

# Thermodynamic Destabilization of Ti-O Solid Solution by H<sub>2</sub> and Deoxygenation of Ti Using Mg

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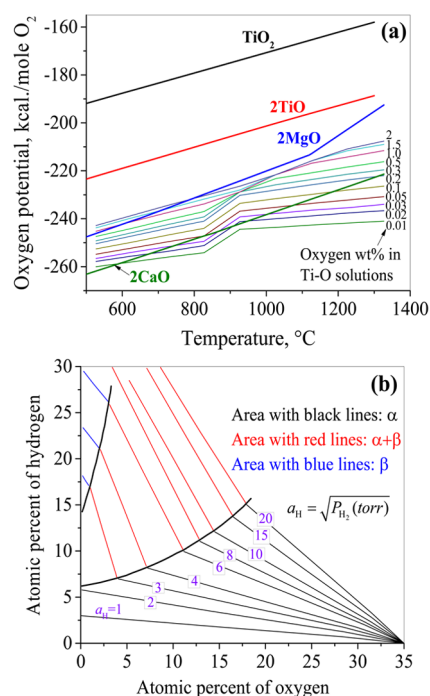
## Supporting Information

**ABSTRACT:** Reactive metals including Ti, Zr, Hf, and V, among others, have a strong chemical affinity to oxygen, which makes them difficult to produce and costly to use. It is especially challenging to produce pure or metal alloy powders of these elements when extremely low oxygen content is required, because they have high solubility for oxygen, and the solid solution of these metals with oxygen is often more stable thermodynamically than their oxides. We report a novel thermochemical approach to destabilize Ti(O) solid solutions using hydrogen, thus enabling deoxygenation of Ti powder using Mg, which has not been possible before because of the thermodynamic stability of Ti(O) solid solutions relative to MgO. The work on Ti serves as an example for other reactive metals. Both analytical modeling and experimental results show that hydrogen can indeed increase the oxygen potential of Ti-O solid solution alloys; in other words, the stability of Ti-O solid solutions is effectively decreased, thus increasing the thermodynamic driving force for Mg to react with oxygen in Ti. Because hydrogen can be easily removed from Ti by a simple heat treatment, it is used only as a temporary alloying element to destabilize the Ti-O systems. The thermodynamic approach described here is a breakthrough and is applicable to a range of different materials. This work is expected to provide an enabling solution to overcome one of the key scientific and technological hurdles to the additive manufacturing of metals, which is emerging rapidly as the future of the manufacturing industry.

Reactive metals including Ti, Zr, Hf, V, as well as some other metals, have a strong chemical affinity to oxygen,<sup>1</sup> which makes them difficult and costly to extract from minerals and to manufacture from stock materials. It is especially difficult to produce pure metals of these elements when high purity and low oxygen content are required, because they typically have a high solubility for oxygen, and the solid solution of these metals with oxygen is often more stable thermodynamically than their oxides. For example,  $\alpha$ -Ti has up to 14.3% solubility for oxygen,<sup>2</sup> and Ti-O solid solutions are more stable than TiO<sub>2</sub>. Moreover, the lower the oxygen content, the more stable a Ti-O is. Therefore, removing oxygen from Ti-O solid solutions, i.e., deoxygenation, is very difficult. This issue is exacerbated when these reactive metals are required in the form of fine powders because of the

high specific surface areas associated with fine particle sizes. It should be noted that Ti metal with low oxygen content in the form of a Ti sponge is industrially produced by the Kroll process, which relies on the reduction of TiCl<sub>4</sub> using Mg. However, Ti powders that are made from Ti sponge or Ti melt are prone to pick up oxygen, exhibiting surface oxidation. This has recently become a glaring challenge for additive manufacturing from Ti and other reactive metal powders, where oxygen content must be <0.15 wt%.

