Hydrogen Assisted Magnesiothermic Reduction of TiO₂

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Abstract: The development of low cost titanium metal production processes has challenged the Ti research and industrial communities around the world for decades. The strong affinity of titanium to oxygen dictates that it is very difficult to produce low-oxygen Ti metal from TiO₂ directly. In this paper, a hydrogen assisted magnesiothermic reduction (HAMR) process for producing Ti metal powder from TiO₂ powder at relatively low temperatures ($\leq 750^{\circ}\text{C}$) is established. The overall approach is based on the thermodynamic tuning of the relative stability of MgO versus that of Ti-O solid solutions by temporarily alloying the system with hydrogen. It is shown that Ti-H-O solid solutions are less stable than their corresponding Ti-O solid solutions, which changes the reaction of Mg with Ti-O from being thermodynamically unfavorable to being favorable. The key steps for producing pure Ti metal powder from TiO₂ involve Mg reduction of TiO₂ in a hydrogen atmosphere which produces porous TiH₂, a heat treatment procedure to consolidate the powder and reduce specific surface area of the powder, and the final step to deoxygenate the powder using Mg in a hydrogen atmosphere to further reduce the oxygen content. This paper systematically examines the changes of oxygen content, phase transformations, and the evolution of the

morphology of the particles during the entire process. The results show that this approach has great potential to be a viable method for the production of low-oxygen Ti metal powder from TiO_2 . In addition, the effect of hydrogen on the oxidation of Ti powder is analyzed using XPS, which reaffirms that titanium hydride is more impervious to surface oxidation than Ti metal, another crucial advantage of using hydrogen atmosphere.

Keywords: Ti metal powder, TiO_2 , reduction, deoxygenation, magnesium, hydrogen

1. Introduction

Titanium metal is a highly coveted and sustainable material owing to its high specific strength, excellent corrosion resistance, and biocompatibility. The combination of these superior properties can account for the widespread adoption of Ti and its alloys in aerospace, defense, biomedical, and chemical industries. However, titanium is also known for being prohibitively expensive for civilian applications, which has limited its use in many industries such as automobiles that would have resulted in a huge benefit for reducing weight and associated energy consumption. Reducing the cost of Ti primary metal production has thus become a major challenge for the Ti research and production communities.

Titanium primary metal has been commercially produced for decades around the world by using the Kroll process. In the Kroll process, purified titanium tetrachloride (TiCl_4) is the precursor, which is reduced by liquid Mg to produce Ti sponge. The main advantage of using TiCl_4 is that it is relatively easy to remove all the undesired impurities from TiCl_4 by distillation, enabling the production of highly purified Ti metal. However, the processes to produce purified TiCl_4 involve a series of highly energy intensive and costly processes [1]. TiCl_4 is also highly corrosive. Even a slight leak can cause serious damage to most metal structures and electrical equipment in its vicinity.

Another alternative for production of Ti primary metal is to reduce TiO_2 , which is safe to work with and can be produced commercially via either the sulfate process or the chloride process. The reduction of TiO_2 can be accomplished by using either electrochemical methods represented by the FFC or Cambridge process [2], or thermochemical reduction of TiO_2 by reactive metals [3,

4]. The focus of this work is on the thermochemical reduction of TiO_2 , while electrochemical approaches are beyond the scope of the present article. It is well known that aluminum and carbon are common reductants. For instance, ferrotitanium and Cr metal are industrially produced by aluminothermic reduction; pig iron and titanium slag are co-produced by carbothermic reduction of Ilmenite. However, neither Al nor C is used to reduce TiO_2 for Ti metal production, since Ti-Al alloys or titanium oxycarbide will be the product instead of Ti metal. Based on the Ellingham diagram for metals' reactions with oxygen, the only two other reducing agents that are both theoretically and practically feasible for reducing TiO_2 are either Ca or Mg. From a practical perspective, Mg has the advantage that it is relatively inexpensive.

Figure 1 compares the oxygen potentials in MgO [5], CaO [5], TiO_2 [5], TiO [5] and Ti-O solid solutions [6]. It shows that MgO and CaO are more stable than TiO_2 and TiO; however, when O is dissolved in a Ti lattice to form a Ti-O solid solution, the Ti-O could be more stable than CaO or MgO, depending on the oxygen content and the temperature. This implies that there are limits to which Ca and Mg can reduce the oxygen content in Ti. Specifically, it can be seen that MgO is less stable than Ti-2%O at temperatures above $\sim 780^\circ\text{C}$, or less stable than Ti-1%O at temperatures above $\sim 600^\circ\text{C}$, and less stable than Ti-0.5%O at all temperatures above room temperature. In other words, Mg cannot reduce O from Ti-O alloys to less than 0.5%O. Ca is a stronger reducing agent, however, even Ca cannot reduce oxygen in Ti to less than 0.02wt% at 700°C . Therefore, the dependence of oxygen potential on temperature represents a primary thermodynamic challenge for producing low oxygen Ti metal through thermochemical reduction of TiO_2 , which is especially difficult when Mg is used as the reducing agent. Note that the discussion on thermodynamic limit above is under the situations of saturated CaO and MgO, i.e.

with an activity of 1.0. The oxygen potentials in MgO and CaO can move downward with decreased activities, and of course the thermodynamic limit changes.

