for oxygen. A quick reference to the Ellingham diagram of oxides¹ will show that, among common metals, only Al, Mg, Ca, and Li form more stable oxides than Ti. The challenges for producing Ti are not only the extractive processes to separate its oxides from other compounds in Ti feed stocks, but more so the process that reduces titanium oxide to metal. Figure 1

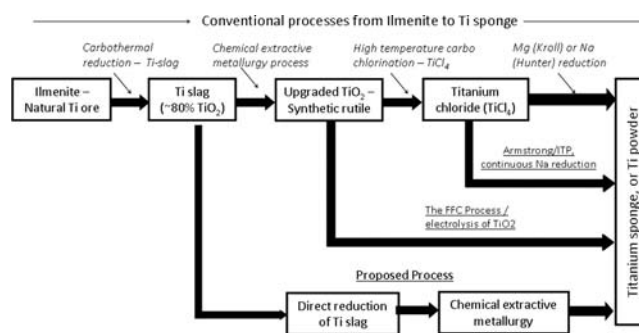


Figure 1. Comparison of conventional and developing processes for production of Ti sponge or Ti powder.

illustrates the major steps of existing methods of producing Ti sponge from ilmenite ore. Over 90% of global titanium reserves is in the form of ilmenite (~45–65% TiO_2 equivalent),² with only 10% occurring as natural rutile (~95% TiO_2). Ilmenite can be smelted using a carbothermal process to yield pig iron and Ti-slag.³ The main component of Ti-slag is ~80% Ti-based oxides which are bonded with other metals in the form of metal titanates,⁴ including Fe, Mg, Ca, Al, Si, and other transition metals. Pig iron is used for making iron and steel, whereas the Ti-slag can be used to produce TiO_2 pigment or Ti metal.

The existing technologies, including both commercial and developmental processes, can be categorized into two groups: those by reduction of TiCl_4 (e.g., Kroll,⁵ Armstrong/ITP⁶) and those by reduction of TiO_2 (e.g., FFC process.⁷) The emphasis in the former approach is to optimize the TiCl_4 reduction processes, while the primary motivation of the latter approach is to avoid the high-temperature chlorination process. The Armstrong process is a significant advancement compared to

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the conventional Hunter⁸ process, as it is a continuous process with molten sodium being pumped continuously into the reactor to reduce TiCl_4 . The FFC process, published in 2000, was also a breakthrough that demonstrated the potential of the electrochemical approach. In either of the two approaches, titanium ore must first be refined through a series of chemical extractive processes to obtain highly refined rutile (TiO_2) before reduction to Ti metal.

The relative cost for each of the processing steps in the Kroll process was reported by Hartman et al.⁹ After upgrading TiO_2 (10% of total), chlorination and Mg reduction are the most costly steps of making Ti sponge (24 and 66%, respectively). As it will be shown, the new approach described in this Communication changes the chemical pathway by first directly reducing TiO_2 to titanium hydride (TiH_2) in the slag to chemically isolate Ti from other compounds and then removing impurities by a series of targeted leaching stages. The new approach eliminates the need for carbo-chlorination of TiO_2 and the reduction of TiCl_4 by Kroll or Hunter types of processes.

Recognizing the energy intensiveness involved in existing technologies, the present authors discovered that the titanium oxide contained in the minerals can be reduced directly with magnesium hydride (MgH_2) to form TiH_2 , which could be purified subsequently by a series of chemical leaching steps. The concept of the new chemical pathway is shown in three primary steps in Figure 2.

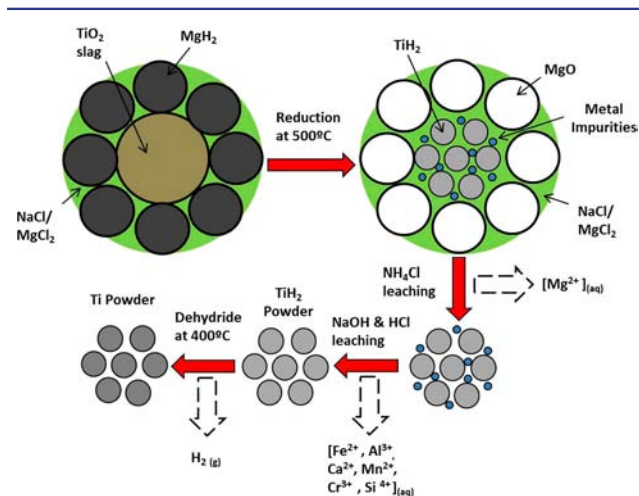
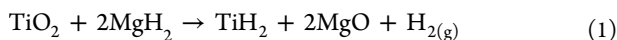