The difficulty of removing oxygen from Ti can be understood based on the thermodynamics of Ti-O system. Figure 1a shows the Ellingham diagram of the Ti-O system<sup>3</sup> compared to that of Ca-O<sup>4</sup> and Mg-O.<sup>4</sup> Because CaO and MgO are more stable than TiO<sub>2</sub>, Ca and Mg are widely used reducing agents for the reduction of TiO<sub>2</sub>. However, as Ti has a high solubility for



**Figure 1.** (a) Comparison of oxygen potential. (b) Isothermal section of the Ti-O-H phase diagram at 700 °C.

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oxygen, the reduction of TiO<sub>2</sub> to pure Ti metal can be broken into two steps (assuming using Mg as the reducing agent): (i) TiO<sub>2</sub> + Mg → Ti(O) + MgO and (ii) Ti(O) + Mg → Ti + MgO, where Ti(O) is solid solution of Ti with oxygen, and Ti is pure metal free of any oxygen. The reduction of TiO<sub>2</sub> has been extensively studied in the literature,<sup>5</sup> while only a few studies deal with removing oxygen from Ti-O solid solutions,<sup>6</sup> which in our view is a more critical and challenging step in order to produce high-purity Ti powders with low oxygen. There have been reports of scavenging oxygen from Ti by adding rare-earth elements to Ti or Ti alloys.<sup>7</sup> However, those methods would introduce additional elements that are not part of the pure metal or specific alloy.

As Figure 1a shows, when O is dissolved in a Ti lattice, Ti-O could be more stable than CaO or MgO, depending on O % and the temperature. In other words, there are limits to which Ca and Mg can reduce the oxygen content in Ti. For example, compared with the Ti-O with 0.5 wt% oxygen, MgO is less stable. Hence at 0.5 wt% of oxygen, Mg cannot remove O from Ti at all. Ca is a stronger reducing agent. However, even Ca cannot reduce oxygen in Ti to <0.02 wt% at 700 °C. In order to reduce oxygen content to lower levels using Mg, beyond such limits, the thermodynamic stability of the Ti-O system has to be altered to make it more susceptible to reactions that remove oxygen, i.e., deoxygenation.

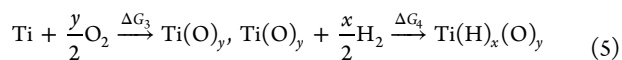
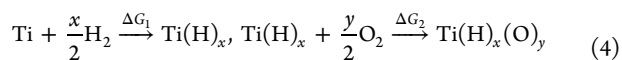
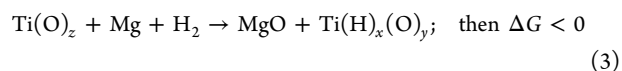
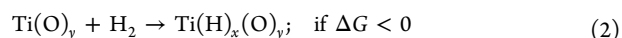
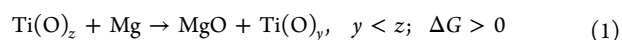
Here we introduce a new approach to thermodynamically destabilize Ti-O solid solutions by introducing hydrogen into the system. It should be noted that thermodynamically, H<sub>2</sub> does not reduce TiO<sub>2</sub> or Ti-O, unless atomic H, such as plasma, is formed at extremely high temperatures.<sup>8</sup> Hydrogen gas has been reported in the reduction of TiO<sub>2</sub> by Mg in a 1964 U.S. patent.<sup>5c</sup> However, that work was only able to reduce oxygen content to ~2 wt%, and did not show a thermodynamic advantage in using H<sub>2</sub> over using Ar.<sup>5c</sup> The results published by the present authors recently did show such an advantage, but the effect of hydrogen is still not understood yet.<sup>5h</sup> We hypothesized that hydrogen may change the relative stability of the Ti-O solid solution versus MgO, even when O content in Ti is very small, thus increasing the driving force for Ti-O to react with a reducing agent such as Mg. We present both analytical modeling and experimental results to demonstrate that hydrogen can indeed increase the thermodynamic driving force for Mg to react with oxygen in Ti, thus enabling Ti to be deoxygenated using Mg which has never been done or reported prior to this work. It is noted that hydrogen can then be easily removed through a simple heat treatment in vacuum or inert atmosphere, thereby leaving pure Ti with extremely low levels of oxygen and hydrogen. In other words, hydrogen is a temporary alloying element used exclusively to destabilize Ti-O and to induce a condition in which oxygen content can be minimized by Mg.