Figure 1 Ellingham diagram showing a comparison of oxygen potential in MgO, CaO, TiO₂, TiO and Ti-O solid solutions (Plotted using the data in references [5, 6])

Calciothermic reduction of TiO₂ has been reported extensively in the literature. The reducing agents based on Ca can be solid hydride CaH₂ [7], vapor-Ca [8], or liquid-Ca [9]. The reduction can also be facilitated by electronically mediated reduction (EMR) [10, 11]. Some literature reports showed that 0.42 wt% of oxygen can be achieved in Ti metal by reducing TiO₂ with the aid of molten CaCl₂ salt at 900 °C [9]. And a wide range of Ti alloys can also be prepared by calcium co-reduction of mixtures of the oxides of alloying elements [12-14]. In contrast, when Mg was used as the reducing agent, the literature showed that the oxygen in Ti can only be reduced to approximately 1.9% [15, 16]. Clearly, if one is to use Mg to reduce TiO₂ to produce low oxygen (< 2 %) Ti metal, additional procedures are necessary to further reduce its oxygen content.

In order to find ways to further reduce oxygen content in Ti, we turn to the phase diagrams of

the Ti-O system. One such diagram shows that Ti metal can dissolve interstitially about 33 atomic percent of oxygen [17]; so the process of preparing pure Ti metal from TiO_2 can actually be divided into two sub-steps: the “reduction” of TiO_2 traversing various Ti_xO_y intermediates to produce a Ti-O solid solution; and the process of further removing the dissolved oxygen in Ti-O to levels less than 0.2%, as required by most industrial standards for Ti alloys. This second step of removing oxygen in Ti is referred to as “deoxygenation”, which is a distinctively different process from “reduction” as defined in chemistry.

Deoxygenation of Ti or Ti alloys by Ca has been reported in the literature as being very effective, where solid Ca, liquid Ca, vapor Ca and Ca-saturated salt were all reportedly used as deoxygenation agents. For example, the so-called deoxygenation in solid state (DOSS) process [18] uses liquid Ca without CaCl_2 flux to remove the alloyed oxygen. This technique has also been applied to reduce oxygen in Ti-Mo and Ti-V β alloys [19]. Similar to the DOSS process, a molten CaCl_2 assisted liquid Ca process was reported to operate at 900-950 °C in Ar. The role of molten CaCl_2 is to dissolve the byproduct of the reaction, CaO, to accelerate the deoxygenation reaction [20]. Ca-saturated salt processing takes advantage of the high solubility of Ca in molten CaCl_2 salt, and conducts the deoxygenation by using the chemically activated salt at 1000-1200 °C through dissolving Ca vapor into CaCl_2 salt, to avoid impurity contamination from Ca metal [21]. In order to reduce the temperature required for the reaction, a Ca vapor process was developed by Oh J. M. et al. to operate in vacuum at relatively low temperatures, in the range of 500-830 °C [22].

Again, in contrast, if Mg is used to deoxygenate Ti, as described earlier, Mg cannot reduce oxygen in Ti to less than 0.5wt% because Ti-O with <0.5wt% O is more stable than MgO. It seems that deoxygenation of Ti to 0.1wt% (1000 ppm) oxygen by Mg is only feasible when the

activity of byproduct MgO can be decreased by a large margin from 1.0 (saturation) to 0.039 at 1000 °C [23]. However, the solubility of MgO in its corresponding halide salt is extremely low [24], compared to that of CaO in the calcium halide flux [25]. In order to lower the activity of MgO, Okabe et al [23] recently reported an electrochemical deoxygenation technique in MgCl₂ salt, by producing Mg metal at a Ti cathode through electrolysis and removing O²⁻ at the anode by forming CO_x. Without the accumulation of MgO and O²⁻ in the molten salt, Mg metal shows deoxygenation capability based on the decreased activity of MgO.

However, almost all of these techniques are conducted at high temperatures of around 900-1200 °C. Having to use such high temperatures can cause many problems, such as the selection of reactor materials to scale up the process, the risk of sintering of the particles, and the possibility of having residual Ca in Ti metal is also a serious concern from the point of view of mechanical properties [26].

Recently, a general approach for converting upgraded Ti slag (UGS) to purified TiO₂ and subsequently to Ti by using Mg for reduction in a H₂ atmosphere was described previously by the present authors [27], which focused on the purification of TiO₂ from UGS. Although the Mg reduction of TiO₂ in H₂ was discussed, it did not go in depth with regard to the reduction process, and it did not explain the deoxygenation process in any detail. A deoxygenation technique using Mg was described in more detail by Zhang et al [28], which is based on the thermodynamic tuning of the relative stability of MgO and Ti-O by introducing hydrogen. It was found that Ti-O, the product of magnesiothermic reduction of TiO₂, can absorb hydrogen to form Ti-O-H solid solution in a hydrogen atmosphere during the process. It was shown that the oxygen potential in the Ti-H-O solid solution is lower than that in the initial Ti-O. Thus the thermodynamic driving force

of the Mg reaction with Ti-O alloys was increased. In other words, Ti-O can be destabilized by absorbing hydrogen. And the higher the hydrogen content in Ti-O-H, the stronger the destabilization effect. This effect of thermodynamic tuning changes the deoxygenation of Ti using Mg from being thermodynamically unfavorable to being favorable.