Figure 2. Schematic illustration of the three-step process for extracting Ti from upgraded Ti mineral (Ti-slag): (1) direct reduction of Ti-slag using MgH_2 , (2) leaching to purify TiH_2 , and (3) dehydrogenation of TiH_2 to form Ti.

The TiO_2 contained within the slag reacts with the MgH_2 reductant as follows:



The strategy of the new method is that, when MgH_2 is used to react with Ti-slag and form TiH_2 , Ti is chemically isolated from the rest of the compounds in slag. Forming TiH_2 , rather than Ti metal, is deliberate and necessary because Ti metal is more prone to forming alloys with other elements such as Fe, which would be extremely difficult to separate. Moreover, TiH_2 has very unique chemical properties. It is insoluble in water, resistant to dilute acid solutions,¹⁰ and has minimal or no solubility for other impurities in the slag. It should be noted

that the insolubility of TiH_2 in water is attributed to its kinetic passivation in water. These properties set up a condition by which the product of the direct reduction of Ti-slag can be sequentially leached to remove impurities and purify TiH_2 .

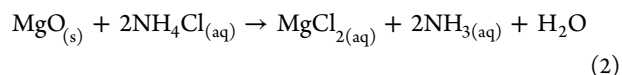
The feasibility of the first step, direct reduction of Ti-slag with MgH_2 (DRTS), lies in several underlying principles. Thermodynamic modeling (HSC Chemistry 5.11, commercial software from Outotec, Finland) showed that when MgH_2 is put in a system with Ti-slag in a hydrogen atmosphere, TiH_2 and MgO are the favored products of the reduction of slag with MgH_2 . Specifics of the thermodynamic analysis are shown in the Supporting Information. Small fractions of other intermetallic compounds may also form as the results of DRTS, which will be removed through leaching processes.

From a kinetics perspective, one of the key concerns regarding the new approach is that the reaction between MgH_2 and TiH_2 is in the “solid” state, and solid-state reactions are usually too slow for such production methods. However, a unique feature of MgH_2 and Mg is that MgH_2 dehydrogenates between 300 and 400 °C, when the hydrogen pressure is at or below 1 atm. Solid Mg has an unusually high vapor pressure at temperatures below its melting point (649 °C). Thus, when the reaction is carried out at approximately 500 °C and 1.0 atm pressure of hydrogen (see results that follows), there is substantial presence of the vapor phase of Mg, which improves the reaction kinetics dramatically.

The reaction kinetics and thermodynamic driving force for forming TiH_2 are further aided by the differences in equilibrium pressure of hydrogen between TiH_2 and MgH_2 . At 500 °C, the equilibrium pressure of TiH_2 is less than 1.0 atm (approximately 0.5 atm), while the equilibrium pressure of MgH_2 is higher than 1.0 atm. Therefore, when the process is carried out at 500 °C and 1.0 atm H_2 , Ti will hydrogenate, while MgH_2 is dehydrogenated, leaving Mg in a solid–vapor phase equilibrium with substantial presence of Mg vapor.

The feasibility of reaction (1) can also be inferred in the literature reports by Borok and Teplenko¹¹ and Froes et al.,¹² who both reported the reduction of purified TiO_2 to Ti and/or TiH_2 using CaH_2 . Our preliminary work showed that, although thermodynamically both CaH_2 and MgH_2 should work at different temperatures, in the experiments CaH_2 did not reduce slag at similarly low temperature conditions. This was attributed to the fact that CaH_2 does not dehydrogenate until much higher temperatures, and solid Ca has a much higher melting point and not as high a vapor pressure as does Mg. Additionally, the recovery of Mg through electrolysis has been reported to consume 13.0 kWh of electrical energy per kg of Mg, much less than the energy required to recover Ca through electrolysis, which is 33–55 kWh/kg.¹³

