A Novel Chemical Pathway for Energy Efficient Production of Ti Metal from Upgraded Titanium Slag

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Abstract

The developments of energy efficient, low cost titanium metal production processes have challenged the metallurgical industry and research community around the world for several decades. The strong affinity of titanium to oxygen dictates that the conventional Ti metal production processes are energy-intensive. In this paper, a new approach that is designed to minimize energy consumption and overall cost for Ti production is presented. The overall approach is based on a chemical pathway that synergistically integrating a series of low cost unit processes to produce Ti that can match the quality of the product produced by the Kroll process commercially to date. The key steps include production of purified TiO₂ with controlled sizes and morphologies, Mg reduction in the presence of hydrogen to form porous TiH₂, heat treatment to close the pores, and Ca de-oxygenation to reduce oxygen content to less than 0.15wt%. The results show that this approach can indeed produce Ti metal powder that has high purity, low oxygen, and meets the specifications by ASTM for general purpose Ti sponge, directly from upgraded titanium slag (UGS) without the high temperature

chlorination step.

Key words: titanium production, upgraded titanium slag, purified TiO_2 , Mg reduction, de-oxygenation

1. Introduction

Titanium metal is a highly coveted material that has been widely used in aerospace, chemical processing, and biomedical industries. However, relative to its potential, Ti is highly underutilized due to the inherent high cost of production of Ti primary metal as well as its alloys, despite the fact that it is the ninth most abundant element and the fourth most abundant metal in the earth's crust [1].

Ti primary metal is primarily produced commercially using the Kroll process today. In the Kroll process, titanium tetrachloride (TiCl_4) is reduced by reacting it with liquid Mg to produce Ti metal. TiCl_4 is a precursor produced by carbothermic reduction of Ti ore to produce Ti slag, followed by chlorination and purification. After the Mg reduction of TiCl_4 at around 800~850 °C, the reduction products containing Ti metal, MgCl_2 , Mg metal, and a small amount of TiCl_3 and TiCl_2 , are refined by vacuum fractional distillation to remove impurities such as MgCl_2 and Mg, yielding purified Ti metal as the final product, which is typically called Ti sponge [2]. The main and arguably the only disadvantages of Kroll process is that it is energy intensive, slow, and expensive due to a number of specific technical reasons including the chlorination process and the high temperature vacuum distillation process to remove the byproduct of the reduction. Therefore, enormous research efforts have been made around the world in the last few decades to develop more energy efficient and lower cost processes.

There are two general approaches for Ti metal production: electrochemical methods and thermochemical methods. A typical example of the electrochemical approach is the FFC or

Cambridge process [3] which relies on the reduction of titanium oxide through electrolysis. The Kroll process is an example of the thermochemical method. The research work of this article describes a new thermochemical method that consumes less energy and would thus be more cost effective than the Kroll process.

Thermochemical production of Ti involves the reduction of a precursor with a reductant. There are two main precursors: TiCl_4 and TiO_2 . Using TiCl_4 as the precursor to produce Ti metal has the advantage that TiCl_4 can be extremely pure in its gaseous state, which logically enables the production of highly purified Ti metal. However, the purification processes to produce TiCl_4 , including the high temperature chlorination process from TiO_2 -bearing minerals involves a series of highly energy intensive and costly processes [4]. Motivated by the aim to avoid the high temperature chlorination process, there have been many investigations involving the use of commercial TiO_2 [5, 6], titania slag, synthetic rutile, or up-graded Ti slag (~95% or higher TiO_2 content) [7] as the precursor. Intuitively TiO_2 would be a lower cost precursor than TiCl_4 because the chlorination step could be avoided. However, the precursor is not the only factor that affects the cost of Ti. The differences in the inherent energies of reduction of either TiO_2 or TiCl_4 , and the selection of reductants also affect the final cost of Ti metal.

Based on the Ellingham diagrams for metals' reaction with oxygen and chlorine, there are three possible reductants, namely Mg, Na and Ca, for reduction of either TiO_2 or TiCl_4 . Figure 1 shows multiple potential thermochemical routes for production of Ti metal from the precursors using Mg, Na, and Ca as reductants.

Due to its extreme chemical affinity to O, Ca metal, rather than Mg, is frequently

employed to reduce TiO_2 . Four different forms of Ca were investigated as options for calciothermic reduction, including solid hydride CaH_2 [8], vapor-Ca [9], liquid-Ca [10], and electronically mediated reduction (EMR) [11]. The oxygen content in Ti can be minimized to a very low level using Ca.

Fig. 1 Thermochemical reduction routes to produce Ti metal through various reductants

Compared to Ca, Na is chemically inert to TiO_2 . It is, however, an effective reductant for reducing TiCl_4 . The power of reduction of Na is equivalent to that of Ca, and both are significantly stronger than that of Mg, which led to the development of a variety of processes based on Na reduction of TiCl_4 , including the Hunter process [12], the Armstrong process [13], Du Pont [14], and Aerosol methods [15].