Based on the previous works [27, 28], the combination of the Mg reduction and Mg deoxygenation as one integrated process for making high purity low oxygen Ti powder from TiO_2 is described for the first time in this manuscript. The integrated process is named as the hydrogen assisted magnesiothermic reduction (HAMR) process, as shown schematically in Figure 2. The process is divided into two main steps: reduction of TiO_2 and deoxygenation of Ti-O. The reaction byproduct MgO is leached using dilute hydrochloric acid solutions after each step. Between the two steps, a heat treatment procedure is carried out to control the specific surface area and particle size of the powder.

To date, although the thermodynamic principle of the destabilizing effect of hydrogen has been demonstrated, a full analysis of the HAMR process has yet to be reported. The effectiveness of the process for producing pure Ti powder with low oxygen content, the mechanisms of the reduction process, and a more detailed understanding on the effect of hydrogen on the reduction (not deoxygenation) of TiO_2 using Mg, are still lacking. In this study, the HAMR process is studied systematically by investigating the changes of the oxygen content and phase compositions as a function of the processing steps. Specific surface areas and morphology of the powder during each critical step of the process are also studied, and a qualitative analysis of the thermodynamic effects of hydrogen on the reduction process is carried out. Additionally, the effects of temporarily alloying Ti with hydrogen to facilitate oxygen removal are also examined by characterizing the

thicknesses of oxide passive layers on Ti and TiH_2 powder using XPS. The results of this study demonstrate that using hydrogen as a temporary alloying element is an effective approach to produce pure Ti metal by reduction of TiO_2 using Mg.

Figure 2 Flowchart of the HAMR process

2. Experimental

Raw materials: The main chemicals used in this research, including anhydrous MgCl_2 , KCl, Mg metal powder with particle size below 300 microns, and hydrochloride acid, were obtained from Sigma-Aldrich (US). Nano sized TiO_2 was purchased from Kronos; TiO_2 powders with an average sizes of 10 μm and 30 μm were prepared via controlled hydrolysis.

Reduction: TiO_2 powder, mono salt of MgCl_2 and Mg metal powder were mixed with a mass ratio of 1: (0.5~1.5) :(0.6~1.8) based on mass balance as well as kinetic considerations, and loaded in a Mo crucible. The total mass of the mixture was no less than 50 grams. Then the Mo crucible was placed into the chamber of a top-loading furnace. After the reaction chamber was evacuated and back-filled with argon and then with hydrogen, the mixture was heated to a temperature between 720~900 $^{\circ}\text{C}$ in pure H_2 gas with a flow rate of 1.5 L/min and held at the temperature for 6 hours, which was considered to be near optimum. The samples were then cooled in H_2 to room temperature. After the reduction, DI water was added first to the powder to make a slurry, then

HCl was added gradually while the pH value of the slurry was monitored in real time, controlled to be higher than 2. After leaching, the powder was filtered and washed with water until the washing liquid was free of any cations. The wet powder was then rinsed using acetone, dried in air, and readied for heat treatment.

Heat treatment: The powder from the Mg reduction step was heated in a H₂ atmosphere to 900-1000 °C, and held for 5~60 minutes before cooling in an argon atmosphere to room temperature. The purpose of the heat treatment is to close the pores in the post-reduction powder after washing and to reduce its specific surface areas.

Deoxygenation: Deoxygenation procedures are similar to the reduction step. Depending on the type of MgCl₂-bearing salt added, the temperature can be in the range of 650-750 °C. A temperature higher than the melting point of Mg metal can kinetically speed up the deoxygenation. However, if the temperature is too high, it will lead to a large amount of evaporation loss of Mg metal. Mono MgCl₂ salt can work well, but the temperature must be higher than its melting point of 718 °C. Using MgCl₂-KCl or MgCl₂-NaCl eutectic salt can lower the deoxygenation temperature by a large margin. In this research, MgCl₂-KCl eutectic salt was used and the temperature was set at 680 °C. The mass ratio of heat treated powder: Mg powder: salt was 1: (0.1~0.5): (0.1~1.0). In order to avoid too much hydrogen absorption during cooling, the cooling gas was switched to Ar. The washing procedure was the same as described above. The deoxygenated Ti powder was stored in a sample container filled with Ar.

Instruments: The H and O/N contents in the dried powder were measured using TGA (TA Instrument Q600) and a LECO analyzer (LECO TCH600) based on the inert gas fusion thermal conductivity/infrared detection method, respectively. X-ray diffraction (XRD) patterns were

collected using a Panalytical X'Pert X-Ray Diffractometer (Cu K α radiation). The morphologies were characterized using a high-resolution scanning electron microscope (HRSEM) FEI NovaNano 630. Specific surface areas were measured by using the Brunauer–Emmett–Teller (BET) method.

The determination of the thickness of the surface's passivated layer was made by using X-ray photoelectron spectroscopy (XPS). XPS was performed with a Kratos Axis Ultra DLD instrument, using the instrument's monochromatic Al K α source (1486.6 eV) for photoelectron excitation. For the samples in this study, wide energy spectra were collected from 1400 eV to 0 eV in order to identify all elements present on the surfaces, in addition to collecting high resolution spectra about primary photoelectron peaks of interest, O 1s, Ti 2p and C 1s. Pass energy was set to 160 eV and 40 eV for wide energy and high resolution spectra respectively. The instrument's charge neutralization system was used to minimize charging artifacts on the sample, with the binding energy of all data corrected to the adventitious C 1s energy of 284.8 eV [29].