The following thermodynamic analysis seeks to demonstrate that Ti-O solid solutions can be destabilized by hydrogen with respect to its stability versus MgO. Eqs 1–3 are used to describe the reactions between Ti-O and Mg in Ar or in H<sub>2</sub>. Eq 3 is the summation of eqs 1 and 2. If the ΔG of eq 2 is significantly more negative than that of eq 1, then the ΔG of eq 3 can be negative, and the reaction can take place thermodynamically.

Another way to evaluate the stability of Ti-O versus MgO is to compare the oxygen potential ( $RT \ln p_{O_2}$ ) in MgO, Ti(O)<sub>y</sub>, and Ti(H)<sub>x</sub>(O)<sub>y</sub>. Higher oxygen potential indicates higher equilibrium oxygen pressure and less stable MO<sub>x</sub> or M-O<sub>x</sub> alloy, where M stands for any metal. The thermodynamic data for MgO and

Ti-O solid solutions with various oxygen contents can be obtained from the open literature. However, thermodynamic data for Ti(H)<sub>x</sub>(O)<sub>y</sub> are not available. Thus, thermodynamic modeling is carried out in this study to derive the oxygen potential in Ti(H)<sub>x</sub>(O)<sub>y</sub>.

Assuming there are two routes to form Ti-H-O solid solutions, as shown in eqs 4 and 5, in which ΔG<sub>1</sub> and ΔG<sub>3</sub> are the Gibbs free energy of formation of Ti(H)<sub>x</sub> and Ti(O)<sub>y</sub>, respectively. The values of ΔG<sub>2</sub> and ΔG<sub>4</sub> are the energy changes during the oxygenation of Ti(H)<sub>x</sub> and hydrogenation of Ti(O)<sub>y</sub>, respectively. The oxygen potential in Ti(H)<sub>x</sub>(O)<sub>y</sub> can be derived from ΔG<sub>2</sub>. Starting and ending with the same materials, the total Gibbs energy change will be the same for the two paths, i.e., ΔG<sub>1</sub> + ΔG<sub>2</sub> = ΔG<sub>3</sub> + ΔG<sub>4</sub>.



In order to determine the oxygen potential in Ti(H)<sub>x</sub>(O)<sub>y</sub>, we must find ΔG<sub>2</sub>, which necessitates establishing ΔG<sub>1</sub>, ΔG<sub>3</sub>, and ΔG<sub>4</sub>. Details of the methods for determining ΔG<sub>1</sub>, ΔG<sub>3</sub>, and ΔG<sub>4</sub> are described in the Supporting Information. A brief description of the core methodology is provided below.

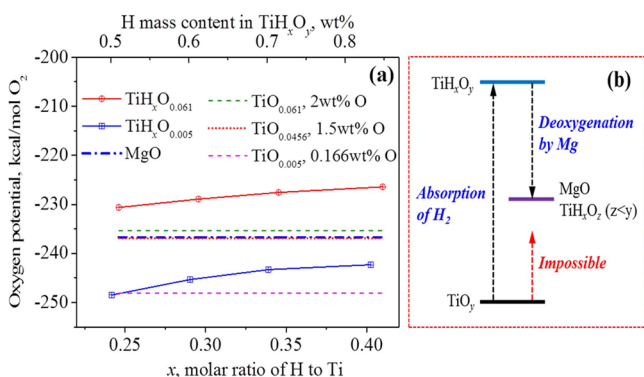
ΔG<sub>1</sub> is related to the relative partial molar free energies of hydrogen ( $\Delta \bar{G}(\text{H}_2) = RT \ln p$ ) integrated over the entire H/Ti range by  $\Delta G_1^0(\text{TiH}_x) = \frac{1}{2} \int_0^x \Delta \bar{G} \, dx = \frac{RT}{2} \int_0^x \ln p \, dx$ , where  $p$  (atm) is the equilibrium hydrogen pressure of Ti(H)<sub>x</sub>,  $x$  is the H/Ti molar ratio.<sup>9</sup> The relationship between pressure, composition, and temperature ( $P$ - $C$ - $T$ ) can be obtained from the open literature, and these values can then be used to derive  $\ln p$  as a function of  $x$  and  $T$ .<sup>9</sup> The modeling also takes into account that Ti may be in either  $\alpha$  or  $\beta$  phase, and therefore the Ti-H phase diagram<sup>10</sup> was used to estimate the phase boundaries at various temperatures. By carrying out the integration, the relationships of the Gibbs free energy of formation of Ti(H)<sub>x</sub> versus temperature can be calculated.