Although Mg is not as strong as Ca or Na for reduction purposes, it is still effective for reduction of both TiO_2 and TiCl_4 . Mg has, of course, been used in the Kroll process for reduction of TiCl_4 . Based on a process energy analysis of the Kroll process reported by Rajiv Kohli [16], almost 2/3 of the total energy for production of Ti using the Kroll process is consumed by the high-temperature vacuum distillation and separation following the actual

reduction process, and 13% is consumed by the chlorination and purification processes. Thus, it is logical to suggest that a process designed to reduce TiO_2 using Mg could be more energy efficient and less expensive than the Kroll process because there will be no need for high temperature vacuum distillation of the byproduct of MgO; and Mg is also the least expensive reductant among Mg, Ca, and Na. The byproduct of the reduction of TiO_2 by Mg is MgO that must be removed using aqueous leaching techniques. The energy consumption and cost of such processes for removing the by-products of the reduction will also impact the final cost.

Recently, a new process was proposed by Fang et al. that produces Ti by direct reduction of upgraded Ti slag (UGS) using Mg under a hydrogen atmosphere [17]. A key consideration of the Fang approach is that it starts with a low cost precursor (UGS) and it employs the least expensive reductant (Mg). An advantage of the Fang approach is that it forms TiH_2 after the reduction which separates Ti chemically from other impurities, thereby facilitating impurity removal by chemical leaching. TiH_2 is known to be impervious to oxygen and less prone to alloying with the impurity elements in the mixture. However, removing impurities, i.e. the purification process is challenging because TiH_2 is prone to dissolution along with the impurities during the post-reduction leaching process. The process of purification is therefore another important factor, in addition to the cost of precursor and reductant.

In short, the energy consumption and cost of Ti metal production from Ti slag depend on several key factors, including the selection of precursor and reductant, the processes for purification, the processes for removing byproducts, and the processes for reclaiming the reductant and other chemical reagents. In this paper, a new chemical pathway is designed to

produce pure Ti from UGS without the energy intensive high temperature chlorination step and without the post-reduction high temperature vacuum distillation step as in the Kroll process. The new chemical pathway integrates a series of low cost purification and reduction processes synergistically to produce Ti with high purity and low oxygen. The aim of this paper is to present the concept and the design of the overall process, and report experimental results of key intermediate steps. The results show that highly purified Ti metal with low oxygen content can be achieved using this new approach.

2. Process design concept

The new process design is shown in Fig. 2. First of all, UGS is selected as the starting raw material. The first part of the overall process is to produce purified titanium dioxide (TiO_2) using hydrometallurgical method. The second step is to reduce the purified TiO_2 using Mg in a hydrogen atmosphere. The last step involves the deoxygenation that is specifically designed to remove oxygen that is dissolved in Ti metal.

2.1 Produce purified TiO_2

The first step of the overall process is the thermal alkaline roasting of UGS with NaOH and subsequent washing with water. There are two objectives for alkaline roasting. One is to transform all metal components into sodium metallate, especially amorphous sodium titanate, which is insoluble in water, but can be readily dissolved in dilute HCl acid solution. The titanic acid will subsequently be selectively precipitated and calcined to produce TiO_2 . The second objective of alkaline roasting is to leach most of the impurities including Si, Al, Cr and V by forming their sodium metallate that are soluble in water and alkaline solutions. The

washed alkaline roasted product will be solid H_2TiO_3 with significantly reduced impurities compared to UGS.

Transition metals such as iron (Fe) and Ti, however, do not dissolve in water or the alkaline solution. Thus the next step of the process is designed to dissolve Fe along with titanate (TiO_3^{2-}) in a dilute HCl solution. Hydrolysis is then instigated to selectively precipitate titanic acid and separate Ti from other impurities. Note Fe does not co-precipitate with Ti and thus it is left in the solution. Additionally, the hydrolysis process is not only a purification technique, but it is also a process that can be used to control particle size and morphology of the product powder. The particle size, size distributions, and morphology depend strongly on the concentration of HCl in the solution, the temperature, time, and agitation of the solution. In order to minimize oxygen content in the final powder, the hydrolysis process parameters are adjusted to produce relatively coarse titanic acid particles (5-50 micrometers). The titanic acid particles are then calcined to transform into relatively coarse TiO_2 . Note that although commercial TiO_2 is readily available as pigment grade TiO_2 , commercial TiO_2 is not chosen for direct Mg reduction because the particle size of pigment grade TiO_2 , typically 200-300 nm, is too fine for controlling oxygen content during the subsequent processing steps. The differences between the purified TiO_2 of this work and the commercial pigment grade TiO_2 will be further discussed later.

2.2 Reduction of TiO_2

The second part of the overall process is to reduce the purified TiO_2 to Ti metal. Mg is selected as the reductant. The reduction process is designed to be conducted in a hydrogen atmosphere in order to form Ti hydride (TiH_2) rather than Ti metal. An important advantage

of forming TiH_2 rather than Ti is that TiH_2 is impervious to oxidation in air. It is also believed that TiH_2 is less prone to alloying with other impurities than Ti metal.