The feasibility of the second step is founded in the principles of fractional chemistry and extractive metallurgy. The impurities can be sequentially leached using common chemical reagents. Many of the specific techniques are already proven in the metallurgical industry. First, to remove MgO from the reduced powder mixture, hot ammonium chloride (NH_4Cl) solutions can be used,¹⁴ and the reaction proceeds according to



It has also been found that adding a chelating agent, such as sodium dihydrogen citrate ($\text{NaC}_6\text{H}_7\text{O}_7$), to the NH_4Cl solution can also significantly improve the solubility of MgO .¹⁵ Similarly, leaching with hot NaOH solution can remove any remaining

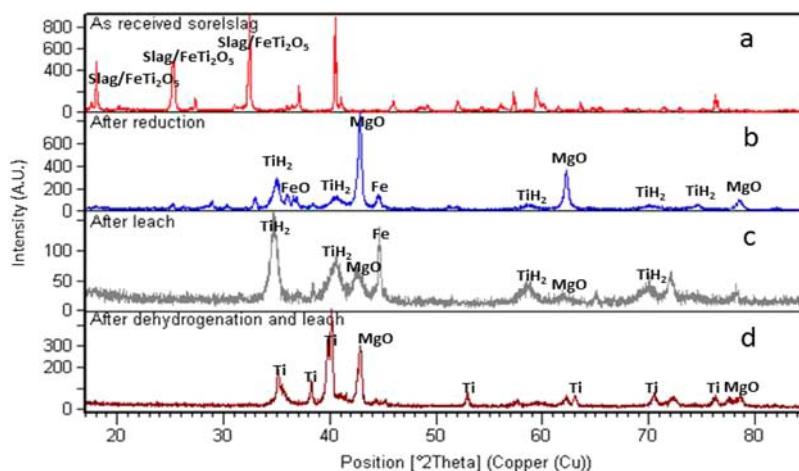
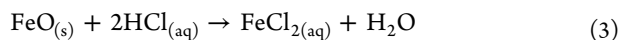


Figure 3. X-ray diffraction patterns of (a) as-received Ti-slag, (b) the product of the reduction of slag with MgH_2 at $500\text{ }^\circ\text{C}$, (c) the product of leaching the reduced powder with NH_4Cl solution, and (d) the product of dehydrogenation at $400\text{ }^\circ\text{C}$ in an inert Ar atmosphere.

silicates from the reduced powder that would otherwise be insoluble in mineral acids other than HF, and will also remove Al_2O_3 with minimal dissolution of TiH_2 . It should be emphasized that the majority of the oxides, including FeO, Al_2O_3 , and SiO_2 , are all reduced along with TiO_2 during the direct reduction process using MgH_2 . Intermetallic compounds such as Fe_2Ti , TiAl , and Ti_3Si_3 may form on the basis of the thermodynamic analysis. Only residual oxides are still of concern.

Any remaining metal or metal oxide compounds such as Fe can be dissolved using a relatively dilute mineral acid,¹⁴ such as HCl:



TiH_2 has been found to have a lower dissolution rate in HCl acid than in H_2SO_4 ,¹⁰ and FeO has been found to have a higher reactivity in HCl than in H_2SO_4 ,¹⁶ therefore, HCl was chosen as the preferred mineral acid. Further, residual MgO in the mixture can also be dissolved by the dilute HCl solution. In the event that other residual contaminants are present at levels that exceed acceptable limits, coordination compounds such as carotenes, porphyrins, supramolecules, polycyclic aromatics, ethylene diamine tetraacetic acid, carboxylic acids, N-heterocyclic carboxylic acids, pyrimidine carboxylic acids, and tetrazole carboxylic acid may be used to improve leaching and impurity separation.

An experimental study was conducted on the reduction of Ti-slag with MgH_2 . The slag used in this investigation is a solid solution of various titanate compounds with a pseudo-brookite structure.⁴ The composition of the slag includes 79.8% total TiO_2 (15.8% Ti_2O_3 reported as TiO_2), 9.1% FeO, 5.6% MgO, 2.7% SiO_2 , 2.2% Al_2O_3 , 0.6% total other metal oxides, and 0.1% metallic Fe, as assayed by Rio Tinto Iron and Titanium. No lanthanide or actinide compounds were detected.