3. Results

3.1 Changes of oxygen content during the hydrogen assisted magnesiothermic reduction of TiO₂

3.1.1 Change of oxygen content vs. process and H₂ partial pressure

As described earlier, TiO₂ powders with different particle sizes were reduced using Mg in a H₂ atmosphere. The products of the reduction were then subjected to heat treatment and deoxygenation as described in Figure 2 (the process flow chart). Figure 3 shows the changes of oxygen content versus the processing steps. Clearly, the oxygen content of Ti was drastically

reduced through the reduction of TiO_2 . It appears that the larger the initial particle size of the TiO_2 powder, the lower is the oxygen level that can be achieved by Mg reduction. The reduced powder, TiH_2 , was also porous with a relatively large specific surface area, which may contribute to higher oxygen content. Higher specific surface areas, which correspond to finer particle sizes, can lead to higher oxygen content in the powder.

Needless to say, the oxygen level in the post-reduction powder was still too high, as required by most industrial standards for Ti and Ti alloys ($<0.2\%$). It was therefore necessary to further reduce the oxygen content in the powder through the deoxygenation process. Prior to the deoxygenation, a heat treatment procedure was carried out, which was designed to consolidate the powder and reduce its specific surface area. The changes of the specific surface areas after heat treatment were shown in Figure 4. The BET values were decreased to less than 1/10 of those of the reduced powders. It is noted that the oxygen level increased slightly in the heat treated powder, which may be attributable to a couple reasons: (1) residual oxygen in the argon and (2) exposure of the powder to air after the heat treatment.

Following the heat treatment, deoxygenation was conducted, also using Mg in a H_2 atmosphere. The oxygen content was reduced to less than 0.15wt%, as shown in Figure 3. As explained earlier in the introduction, the use of hydrogen plays a critical role in enabling the deoxygenation of Ti using Mg [28]. As described in the experimental section, MgCl_2 -bearing salt was added for the deoxygenation as it was for the reduction, aiming to improve the kinetic rates of the reaction. Even though the preliminary work has shown that the deoxygenation process may be carried out without using salt to achieve a similar result, the exact effect of salt on the kinetics of the deoxygenation is yet to be investigated.

The results of this study show that the use of hydrogen during the reduction also plays a very important role in lowering the oxygen content in Ti in the as-reduced state. Figure 3 shows that the oxygen content in the as-reduced powder is between 0.78 and 1.28 wt%, which is significantly lower than what can be predicted according to the Ellingham diagram (Figure 1), which shows that TiO_2 can only be reduced to Ti-O solid solution with an oxygen content between 1.5 and 2 wt% at 750 °C by using Mg in Ar. This result suggests that there is a thermodynamic advantage of reducing TiO_2 using Mg in H_2 compared to Ar.

In order to further elucidate the effect of hydrogen, a series of experiments were carried out to reduce TiO_2 using Mg in hydrogen at different partial pressures. In order to ensure that the reaction reached its thermodynamic equilibrium, a long holding time of 12 hours was used. In addition, 50 wt% excess amount of Mg powder was added to avoid the adverse effect of the evaporation loss of Mg on reduction equilibrium. Figure 5 quantitatively compares the effect of H_2 partial pressure on the magnesiothermic reduction, as indicated by the oxygen content in the as-reduced powder. The experimental results show that the oxygen content in the reduced powder depends strongly on the partial pressure of hydrogen. Increasing the hydrogen partial pressure can move the reduction reaction forward. The oxygen level in the as-reduced powder can be 0.5 wt% when pure hydrogen is used, compared with that of 4.26 wt% in pure Ar. This result indicates that the alloying of Ti by hydrogen changes the thermodynamic limit for the reduction of TiO_2 by Mg.

The correlation of H content in the reduced powder vs. the partial pressure of hydrogen was also plotted in Figure 5, showing that the trend is opposite to that for the oxygen content. Note that about 1000 ppm of H in the powder that was reduced in pure Ar gas is attributed to the moisture introduced by the salt. The H/Ti molar ratio in the reduced powder was calculated and compared

with that of the theoretical values derived from the Ti-H phase diagram. It shows that the real hydrogen content in the reduced powder is lower than that of the theoretical values, which can be explained by the operations after the reduction. Prior to pull the post-reduction crucible to the cold area for fast cooling in Ar in order to retain the hydrogen in the reduced product, the reduction chamber was purged with Ar gas with a high flow rate (5 L/min) to expel H_2 gas out. Thus the discrepancy between the H/Ti molar ratios in Figure 5 results from the dehydrogenation during the post-reduction operation.

H_2 partial pressure affects the deoxygenation of Ti-O by Mg too, which has been previously reported by the present authors [28]. It was shown that the higher the hydrogen partial pressure, the lower the oxygen content in the deoxygenated powder. The effects of hydrogen partial pressure on both the reduction and the deoxygenation processes are consistent, as the limits for both cases are determined by the equilibrated oxygen potential between MgO and the Ti-O-H solid solution, which will be further discussed in section 4.1 of this paper.