After Mg reduction in H_2 , the byproduct of MgO and unreacted Mg metal are leached using aqueous HCl solution. The acidity of the slurry during leaching must be carefully controlled to avoid the dissolution of TiH_2 .

After the reduction and subsequent leaching, TiH_2 powder is obtained. A heat treatment step is incorporated to reduce the surface area and obtain dense particles. Increasing particle size or minimizing specific surface area is beneficial for minimizing oxygen pick up during subsequent handling of the powder. During the heat treatment, the TiH_2 powder will also be dehydrogenated.

2.3 Deoxygenation

Commercial specifications require the oxygen content of Ti sponge to be less than 0.15%. The oxygen content of Mg reduced TiO_2 is expected to be greater than 1% [18]. Therefore, a de-oxygenation process is necessary and integrated as a part of the overall process. De-oxygenation can be carried out by mixing the powder with Ca metal and heating the mixture to elevated temperatures to reduce its oxygen content according to existing processes as reported in literature [19-21]. In this work a low temperature molten salt (LTMS) process was applied by which the deoxygenation process is designed to operate at temperatures lower than the melting point of Ca. Molten CaCl_2 is used as a medium to facilitate the reaction. Details of the LTMS process can be found in reference [22]. The by-product of the de-oxygenation process will be CaO which can also be leached using a dilute HCl solution.

In short, the process for production of Ti metal from UGS involves making purified

TiO₂, the reduction of purified TiO₂ by Mg in hydrogen, and de-oxygenation using Ca. Both the concept of the overall chemical pathway and the details of the individual techniques are designed to work synergistically to accomplish the tasks of both purification and reduction of titanium oxide to produce Ti metal. Details of each processing step and the effectiveness of the entire process are further illustrated through the experimental results and discussions as follows.

Fig. 2 Flow chart of the new approach for Ti powder production

3. Experimental

3.1 Procurement of raw materials and chemicals

Up-graded Ti-slag (UGS), assaying 94.5% TiO₂, was provided by Rio Tinto and used as the raw material in this work. The chemical composition of UGS is given in Table 1, which shows that the impurity contents including Fe, Si, Mg and Al were all relatively high. UGS is commercially used as the feedstock for the chloride process of making TiO₂ pigment. The particle size of as-received UGS is in the range of several hundred microns. Thus, it was wet milled and screened to minus 20 microns before alkaline roasting.

Table 1 Chemical composition of original UGS (wt%)

Ti	O	Fe	Mg	Al	Ca	Si	Cr	Mn	V
56.7	40.4	1.0	0.42	0.26	0.09	0.84	0.05	0.03	0.22

Other chemicals involved in this study include NaOH, concentrated HCl solution, Mg metal, MgH₂ powder, Ca metal, anhydrous MgCl₂, CaCl₂, KCl, and compressed hydrogen and argon. Mg and anhydrous salts were purchased from Alfa Aesar and preserved in an glove box with constant circulation of Ar to avoid oxidation and absorption of moisture. Water is purified with Milli-Q (Millipore Corp.) equipment before use. Standard solutions for ICP-OES test are purchased from Inorganic Ventures.

3.2 Analytical methods, measurement of physical and chemical properties

Through the whole process, the chemical compositions and interstitial element contents of the solid and liquid intermediates and final product were monitored. Solid samples were totally dissolved by 6 mol/L HCl solution after being fused by the mixture of sodium carbonate and boric acid in a Pt crucible, then the solutions were analyzed using ICP-OES. The concentrations in the liquid samples were directly determined by using ICP-OES after being diluted. The contents of O, N, H, C interstitial elements were determined by using LECO analyzers.

A Philips 1140 diffractometer (Cu K α) X-Ray diffraction (XRD) unit, was used to determine the phase compositions of the precursor, intermediates, and final products. The

morphologies and the particle size of the solid samples were examined using a scanning electron microscope (SEM, FEI NovaNano 630). Particle size and size distributions were determined using a Shimadzu particle size analyzer. The specific surface area was evaluated by using a BET analyzer (TriStar II). The density of the powder was measured using AccuPyc II 1340 Series Pycnometers.

4. Results and Discussion

4.1 Production of purified TiO₂ from UGS

4.1.1 Alkaline roasting

As described earlier, alkaline roasting is the first step of the process to produce purified TiO₂. The impurities in UGS can be classified into two categories, alkali-soluble impurities including Si, Al, V, Mn and Cr, and acid-soluble impurities including Fe, Al, V, Ca, Mg, Si, Mn and Cr. However, except for Si, most of the impurities in UGS do not exist as stand-alone phases; rather, they form solid solutions with TiO₂ in the form of rutile. The reported empirical formulas for the core and the rim of the rutile grains are Ti_{0.896}Fe_{0.045}Mg_{0.089}Al_{0.024}V_{0.006}Cr_{0.002}Mn_{0.002}O₂ and Ti_{0.993}Fe_{0.003}V_{0.005}Cr_{0.001}O₂, respectively [23]. In other words, some impurities such as Fe, Mg, Al, and V, are hosted within the lattice of rutile. With regard to Si, it exists as a glassy silicate phase and fills the cracks between rutile grains [23]. Based on the above, it is plausible to leach the impurities by destroying the structure and chemically separating them from the titanium dioxide. Other procedures were also applied in addition to alkaline roasting to minimize Si content.