ΔG<sub>3</sub> can be derived by multiplying  $\overline{\Delta F}_{(\text{O})}$ , which is the partial molar free energy of oxygen in Ti-O solutions,<sup>2</sup> by the molar fraction of oxygen ( $N_{(\text{O})}$ ) in Ti(O)<sub>y</sub>.

ΔG<sub>4</sub> is the energy change during hydrogenation of Ti(O)<sub>y</sub>. The equilibrium data between  $x$  (H/Ti molar ratio) and  $p_{\text{H}_2}$  (equilibrium H<sub>2</sub> pressure) at different O/Ti molar ratios and at various temperatures can be obtained from Ti-O-H phase diagrams.<sup>11</sup> Similar to that in the Ti-H system, Sieverts law<sup>12</sup> was used to describe the relationship between  $x$  and  $p_{\text{H}_2}$  in  $\alpha$  phase; equation  $\ln p = a + bx + 2\ln[x/(2-x)] - c/T$  was used in  $\beta$  phase and ( $\alpha + \beta$ ) phase, in which  $a$ ,  $b$ , and  $c$  can be numerically fitted by using those sets of data of ( $x$ ,  $\ln p$ ) at different temperatures. Then, the ΔG<sub>4</sub> at any designated  $y$  and  $x$  values can be obtained by carrying out the integration. In this study, ΔG<sub>4</sub> with  $y$  values of 0.005 and 0.061 were calculated, which correspond to 0.166 and 2.0 wt% oxygen, respectively. These two values were selected because 2.0 wt% is the experimentally observed limit at which Mg can remove oxygen from Ti-O solid

solutions in Ar, and 0.166 wt% is near the maximum value of oxygen content allowed by ASTM and AMS standards for titanium alloys.

Using the method described above, the oxygen potential in  $\text{Ti}(\text{H})_x(\text{O})_y$  was estimated and plotted in Figure 2, comparing



**Figure 2.** (a) Comparison of oxygen potential in  $\text{Ti}(\text{H})_x(\text{O})_y$ ,  $\text{MgO}$  and  $\text{Ti}(\text{O})_x$  at 700 °C. (b) Schematic illustration of the destabilization of  $\text{Ti-O}$  by hydrogen.

the oxygen potentials in  $\text{MgO}$ ,  $\text{Ti}(\text{O})_x$ , and  $\text{Ti}(\text{H})_x(\text{O})_y$  with  $\sim 2$ , 1.5, and 0.166 wt% oxygen, respectively. At 700 °C, without hydrogen, the oxygen potential in  $\text{MgO}$  equals approximately that in  $\text{Ti}(\text{O})_{0.0456}$  (1.5 wt%O), while the oxygen potential in  $\text{Ti}(\text{O})_{0.005}$  (0.166 wt%O) is significantly lower than that in  $\text{MgO}$ , i.e.,  $\text{Ti}(\text{O})_{0.005}$  is more stable than  $\text{MgO}$ , and Mg cannot remove oxygen from  $\text{Ti}(\text{O})_{0.005}$ .