Figure 3 Change of oxygen content vs. process

Figure 4 Specific surface areas vs. process (reduction and heat treatment)

Figure 5 Effect of hydrogen partial pressure on the reduction of TiO₂ using Mg

3.1.2 Surface oxygen vs. lattice oxygen

It is widely recognized that Ti metal forms a passive oxide layer when it is exposed to air or water. Therefore, part of the total oxygen content in a Ti powder is logically in the form of oxides

on the surface of each particle. There have been reports of studies on the thickness of the oxide layer on Ti metal particles by using the X-ray photoelectron spectroscopy (XPS) technique, and the oxide layer can change its thickness and composition depending on the aging time and temperature [30], ranging from 3-8 nm at room temperature [31]. It has been estimated that for Ti a spherical particle of 2 μm in diameter and 3 nm in surface layer thickness, the surface oxygen content can be around 3900 ppm [32]. Therefore, for a Ti particle of any size with known specific surface area, the contribution of surface oxygen to the oxygen content in the particle can be estimated. Figure 6 shows the estimated oxygen content attributable to the surface oxide layer as a function of its specific surface area. It shows that, in order to control the oxygen in Ti metal to be less than 1500 ppm, the specific surface area must be at least smaller than 0.256 m^2/g , or 0.17 m^2/g to be less than 1000 ppm.

Assuming that the thickness of the surface passivation layer on the titanium hydride powder (which is of interest in this work) is the same as that on Ti metal powder, the oxygen contents in the samples of this work attributable to the surface oxide layer can then be estimated. Figure 7 shows the estimated oxygen content due to surface oxides compared to the measured oxygen content of the as-reduced powder and the powder after deoxygenation. Note that these powders all contain a significant amount of hydrogen because both the reduction and deoxygenation processes were conducted in H_2 . Figure 7 shows that the measured oxygen content is less than the estimated oxygen content attributable to the surface oxide. The higher the specific surface area, the larger the difference between the estimated and measured oxygen content. This is counter intuitive because the total oxygen content should be the surface oxygen plus that dissolved in the bulk. A possible reason for this phenomenon is that the thickness of the oxide layer on Ti-H particles with

a significant amount of hydrogen content may be thinner than that on equivalent Ti metal particles.

Further, the surface layer may be partially composed of suboxides of Ti.

Figure 6 The relationship of specific surface area vs. surface oxygen content and particle size

Figure 7 The estimated oxygen content due to surface oxides vs. the measured oxygen content of the as-reduced and as-deoxygenated powders

3.1.3 Dehydrogenation

As hydrogen is used in the entire process, the variation of H content in all intermediates was monitored, as shown in Figure 8(a). Using the powder sample with the coarsest size cut as an example, the hydrogen content was approximately 3.8 wt% in the as-reduced powder, which is almost the level of hydrogen in stoichiometric TiH_2 (4 wt%), indicating that the hydride phase was formed as a result of the reduction process. The hydrogen content in the powder after heat treatment, and after deoxygenation, were 1.7 and 2 wt%, respectively. These results are consistent with the Ti-H phase diagrams as functions of both temperature and partial pressure of hydrogen. Furthermore, if the deoxygenated powder is cooled in H_2 it will end up being pure hydride phase with a hydrogen content of 3.82 wt%.

Figure 8 (a) The variation of H content in all intermediates, (b) The TGA-DSC curve for dehydrogenation of heat treated powder

The deoxygenated powder has to be dehydrogenated to produce pure Ti powder. It is well known that TiH_2 can be readily dehydrogenated at moderately high temperatures ($>400\text{ }^\circ\text{C}$) in vacuum or in a protective atmosphere in which the partial pressure of H_2 is lower than its equilibrium pressure. In this work, the deoxygenated powder with 2 wt% of hydrogen was dehydrogenated at $600\text{ }^\circ\text{C}$ under high vacuum. The H wt% was less than 100 ppm (0.01 wt%)

after the dehydrogenation, which is sufficiently low to satisfy industrial standards.

To verify the stability of the powder after the dehydrogenation, an oxidation test was carried out by using the TGA to measure the weight gains of the powder when heated to the temperature range of RT to 800 °C in air. The result as shown in Figure 9 demonstrates that Ti powder produced with the given particle size and specific surface area is relatively stable in air. It can oxidize rapidly only when the temperature is raised to higher than 500 °C.

Figure 9 The oxidation curve of Ti powder produced by HAMR process

3.2 Phase transformations during the entire process

The hydrogen assisted magnesiothermic reduction process, as described above, involves not only changes in chemical composition, but also a series of phase transformations. Figure 10 shows the XRD patterns of as-reduced, as well as heat treated, and deoxygenated powders. For the as-reduced powder, Figure 10(a) shows that the main peaks matched well with that of $\text{TiH}_{1.924}$. However, there are also other phases such as $\text{TiH}_{1.5}$ and $\alpha\text{-Ti}$ in the powder made from the

nano-sized TiO_2 . The titanium hydride phase is not pure hydride, but with dissolved oxygen. As a result of the dissolved oxygen, the lattice parameters of TiH_x changed compared to those obtained from the powder diffraction file (PDF) cards (00-025-0982 and 01-078-2216) for pure TiH_x , as shown in Figure 10(a).