It was found that the extent of reduction of Ti-slag with MgH_2 was facilitated by the inclusion of a eutectic mixture of sodium and magnesium chloride salts that would be molten at the reaction temperature. Molten salts have very high conductivity and appear to facilitate electron transfer during the reduction reaction. The exact molten salt composition was determined after several trials using either single or mixed chlorides salts. More details on the compositions of the chloride salts are given in the Supporting Information. It was

also found that milling the slag also greatly enhanced the degree of conversion. Ti-slag was ball-milled with 20 wt% of the eutectic salt mixture and then mixed with MgH_2 . The slag/reductant mixture was heated in a tube furnace with flowing hydrogen to $500\text{ }^\circ\text{C}$. Figure 3 compares the X-ray diffraction (XRD) spectra of the reaction product and the as-received Ti-slag, as well as those of the products after selected steps of leaching and purification. It is evident that the primary phase in the reaction products is TiH_2 , which was not present in as-received Ti-slag. The other main compound in the reduction product is MgO.

The total composition of the reduced powder was determined using microwave digestion in concentrated HNO_3/HF acid solution and ICP-MS analysis. Another sample of reduced powder was leached in an HCl solution at an optimized concentration and temperature that allowed for the dissolution of converted TiH_2 but minimal Ti from any unreacted slag. The Ti measured in the leach solution is divided by the total Ti content in the powder to obtain the degree of conversion. Conversions as high as 95% have been obtained.

The product of the direct reduction experiment was then subjected to leaching as described above. MgO is removed from the reduced powder mixture by NH_4Cl solutions according to eq 2. In Figure 3, a sharp decrease in the intensity of the MgO peaks is observed after NH_4Cl leaching. Remaining metal and metal oxide compounds such as Fe were dissolved using dilute HCl, as shown in eq 3. Figure 4 shows the morphology and particle size of the TiH_2 powder after leaching and purification.

The chemical compositions of the powder after all leaching steps were analyzed using the energy-dispersive spectroscopy (EDS) technique. Figure 4 shows that the TiH_2 particles are 99% pure, free of impurity particles. The exact compositions of impurity elements, however, were not determined because their composition levels were below the accuracy capability of the EDS technique. Ongoing efforts are focused on developing methods to measure exact impurity compositions of the powder.

The resulting hydride powder was dehydrogenated to produce Ti metal by heating it above $400\text{ }^\circ\text{C}$ in an argon atmosphere. The XRD spectrum of reduced powder after NH_4Cl leaching and dehydrogenation at $400\text{ }^\circ\text{C}$ is shown in Figure 3. The hydride peaks have clearly been replaced by

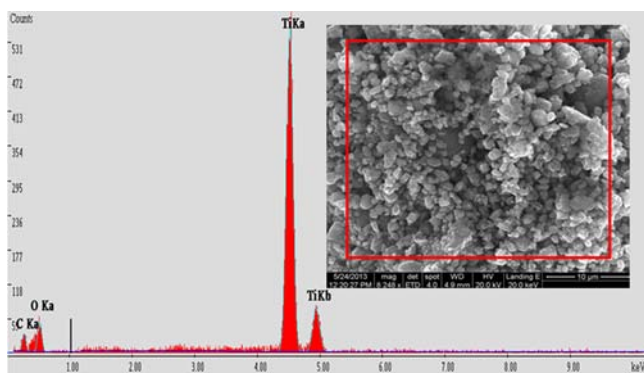


Figure 4. SEM/EDS analysis of final titanium hydride product using the DRTS process as described.

alpha-Ti peaks, demonstrating the flexibility of the process to make either Ti metal or TiH_2 powders.

Finally, the change in the chemical pathway for Ti extraction facilitates the potential for substantial energy reductions. The DRTS approach is based on low-temperature and ambient-pressure processes that eliminate the need for high-temperature carbo-chlorination, molten Mg reduction, and vacuum distillation. The energy-saving potential of the DRTS process was estimated to be approximately 62% less than that of the Kroll process. Details of the analysis of energy consumption are included in the Supporting Information

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures and energy analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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