However, with hydrogen, the oxygen potentials in both  $\text{Ti}(\text{H})_x(\text{O})_{0.005}$  and  $\text{Ti}(\text{H})_x(\text{O})_{0.061}$  are less negative than that in  $\text{Ti}(\text{O})_{0.005}$  and  $\text{Ti}(\text{O})_{0.061}$ , respectively, indicating that hydrogen destabilizes  $\text{Ti-O}$  solid solutions, thus increasing the driving force for Mg to capture oxygen from the  $\text{Ti-O}$  solutions. Figure 2b schematically illustrates the destabilization effect of hydrogen. In general, Figure 2a shows that the oxygen potential is a function of both oxygen and hydrogen content. When oxygen content is low,  $\text{Ti}(\text{H})_x(\text{O})_y$  may still be more stable than  $\text{MgO}$ . At a given oxygen content, the oxygen potential increases with the increase of hydrogen. However, it is noted that the data in Figure 2a is limited to the hydrogen content up to 0.83 wt%, which is low. This limit is due to the availability of data in the published phase diagram (Figure 1b). In practice, the hydrogen content can be significantly higher than 1.0 wt%. This will be discussed more below. Moreover, the temperature at 1 bar hydrogen pressure ( $T_{1 \text{ bar}}$ ) of pure  $\text{MgH}_2$  is 278.9 °C. The thermodynamic calculation of this work is focused on 700 °C, a temperature at which Mg metal is in the liquid phase, and the solubility of H in Mg is extremely low at this temperature ( $\sim 0.0047$  wt%).<sup>13</sup> Thus, Mg will not form  $\text{MgH}_2$ , and the thermodynamic relationships discussed above will not be affected.

It should be noted that the destabilization effect could be a function of temperature and composition. Peterson et al.<sup>14</sup> and Yamanaka et al.<sup>15</sup> observed that the solubility of H in V-O alloys can decrease or increase depending on the temperature and O/V atomic ratio. Similar phenomenon could also be true for the  $\text{Ti-O-H}$  system. However, it is beyond the scope of the present work to examine all temperature and composition ranges. The results of this work are valid within the temperature and composition ranges presented.

Experimental studies were further carried out to empirically test the thermodynamic predictions. Table 1 compares the

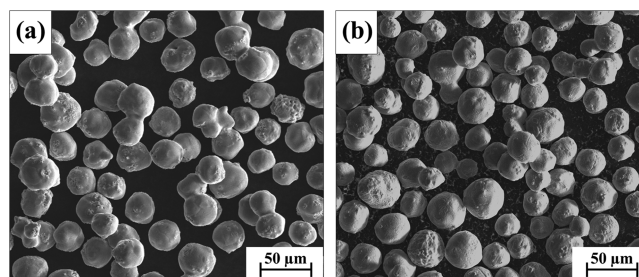
**Table 1.** Comparison of Deoxygenation by Mg in  $\text{H}_2$  and Ar Atmosphere<sup>a</sup>

atmosphere, temp (°C)	$\text{H}_2$ , 670	Ar, 670	$\text{H}_2$ , 750	Ar, 750
O content after deox (wt%)	0.0555	2.22	0.0503	2.00

<sup>a</sup>Initial O content in  $\text{Ti-O}$  alloy powder was  $(4.19 \pm 0.01)$  wt%; size range of the powder was from 45 to 74  $\mu\text{m}$ ; mass ratio of powder:salt:Mg was 2:1:0.378; the deoxygenation time was set at 12 h.

results of the deoxygenation of  $\text{Ti-O}$  alloy ( $\alpha\text{-Ti}$ ) powder by Mg in pure  $\text{H}_2$  and Ar atmosphere. It shows that the oxygen content in  $\alpha\text{-Ti}$  powder can be reduced to as low as 0.05–0.06 wt% by Mg in  $\text{H}_2$ , which is significantly lower than that required by the ASTM standard for Ti sponge (0.15 wt% O). However, the oxygen content in the sample that was deoxygenated using Mg in Ar was 2 wt%, which is consistent with the thermodynamic analysis as discussed earlier. The comparisons between the samples run in  $\text{H}_2$  and in Ar clearly demonstrated that the  $\text{Ti-O}$  system was indeed destabilized by the presence of hydrogen.

The effect of hydrogen also depends on the partial pressure of hydrogen (Supplementary Figure 8a). Hydrogen partial pressure was varied from 5% to 100%. The results show that oxygen can be reduced to 0.26 wt% even if the hydrogen pressure is only 5%. Additionally, the higher the hydrogen partial pressure, the higher the oxygen removal ratio. Needless to say, the hydrogen content in the powder would increase with the increase of hydrogen partial pressure. However, as pointed out earlier, the hydrogen in the powder can be easily removed when desired. Figure 3 shows the morphology of the Ti powder before and after deoxygenation, showing roughly spheroidal particles in both samples.