The phase compositions of the heat treated powders are shown in Figure 10(b). The main phases in this sample are $\text{TiH}_{1.5}$ (δ -phase) and α -Ti. Based on the thermal history of this powder, it can be predicted that the powder is partially hydrogenated during cooling. According to the Ti-H phase diagram, we know that β -phase Ti with dissolved oxygen and hydrogen is the stable phase at temperatures above the eutectoid transformation, while $\text{TiH}_{1.5}$ and α -Ti phases are the stable phases at lower temperatures. This can also be observed from Figure 8(b), which shows a eutectoid transformation at 300 °C forming β -phase (endothermic peak I) prior to the dehydrogenation (endothermic peak II). Furthermore, the relative fractions of the two phases can be calculated based on the hydrogen content in the heat treated powder, which was determined to be approximately 56 wt% of $\text{TiH}_{1.5}$ and 44 wt% of α -Ti.

No obvious phase composition changes were observed for the powders before or after the deoxygenation process (Figure 10(c)). Note, those powders contained hydrogen. The two powders were dehydrogenated and tested again (Figure 10(d)). It is obvious that both are α -Ti phases after dehydrogenation, but the peaks for α -Ti with higher oxygen were shifted to the left compared with the α -Ti standard (PDF card 01-089-2762) (Figure 10(e) and (f)). The shifting of the peak positions is attributed to the expansion of the unit cells [33]. Specifically, as it was reported, the increase of oxygen content in Ti will increase the c value of its unit cell [34], which was also evidenced in this work using the Rietveld refinement method.

As a summary, the phase transformations during the entire process of producing Ti metal from TiO_2 powder is illustrated in Figure 11. The phases stable at room-temperature were directly determined by using the XRD technique, while the high-temperature phases were identified by reasoning, using the Ti-H and Ti-H-O phase diagrams. The β -phase Ti-H-O solid solution with various oxygen contents is the most important intermediate.

Figure 10 (a) Comparisons of the XRD patterns of the post-reduction powders, (b) heat treated powders, (c) deoxygenated powder before dehydrogenation, (d) deoxygenated powder after

dehydrogenation, (e and f) local enlarged images for (d)

Note: all powders were leached and washed to remove MgO.

Figure 11 Phase transformations during the hydrogen assisted magnesiothermic reduction process

for producing Ti metal from TiO_2 powder

3.3 Evolution of the morphology of particles during reduction and heat treatment

The size and morphology of particles are important aspects of any powder production process.

Figure 12 illustrates the evolution of the morphology of the particles studied during this work, and indicating that the morphology of the as-reduced powder inherits the morphology of the initial TiO_2 powder. However, the particle size of the titanium hydride powder formed by reducing the nano-sized TiO_2 grew significantly at the reduction temperature (Figure 12(d)). When the coarse TiO_2 powder was used as the starting material, the titanium hydride powder was also coarse and discrete. The coarse powder also exhibited a porous structure (Figure 12(f)), and thus higher specific surface area. This phenomenon can be attributed to the volume shrinkage from TiO_2 to Ti, and the formation of the byproduct MgO inside (Figure 12(n)) and outside (Figure 12(m)) the

particle, preventing physical contacts and sintering between particles, and self-densification of the particles [35].

In order to minimize oxygen pick up in the final product powder, the heat treatment procedure was designed to close the pores within each particle and minimize the specific surface area. Figure 10 shows that the heat treated powders from three different initial powders exhibited significant differences in their responses to the heat treatment procedure. For the powder from the nano-sized TiO_2 , the titanium hydride is in the submicron size range in the as-reduced state. Upon heat treatment, this powder experienced considerable sintering among particles, Figure 12(g) and (j). The discrete loose fine powder formed porous chunks (Figure 12(g)). The specific surface area of this powder decreased significantly as a result of the heat treatment, from $4.98 \text{ m}^2/\text{g}$ to $0.08\sim 0.21 \text{ m}^2/\text{g}$ varied by the size range. For the medium sized titanium hydride powder, the situation was a bit similar to the submicron sized powder. However, the sintering between particles was not as extensive (Figure 12(h) and (k)), which is understandable due to the increase in particle size. The coarsest hydride powder experienced extensive densification within each particle, while the sintering between particles was minimal (Figure 12(i) and (l)). The particles remained discrete after the heat treatment and the particle surfaces appeared smooth and free of open pores, when the BET decreased from $2.13 \text{ m}^2/\text{g}$ to $0.19 \text{ m}^2/\text{g}$. These results shed light on the effects of particle sizes and specific surface areas. However, a comprehensive study is needed to fully investigate the effects and evolution of particle sizes and morphologies as a function of the processing parameters.

Figure 12 SEM images of three different TiO_2 powders (*a* nano-sized, *b* 10 μm , and *c* 20-45 μm); the same three powders post-reduction (*d*, *e* and *f*); after heat treatment at low magnification (*g*, *h* and *i*) and at higher magnification (*j*, *k* and *l*); EDS results of the surface (*m*) and the cross section

(n) of the post-reduction powders after water washing

4. Discussion

4.1 Effect of hydrogen on thermodynamic tuning of Mg reduction capability

As the results described above indicate, the reduction of TiO_2 and the deoxygenation of $\text{Ti}(\text{O})$ can be significantly enhanced by carrying out the reactions in the presence of hydrogen. The effect of hydrogen can be analyzed from a thermodynamics point of view, as follows.