With the aim to digest the titanium feed stocks, including ilmenite, titania slag or

upgraded titania slag, typical hydrometallurgical methods, such as the sulfate process [24], use highly concentrated sulfuric acid to dissolve titanium and all impurities into solution. Concentrated HCl may also be used [25]. To avoid using concentrated acid, the process of pretreating the feedstock with an alkaline roasting step by NaOH, followed by dissolving the material in a low-concentration acid [26] was selected for this work. The principle of NaOH roasting is as follows. On the one hand, titanium dioxide and alkali-soluble impurities can be transformed during roasting into their sodium metallate salts, mainly Na₂TiO₃ accompanied by Na₂SiO₃, NaAlO₂, Na₃VO₄, Na₂CrO₄, Na₃MnO₄. On the other hand, alkali-insoluble impurities can also be hosted by their sodium metallate salts or metal hydroxide compounds, such as NaFeO₂ [27], Na₂MgO₂ [28] and Ca(OH)₂. After roasting, the reaction product can be washed using water during which the excess NaOH will be dissolved, and most of the sodium combined with Na₂TiO₃ will be released to form water-soluble NaOH and alkali-insoluble metatitanic acid (H₂TiO₃). Additionally, the alkali-insoluble metals will be retained with metatitanic acid in their metal hydroxide compounds of Fe(OH)₃, Mg(OH)₂ and Ca(OH)₂. The reactions involved in this process are listed as Eq. (1) to Eq. (8). Thus, the goal of chemically separating titanium and other impurities is achieved.

Alkaline roasting:

Water washing:

Experimental investigation of the NaOH roasting process was conducted at 500 °C for 1 hour with a mass ratio of NaOH to UGS of 1.5:1. The parameters of the roasting process were determined based on the present authors' prior research [26] as well as published reports by their research peers [29]. The phase composition of the dried water-washed residue is shown in Fig 13 (B). Figure 13 shows that the UGS with XRD pattern in Fig. 13 (A) was completely transformed during roasting without any leftover rutile. The chemical composition of the residue was analyzed using ICP and the results are shown in Table 2. Based on the composition it is deduced that the residue is primarily composed of H_2TiO_3 . The effectiveness of the alkaline roasting process in terms of the removal rates of the impurities were calculated and they are as high as 97.5%, 94.5%, 88.8%, 83.0% and 78.8%, for Si, Al, V, Mn and Cr respectively. Even Fe and Mg were partially dissolved by the alkaline solution, which may be attributed to their limited but detectable solubility in the alkaline solution.

It should be noted that oxidation is a necessary step during roasting because some of the impurities including V, Mn and Cr in the original UGS are in their reduced states of V^{4+} , Mn^{2+} and Cr^{3+} , while only their sodium salts with high valence could be readily dissolved in the alkaline solution. This is attributed to the processes that produce UGS which include oxidation, reduction, and high pressure HCl leaching. Thus, the roasting was conducted in air.

Table 2 Chemical composition of the dried residue and the impurity removal rates

Element	Ti	Fe	Mg	Al	Ca	Si	Cr	Mn	V
wt%	40.00	0.483	0.156	0.010	0.072	0.038	0.008	0.004	0.017
Removal rate (%)	0	31.5	47.3	94.5	0	97.5	78.8	83.0	88.8

4.1.2 Dissolution

After the roasting process described above, the transition metal species such as Fe are still in the residue of water-washed alkaline roasted product, which is a mud-like intermediate (referred to as “mud” hereafter). These impurities have to be further separated from metatitanic acid. The only plausible pathway to achieve that is through total dissolution of the mud and re-precipitation of titanium dioxide from the Ti-bearing acid solution. As the result of the alkaline roasting, the chemically stable rutile in the original UGS has been transformed into extremely active metatitanic acid, which can be readily dissolved in diluted acid solutions (HCl or H₂SO₄) at a low temperature. In this research, the wet mud, containing 50% water mass content, was immersed in HCl solution to dissolve it. The initial HCl concentration of the solution was 6 mol/L and the experiment was conducted at 50 °C for 30-60 minutes [30]. The total amount of HCl used is based on the total mass of Ti in the wet mud. It should be noted that the water in the wet mud was taken into account for determining the concentration of HCl solution.

After the dissolution, the leachate was filtered to remove insoluble particles and a

transparent Ti-bearing solution was obtained in preparation for the hydrolysis step.

The typical composition of the solution before hydrolysis is shown in Table 3.