**Figure 3.** Morphology of Ti powder before (a) and after (b) deoxygenation.

Hydrogen contents in the samples of this study ranged from 1.09 to 1.62 wt%, depending on the partial pressure. This range is significantly higher than those thermodynamically calculated in Figure 2a. The range of H wt% in Figure 2a is limited due to the available phase diagram data. However, the experimental results are consistent with the predictions of Figure 2a, i.e., the oxygen potential in  $\text{Ti-O}$  solid solution increases with the increase of the hydrogen or oxygen contents. Furthermore, during reactions between  $\text{Ti-O}$  with Mg, the oxygen potential in  $\text{Ti}(\text{H})_x(\text{O})_y$  will equilibrate with that in  $\text{MgO}$  at a given set of  $x$  and  $y$  values, i.e., a combination of oxygen and hydrogen content. At equilibrium, the higher the hydrogen content is (higher  $x$ ), the lower the oxygen content (lower  $y$ ). Therefore, the capacity of Mg for deoxygenating Ti increases as the hydrogen content increases.

It is further noted here that a number of other process parameters also affect the deoxygenation of Ti using Mg, including temperature, time, and particle size, which is shown in Supplementary Figure 8b–d. When reduced at a relatively low temperature that is lower than the melting point of Mg metal

(649 °C), a longer dwell time of 24 h was applied. Otherwise, a shorter dwell time of 12 h was used. It was demonstrated that oxygen content as low as 0.05 wt% can be achieved at temperatures between 670 and 750 °C. However, when the temperature was increased to 800 °C, the sample that was held for 1 h at the temperature had lower oxygen content than the one held for 12 h, which is attributed to the limited evaporation loss of Mg in a shorter time. Thermodynamically, the oxygen content in titanium is a function of the reaction temperature. The lower the reaction temperature, the lower the oxygen content in titanium. However, using lower temperatures will inevitably encounter kinetic hurdles. Thus, it is reasonable to assume that there is an optimum temperature at which one can not only maximize the potentials afforded by the thermodynamics but also improve the kinetic rate of reduction. Overall, the kinetic rate of the reactions in this research was rapid in practice sense, which can at least be partially credited to the use of hydrogen and the use of MgCl<sub>2</sub>-bearing salt.

Supplementary Figure 8d further shows that the oxygen content is also a function of the particle size. The finer the particles, the higher the oxygen content in the powder. This is expected for Ti powder because finer powders have high specific surface areas. However, it is worth noting that the oxygen content of the powder with <20 μm particle size still has a oxygen content <0.1 wt%, which is remarkable for Ti powders, far exceeding the industry specifications for Ti powder.

The effect of hydrogen on the reaction between Ti-O and Mg can also be partially affected by the phase transformations induced by the addition of hydrogen. Hydrogen is known to be a β phase stabilizer.<sup>16</sup> Figure 1a also shows that β-Ti(O) is less stable than α-Ti(O). Moreover, the diffusion coefficient of oxygen in Ti is higher in β than in α,<sup>17</sup> which may enhance the kinetics of the reaction.

To the best of our knowledge, this is the first demonstration that Mg can be effectively used to deoxygenate Ti. Mg was not considered as an agent for deoxygenating Ti because Ti(O) solid solutions can be more stable than MgO at relatively low oxygen levels. Calcium has been reportedly used in the industry to deoxygenate Ti or Ti alloys. However, the processes using Ca require significantly higher temperatures which can cause many undesirable issues, such as contamination from reactors, and sintering of particles which are especially problematic for making spherical powders for additive manufacturing. Therefore, the capability to deoxygenate Ti using Mg represents a significant breakthrough technology with broad implications for the practical use of titanium and other reactive metals including Zr, Hf, and V.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00845.

Experimental details and data (PDF)

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### Notes

The authors declare no competing financial interest.

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