It has been mentioned earlier that the production of Ti metal from TiO_2 can be divided into two sub-steps, reduction and deoxygenation. The reactions in Table 1 represent the typical chemical reduction of TiO_2 by Mg in an inert atmosphere (Ar) or H_2 . Reactions (1) and (2) assume that the titanium metal free of oxygen is prepared through reducing TiO_2 by Mg, whereas reactions (3) and (4) consider that Ti with alloyed oxygen is produced after Mg reduction, which is the true situation.

According to the database of Gibbs free energy of formation for oxide compounds [5], $\Delta G_r^\theta(1)$ for reaction (1) equals to $0.0397 \times T - 251.94$ kJ, in the temperature range from 0 °C to 1000 °C, where T is the temperature in °C. $\Delta G_r^\theta(1)$ is always negative, i.e. smaller than zero.

Regarding $\Delta F_{\text{Ti}(\text{H})_x}$ in $\Delta G_r^\theta(2)$ in Table 1, the Gibbs free energy of formation of $\text{Ti}(\text{H})_x$ as a function of temperature and x can be calculated by integration [36]. The calculated result was reported [28] and replotted in Figure 13(a). It shows that $\Delta F_{\text{Ti}(\text{H})_x}$ is always negative, and the larger the value of x , the more negative the formation energy is. Thus, theoretically, $\Delta G_r^\theta(2)$ is always more negative than $\Delta G_r^\theta(1)$, and the higher the hydrogen content in $\text{Ti}(\text{H})_x$, the stronger the thermodynamic driving force for reaction (2).

Similarly, the relative magnitude of $\Delta G_r^\theta(3)$ and $\Delta G_r^\theta(4)$ for reaction (3) and reaction (4) is determined by $\Delta F_{\text{Ti(O)}_y}$ and $\Delta F_{\text{Ti(H)x(O)y}}$, or by $\Delta G_r^\theta(5)$, which is the Gibbs energy change of hydrogenation of TiO_y . $\Delta G_r^\theta(5)$ for Ti-O solid solution with O/Ti molar ratios of 0.005 and 0.061 at 600, 700 and 800 °C was calculated [28] and replotted in Figure 13(b), illustrating that $\Delta G_r^\theta(5)$ is always negative, and the larger the value of x , the more negative the energy change of hydrogenation. Thus, $\Delta F_{\text{Ti(H)x(O)y}} < \Delta F_{\text{Ti(O)y}}$, and further $\Delta G_r^\theta(4)$ is smaller than $\Delta G_r^\theta(3)$. In addition, the higher the hydrogen content in Ti(H)x(O)y , the larger the gap between $\Delta G_r^\theta(3)$ and $\Delta G_r^\theta(4)$.

Thus, it can be qualitatively concluded that the thermodynamic driving force for the reduction of TiO_2 by Mg can be enhanced by alloying Ti or Ti-O with hydrogen, and the more hydrogen is used, the stronger the driving force. This is also the reason that the reduction and the cooling in these experiments were conducted in a hydrogen atmosphere, to promote formation of the hydride phase. The oxygen content in the as-reduced powder, which is titanium hydride, is lower than the predicted oxygen content if the reduction product was Ti metal.

Table 1 Chemical reactions of reducing TiO_2 by Mg

Reaction (1) to (5)	ΔG_r^θ
(1) $\text{TiO}_2 + 2\text{Mg} \rightarrow \text{Ti} + 2\text{MgO}$	$\Delta G_r^\theta(1) = 2\Delta F_{\text{MgO}} - \Delta F_{\text{TiO}_2}$
(2) $\text{TiO}_2 + 2\text{Mg} + \frac{x}{2}\text{H}_2 \rightarrow \text{Ti(H)}_x + 2\text{MgO}$	$\Delta G_r^\theta(2) = 2\Delta F_{\text{MgO}} - \Delta F_{\text{TiO}_2} + \Delta F_{\text{TiH}_x}$
	$\therefore \Delta G_r^\theta(2) < \Delta G_r^\theta(1)$
(3) $\text{TiO}_2 + (2-y)\text{Mg} \rightarrow \text{Ti(O)}_y + (2-y)\text{MgO}$	$\Delta G_r^\theta(3) = (2-y)\Delta F_{\text{MgO}} + \Delta F_{\text{Ti(O)}_y} - \Delta F_{\text{TiO}_2}$
(4) $\text{TiO}_2 + (2-y)\text{Mg} + \frac{x}{2}\text{H}_2 \rightarrow \text{Ti(H)}_x(\text{O})_y + (2-y)\text{MgO}$	$\Delta G_r^\theta(4) = (2-y)\Delta F_{\text{MgO}} + \Delta F_{\text{Ti(H)}_x(\text{O})_y} - \Delta F_{\text{TiO}_2}$

$$\Delta G_r^\theta(5) = \Delta F_{\text{Ti(H)}_x(\text{O})_y} - \Delta F_{\text{Ti(O)}_y}$$

$$\therefore \Delta G_r^\theta(4) < \Delta G_r^\theta(3)$$

Note: Ti(H)_x stands for titanium hydride or Ti-H solid solution; Ti(O)_y stands for Ti-O solid solution; $\text{Ti(H)}_x(\text{O})_y$ represents Ti-H-O solid solution. ΔG_r^θ is the Gibbs free energy of a reaction, and ΔF is the Gibbs free energy of formation.