Table 3 Main metal concentrations in the HCl leachate (mg/L)

Ti	Mg	Al	Fe	Si	Ca	Cr	V	Mn
49000	222	7	664	18	45	7	19	4

The reason for 6 mol/L HCl of the leaching medium is based on the following considerations: (1) Over exorbitant lixiviant, such as concentrated HCl, will make the handling more difficult and the lack of water molecules has an adverse effect on dissolution; (2) Ti ions are not stable in weak acid solution and the generation of water during dissolution will further dilute the acid, which could create a risk of premature hydrolysis. The free HCl concentration in the leachate after the present dissolution was still as high as around 2 mol/L; (3) Even though it has been shown that 4 mol/L HCl also works for the purpose of this work [31], the lower the HCl concentration, the lower the Ti concentration and corresponding hydrolysis ratio. Thus, 6mol/L HCl was determined to be the optimum concentration.

4.1.3 Hydrolysis and calcination

Hydrolysis is a process of selective and spontaneous precipitation of Ti species from the Ti-bearing acid solution in the form of titanic acid. Various titanic acids with a general formula of $\text{TiO}_x(\text{OH})_{4-2x}$ depending on the water content in them can be obtained by controlling hydrolysis parameters. The general chemical reaction involved is shown as Eq.

(9). The product of hydrolysis can be metatitanic acid ($\text{TiO}(\text{OH})_2$), orthotitanic acid ($\text{Ti}(\text{OH})_4$), or pyrotitanic acid ($\text{H}_2\text{Ti}_2\text{O}_5$), and so forth.

In this study, the liquid after dissolution of wet mud is a TiCl_4 -bearing solution. In this solution, an equivalent concentration of TiO_2 based on the concentration of Ti^{4+} was controlled to be around 80 g/L. The hydrolysis was carried out at 95-100 °C for 16 hours. The solution was continuously stirred.

The product of hydrolysis was solid titanic acid particles, with particle sizes ranging from approximately 10 to 50 microns using the above parameters. The morphology and particle size distribution are shown in Fig. 3 and Fig. 4. Particles are mostly aggregates of fine crystals.

Fig. 3 Morphology of the hydrolyzed titanic acid particles

Fig. 4 Particle size distribution of the hydrolyzed titanatic acid particles

After the hydrolysis, the titanatic acid precipitate was subjected to calcination by heating up gradually to dehydrate the precipitate particles and to obtain rutile at 900 °C in air. Rutile is the high-temperature stable phase that is easier to reduce than Anatase [32]. The XRD pattern of the post-calcination particles is shown in Fig. 13 (C). According to the weight loss during calcination, it was confirmed that the water content in the precipitate was approximately 10%, suggesting that the precipitate was pyrotitanic acid. The morphology of rutile particles inherits that of the titanatic acid. And the purity of rutile, or impurity contents in the material were analyzed by using ICP and the results are shown in Table 4, which is also compared with commercial rutile. It is apparent that the purity of TiO₂ produced by this process is comparable to that of commercial rutile.

Table 4 Comparison of the impurity contents in rutile prepared by this work and in

commercial pigment grade rutile [31] , wt%

Mg	Al	Fe	Si	Ca	Cr	V	Mn	C

This work	0.048	0.006	0.043	0.030	0.029	0.018	0.037	0.005	0.0035
Commercial	0.030	NA	0.0012	0.0386	0.0112	<0.0013	NA	<0.0007	NA

There are two critical issues during hydrolysis: purifying the material, especially the removal of iron, and controlling size and morphology of the particles. The purity of TiO_2 has a direct impact on the purity of Ti metal in the end. In this study, the ferric ion in the pre-hydrolysis solution was reduced by Ti^{3+} ion to ferrous ion. During the precipitation of titanic acid, ferrous ion will remain in the leaching solution, thus separating Fe from Ti, thereby minimizing iron content in TiO_2 . Table 5 compares the Fe content as well as other compositions before and after the hydrolysis. Clearly the Fe content is significantly and sufficiently minimized in TiO_2 .

Table 5 Chemical composition comparison of the solution before and after hydrolysis (mg/L)

	Ti	Mg	Al	Fe	Si	Ca	Cr	V	Mn
Pre-hydrolysis	49000	222	7	664	18	45	7	19	4
Post-hydrolysis	880	231	8	690	4	52	5	4	5

Theoretically, commercial pigment grade TiO_2 could be used as a raw material for making Ti metal according to the process of this paper. However, there are several reasons that it is believed to be more advantageous to prepare TiO_2 according to the process described above.

First, commercial TiO_2 that are currently available in large quantities are almost all

exclusive produced for TiO_2 pigment, which have particle sizes in the range of 200-300 nm in diameter [33], which the most efficient size for scattering yellow-green light that the human eyes are most sensitive to [34]. This particle size is too fine to be used directly in the Mg reduction process of this work for the purpose of producing Ti metal, because the reduced product (TiH_2 in this process) will be prone to oxidation as soon as it is exposed to air.

Second, the oxygen content of Ti metal powder is a direct function of the particle size due to the formation of TiO_2 passive layer. For instance, for Ti spherical particles of 2 μm in diameter with a surface oxide layer of 3 nm in thickness, the oxygen content can be around 3900 ppm [35]. Hence, in order to produce Ti metal with oxygen content less than 1500 ppm as required for Ti sponge, the particle size of Ti metal powder must be greater than 5.2 micrometers assuming the thickness of the passive oxide layer remains at 3 nm. Thus, this process is deliberately designed to produce relatively coarse TiO_2 with particle sizes in the range of 10 to 50 microns so that when it is reduced, it will retain the same relatively coarse particle size and form relatively coarse Ti metal powder in the end.

Third, for pigment production, iron is one of the detrimental impurities [36]. With a Fe_2O_3 content of 30 ppm, TiO_2 will present a light yellow color. Usually 90 ppm of Fe_2O_3 is considered as a threshold value at which Fe_2O_3 affects the whiteness of A-type TiO_2 [37]. However, iron content in Ti metal does not need to be so low. ASTM specification for general purpose Ti sponge requires Fe content only to be less than 1500 ppm, which is much easier to achieve. Consequently, a process as described above which is a lower cost process as compared to the chloride process for making pigment TiO_2 can and should be used to prepare TiO_2 for the purpose of producing Ti metal.

4.2 Mg reduction

Mg is one of the reductants that can form more stable oxides than TiO_2 . Even though the reported results to date show that the ability of Mg for reduction is limited [18, 38] as compared to Ca, Mg is selected for this work because of a number of factors including that the cost of Mg is significantly lower than that of Ca, the potential reaction temperature is lower, and controllability of the reduction process of using Mg will be better than using Ca. However, the challenge is how to reduce the oxygen content to a satisfactory level by using a Mg based process.

To improve the efficiency and effectiveness of the reduction of TiO_2 using Mg, previous work by the present authors [17] showed that the Mg reduction should be conducted in a hydrogen atmosphere using magnesium chloride salt as a medium. When the reaction is conducted in H_2 , TiH_2 is formed. As pointed out in the earlier section on the design of the overall process, forming TiH_2 powder as the product of the reduction reaction is viewed as being more advantageous than forming Ti metal powder with respect to both oxygen content and purity of the product.

In this work, the same general approach for reduction is adopted. Purified TiO_2 was mixed with Mg metal and alkaline salt including MgCl_2 . The mixture was heated and held at various temperatures in H_2 atmosphere. The reaction product included TiH_2 and MgO . MgO was leached using a dilute HCl solution. The objective of the process is to minimize oxygen content. The following descriptions of the results show the effects of hydrogen, salt, and temperature on the reduction.

Additionally, magnesiothermic reduction generates a large amount of exothermic heat, which could lead to a system temperature as high as 1600 °C when the reduction is initiated [39]. Consequently, one of the goals of this work is to control the reaction at a relatively low temperature and with an acceptable reduction rate, avoiding any severe temperature spike.

4.2.1 Effect of MgCl₂-bearing salt

In order to understand the effect of salt, TGA-DSC analysis techniques were used. Figure 5 presents the DSC curves during heating of a TiO₂ mixture with MgH₂ (compared to Mg metal, MgH₂ powder is easier to grind to finer sizes) with and without MgCl₂/KCl eutectic salt (molar ratio of MgCl₂ to KCl was 2:3), which shows a significant difference with respect to the exothermic heat due to the reduction reaction. In the presence of salt, an exothermic peak at 538°C (c1) attributable to the reduction reaction was clearly visible. The reaction happened before the melting of Mg (d1 and d2). Furthermore, the peak that indicates the solidification of metallic Mg (e1 and e2) was notably smaller when the salt was added in the system, suggesting that there is little residual unreacted Mg; in other words, the reaction was more complete when the salt was used. Thus, it appears that the initial reaction temperature of Mg reduction was lowered and the kinetic rate was improved when the salt with a lower melting point than Mg was used.

Fig. 5 DSC curves when reducing TiO_2 by MgH_2 in the presence or absence of MgCl_2/KCl eutectic salt. [red line: with the presence of salt; dark line: with the absence of salt; a1 and a2: dehydrogenation of MgH_2 ; b1: melting of the salt; c1: exothermic reduction; d1 and d2: melting of Mg metal; e1 and e2: solidification of remaining Mg metal; f1: solidification of salt]

Furthermore, the TGA-DSC technique is also used to screen salt with different compositions. The DSC curves of salt mixtures with different ratios of $\text{MgCl}_2 : \text{KCl}$ were compared in Fig. 6. The mixed salts of MgCl_2 with KCl were considered because they generally possess lower eutectic temperatures. Figure 6 shows that the peak temperature positions for the exothermic reactions were not affected significantly by the compositions of the salts. However, the intensity of the exothermic reaction varied. The peak intensity grew stronger when the molar ratio changed from 1:0.25 to 1:0.5, followed by a gradual weakening until the ratio reached 1:4. The stronger the exothermic peak, the smaller the remaining quantity of Mg, determined by the peak intensities for the solidification of remaining Mg.