Figure 13 (a) The Gibbs free energy of formation of TiH_x , (b) the Gibbs energy change of hydrogenation of TiO_y

As mentioned earlier, the US patent 3140170 [15] also disclosed the technique of using Mg to reduce rutile, which consists of primarily TiO_2 , in a H_2 atmosphere. The reported oxygen content in that work was about 2.0 wt% or more, higher than the results of this work. Although the fundamentals of both works are similar, several factors may have affected the outcome. These factors include the type of raw materials, the amount of reducing agent Mg, the amount of salt, time and temperature, all affecting the thermodynamic equilibrium as well as the kinetics of the reduction. The relatively lower oxygen content achieved in this work was reached through a combination of near optimum conditions. However, a comprehensive investigation is still needed to determine the true optimum conditions.

4.2 Surface oxygen control by alloy Ti with hydrogen

As mentioned earlier, both TiH_2 and Ti metal particles are expected to have an envelope of titanium oxide on their surfaces. It is believed here that the passivation layer on the surface of fresh TiH_2 powder should be thinner than that of fresh Ti metal powder, according to the relationship of oxygen content versus BET value; however, opposing positions have been taken by others [37]. X-Ray Photoelectron Spectroscopy (XPS) analysis was therefore used to study the oxide film of the fresh TiH_2 and Ti metal powders in this study, which are stored in glove box filled with Ar gas.

Wide energy spectra taken by XPS on both samples showed the expected Ti, O and C, shown in Figure 14 and Table 2, and both samples showed significant amounts of C. Here, all results were calculated from the high resolution spectra using standard Shirley type background subtraction. More relevant to this study is to understand the changes in Ti oxidation based on fitting the Ti 2p spectra. For each sample, the Ti 2p spectra were fit following a procedure largely based on work done by Biesinger et. al [38]. A least squares fitting algorithm was employed using the program CasaXPS. Fitting results for the TiH_2 and Ti samples are shown in Figures 15 (b) and (c), respectively.

For each sample, Ti was found to contain IV and metallic states. In addition, both samples showed sub-oxidation states of II and III. These assignments are in good agreement with reported literature values on these binding energies [39]. What can clearly be seen when comparing the Ti 2p spectra from both spectra is that, in the case of TiH_2 sample, the low binding energy peak at approximately 454 eV is relatively larger. This peak corresponds to metallic Ti, indicating that the

extent of Ti oxidation in the TiH₂ sample is less than that in the Ti sample, with 18.33% and 5.41% of the Ti in the sample surface measured in a metallic state for TiH₂ and Ti samples, respectively. Furthermore, the amount of Ti as Ti IV (likely TiO₂) is 56.68 % vs. 83.48 % for TiH₂ and Ti samples. As for the sub-oxides, both samples showed relatively similar amounts of Ti II but the TiH₂ sample shows more Ti III.

Further, in order to gauge oxide layer thickness, the ratio of Ti^{ox} to Ti⁺⁰ signal intensity can be modelled in a layer by layer fashion, and compared to the relative peak fit areas for the Ti 2p region that corresponds to these oxidation states. Based on a model described by Van Devener, et al. [40], it is calculated that TiH₂ powder has an oxide layer thickness of only 2.1 nm, whilst Ti powder has an oxide layer thickness of 4.1 nm. These results are generally in agreement with recently published data by Hryha E. et al of 2.9 nm for Ti powder [30]. Because of the thinner passivation layer of the fresh TiH₂ powder, the contribution of oxygen from the surface is weaker, which is beneficial for total oxygen content control.

Figure 14 XPS survey spectra of TiH₂ and Ti powders without Ar⁺ etching

Table 2 Basic elemental composition by XPS (Atomic %)

	Ti	O	C
TiH ₂ powder	13.62	42.54	43.84
Ti powder	16.05	46.22	37.73

Figure 15 XPS data showing the position of the Ti2p peak on the as-received surface of TiH₂ and Ti powders (a); Ti 2p peak fitting for TiH₂ powder (b); Ti 2p peak fitting for Ti powder (c).

5 Conclusions

A hydrogen-assisted magnesiothermic reduction (HAMR) process for producing Ti metal

powder from TiO_2 powder is described in this article. The key steps include Mg reduction of TiO_2 in a hydrogen atmosphere, a heat treatment procedure, and a final deoxygenation step using Mg in a hydrogen atmosphere. The results show that this is a viable approach for the production of low-oxygen Ti metal powder from TiO_2 . The key enabling factor for the effectiveness of the HAMR process is the use of hydrogen during the reduction of TiO_2 and during the deoxygenation of the Ti-O solid solution. The results and analysis demonstrated that the thermodynamic driving forces for Mg reduction of TiO_2 , and Mg deoxygenation of Ti-O, can be enhanced with the aid of hydrogen. In particular, the alloying of Ti-O solid solution by hydrogen can destabilize Ti-O, enabling the reaction of Mg deoxygenation to shift from thermodynamically unfavorable to become favored. The thermodynamic destabilization effect of hydrogen is the scientific basis for the feasibility of production of low oxygen Ti from TiO_2 by the hydrogen assisted magnesiothermic reduction process.

Further, the results demonstrate that forming hydride during reduction is advantageous over forming Ti metal powder because TiH_2 is more impervious to oxidation than Ti metal. The thickness of the surface passivation layer on fresh titanium hydride is considerably thinner than that on Ti metal powder.

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Graphical Abstract