Hence, it seems that the most suitable molar ratio of MgCl_2 to KCl was 1:0.5 with respect to the kinetics of the reduction reaction.

Fig. 6 DSC curves when reducing TiO_2 by MgH_2 with the presence of eutectic salt with various compositions

The effects of the compositions of salts are also compared by measuring the oxygen

content after reduction. The reduction was conducted by holding the sample for 6 hours at 750 °C in H₂ atmosphere. The oxygen content in the reduced powder as measured using a LECO oxygen analyzer are shown in Fig. 7. Clearly, the compositions of salts affect not only the kinetic rate, but also the oxygen content after the reduction. The oxygen level in the reduced powder can be reduced to 1.5% when the MgCl₂ : KCl molar ratio is greater than 1:0.5 at 750 °C.

Fig. 7 Variation of reduction efficiency with the chemical composition of the eutectic salt

It should be noted here that although the positive effects of salt on the kinetics of the reduction of TiO₂ by Mg is clear from the above the results, the fundamental mechanisms of the effects of salt on reduction is still not fully understood. Preliminary study has showed that the reduction of TiO₂ by Mg can take place without the direct contact between TiO₂ and Mg. It suggests that the salt can facilitate the mass transfer of the reductant, thus enhance the kinetic rate of the reduction. However, a comprehensive discussion of this issue is beyond the scope of this article.

4.2.2 Effect of reduction temperature

The DSC analysis showed that the reduction temperature with $\text{MgCl}_2\text{-KCl}$ eutectic salt as medium should be set higher than $550\text{ }^\circ\text{C}$ which is the temperature at which the exothermic peak appears. The effect of temperature was further investigated by experiments at various temperatures, namely $550\text{ }^\circ\text{C}$, $590\text{ }^\circ\text{C}$, $630\text{ }^\circ\text{C}$, $680\text{ }^\circ\text{C}$, 750°C and 800°C . The temperatures were selected to cover the range of exothermic peaks and to be either higher or lower than the melting point of Mg.

The effect of temperature is evaluated by measuring the titanium contents in the powder after MgO is leached, as shown in Fig. 8. It shows that Ti content increased dramatically with the elevation of the reduction temperature, indicating that a temperature higher than the peak point in the DSC curve is necessary to guarantee a relatively high degree of reduction.

Additionally, the Mg contents were found to be high in samples that were reduced at lower temperatures. This is attributed to the formation of magnesium titanate that is insoluble in the acid solutions.

Based on the above results, $750\text{ }^\circ\text{C}$ was adopted as the optimum temperature for reducing TiO_2 with Mg.

Fig. 8 Ti and Mg contents in the leached powders reduced at various temperatures

(The mass ratio of TiO_2 to salt was 1:0.5, and the excess coefficient of Mg was 1.5)

4.2.3 Effect of hydrogen

As mentioned earlier, the Mg reduction is conducted in hydrogen atmosphere in this work. The effect of hydrogen is shown in Table 6. It shows that the oxygen content of the product powder that was reduced in hydrogen atmosphere is significantly lower than that reduced in argon atmosphere. It can be shown that the thermodynamic equilibrium between Ti containing oxygen and Mg is different under hydrogen atmosphere than under inert atmosphere or vacuum, favoring the reduction of TiO_2 . However, further in-depth research is needed to elucidate the underlying thermodynamics, which is the subject of a parallel investigation by the present authors.

Furthermore, as described in the process design, the process is deliberately designed to form TiH_2 instead of Ti metal after reduction because TiH_2 is known to be impervious to

oxygen as compared to Ti metal. This has strong practical implications for handling of powders after the reduction.

The remaining oxygen in the reduced product will need to be removed through a deoxygenation process using Ca which will be discussed in the next section. As mentioned earlier, one of the reasons that Mg was chosen as the reductant for this process is that it is less costly than Ca. Needless to say that the lower the oxygen content in the powder prior to the deoxygenation process, the less Ca will be needed, thus the lower the cost.

Table 6 Oxygen content of the powder after Mg reduction in H₂ and Ar atmosphere*

	H ₂ atmosphere	Ar atmosphere
Oxygen content, wt%	1.37%	2.90%

* Other reduction parameters: the mass ratio of TiO₂ to salt was 1:0.5, the excess coefficient of Mg was 1.2, and reduction temperature and time were 750 °C for 6 hours.

4.2.4 Reduction of TiO₂ by Mg and the production of porous TiH₂

Based on the understanding of the effects of key parameters above, the reduction of TiO₂ is carried out as follows. Rutile particles with particle sizes in the range of 10-50 micrometer were used. The TiO₂ particle were mixed with the same mass of salt (mole ratio of MgCl₂ to KCl was 1:0.5) and 1.2~1.5 times of theoretical amount of Mg needed for reduction. The reduction was conducted at 750 °C in H₂ atmosphere for 6 hours.

After reduction, the reduced powder was pulped by high-purity water first, and then leached by concentrated HCl using a peristaltic pump controlled dripping technique to

remove MgO and unreacted Mg metal. The slurry was stirred for 30 minutes until the pH value of the leachate reached 3 to 4. Finally, TiH₂ intermediate was obtained after filtration, water washing, and drying. The phase composition of the product powder was determined by using XRD as shown in Fig.13 (D). The critical metal and interstitial impurity contents in TiH₂ were analyzed using ICP as presented in Table 7. The morphology of TiH₂ was irregular and large in size with a porous structure having a BET determined specific surface area of 3.46 m²/g.

Table 7 Impurity contents in TiH₂ intermediate

Mg	Al	Fe	Si	Ca	Cr	V	Mn	O	C
0.123	0.012	0.058	0.035	0.030	0.024	0.057	0.005	1.50	0.015

Fig.9 Morphology of the porous TiH₂ produced by reducing coarse TiO₂ by Mg

4.3 Heat treatment and de-oxygenation

As indicated above, the oxygen content of the TiH₂ powder after the reduction of TiO₂ by Mg was over 1%, which is too high for commercial Ti. Therefore, further measures are

needed to reduce oxygen content. First of all, the oxygen content of Ti powder is typically a function of the particle sizes, which is inversely proportionally to specific surface areas of the powder. Therefore, one of the measures to reduce the final oxygen content is to reduce the specific surface area of the TiH₂ powder, which is the product of the reduction.

As shown earlier, the TiH₂ powder was porous. The sizes of the pores range from 400 to 600 nm. Consequently the specific surface area of the porous TiH₂ is extremely large. To reduce the surface area, the porous TiH₂ was heat treated in argon at 900 °C for 10 minutes (Fig. 10). TiH₂ particles were also dehydrogenated at temperatures above 700 °C. The volume of individual Ti particles shrank compared to original TiH₂ particles. The sizes are still as large as around 20 µm. The BET values of the powders were significantly decreased, from 3.46 m²/g to 0.09 m²/g. The cross section of the Ti particles is shown in Fig. 11, illustrating that the porosity was eliminated after heat treatment. The high relative density of the powder was measured using a Pycnometer as 98.2% of the theoretical density of pure Ti. The oxygen content of the Ti particles after the heat treatment was measured at 1.52 wt%, which is similar to that of the TiH₂ powder before the heat treatment.

To further reduce the oxygen content of the Ti particles, a de-oxygenation step was applied to the powder after the heat treatment. As mentioned earlier, Ca de-oxygenation is widely reported in literatures. However, in order to avoid using high temperatures above 900 °C, a new low temperature molten salt (LTMS) process was developed and used in this work [22]. In this process, de-oxygenation was carried out by mixing the powder with Ca metal and anhydrous CaCl₂-KCl mixed salt, followed by treatment in argon at around 750-800 °C

for 12 hours. After de-oxygenation, the remnant Ca, CaO (byproduct), and salt were leached by using an HCl solution and washed using high-purity water.

The morphology of final Ti metal powder is shown in Fig. 12, which inherited the shape of heat-treated Ti particles. The oxygen content of the powder was decreased drastically from 1.5% to 0.11% (Table 8). The chemical composition of the Ti powder produced by using this process is compared with the ASTM standard specifications for Ti sponge as shown in Table 8. Clearly that the Ti powder produced using the process described in this paper meets the requirements of the ASTM standard.

Fig. 10 Morphology of Ti particles obtained by heat treating porous TiH_2

Fig. 11 Cross section of Ti particles obtained by heat treating porous TiH_2

Fig. 12 Morphology of final Ti metal powder after de-oxygenation

Table 8 Chemical composition of final Ti metal powder produced by this process, wt%

	Mg	Al	Fe	Si	Cl	Water	O	N	C	H
This work	0.067	0.021	0.044	0.036	0.001	/	0.11	0.019	0.03	0.028
ASTM-B299-13										
(GP)	0.5	0.05	0.15	0.04	0.2	0.02	0.15	0.02	0.03	0.03

Fig. 13 XRD patterns for the original UGS (A), intermediates (B, C,D and E) and final product (F)

5. Summary

A new chemical pathway for producing high purity low oxygen Ti metal powder directly from UGS is demonstrated. The new process is based on integrating synergistically a series of unit processes that are designed to accomplish the tasks of purification, reduction, and

deoxygenation sequentially. The overall process includes three key steps: production of purified TiO_2 , Mg reduction of TiO_2 in hydrogen atmosphere, and de-oxygenation of Ti powder using Ca. A key step is the hydrolysis process that produces relatively coarse TiO_2 with controlled sizes and morphologies that allows Mg reduction in the presence of hydrogen to form porous TiH_2 . The de-oxygenation process using Ca enables the production of powder with less than 0.15% oxygen. The purity of Ti, or the impurity content of the powder produced using this process, meets the specifications by ASTM for Ti sponge.

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