

# Calciothermic Reduction of $TiO_2$ : A Diagrammatic Assessment of the Thermodynamic Limit of Deoxidation

K.T. Jacob and Sapna Gupta

*Calciothermic reduction of  $TiO_2$  provides a potentially low-cost route to titanium production. Presented in this article is a suitably designed diagram, useful for assessing the degree of reduction of  $TiO_2$  and residual oxygen contamination in metal as a function of reduction temperature and other process parameters. The oxygen chemical potential diagram à la Ellingham–Richardson–Jeffes is useful for visualization of the thermodynamics of reduction reactions at high temperatures. Although traditionally the diagram depicts oxygen potentials corresponding to the oxidation of different metals to their corresponding oxides or of lower oxides to higher oxides, oxygen potentials associated with solution phases at constant composition can be readily superimposed. The usefulness of the diagram for an insightful analysis of calciothermic reduction, either direct or through an electrochemical process, is discussed. Identified are possible process variations, modeling and optimization strategies.*

## INTRODUCTION

Titanium is usually extracted by the Kroll process<sup>1</sup> in which titanium tetrachloride is reduced by magnesium to form titanium sponge and magnesium chloride. This is an expensive and time-consuming process, which makes titanium a costly metal. Although titanium and its alloys have very useful properties such as high strength, low density and very good corrosion resistance, their application is restricted by the high cost of production. A process for direct metallothermic reduction of  $TiO_2$  can eliminate the chlorination step and reduce cost. Electroreduction is a very simple technique in which the oxide to be reduced is made the cath-

ode in a fused salt of an alkaline-earth chloride. By applying a voltage below the decomposition potential of the salt at temperatures in the vicinity of 1,200 K, the oxide is reduced to metal through several intermediate steps. Depending on the voltage employed, the calcium metal for reduction is generated in the vicinity of the cathode either in the pure form or in the dissolved state

at low activity in the fused salt. In the laboratory, this technique has been applied to a large number of metal oxides, including titanium dioxide, by several investigators.<sup>2-7</sup> A number of different calciothermic and electroreduction processes have been suggested, differing in process details and mechanisms of reduction. An interesting aspect of the electrochemical process is that when an intimate mixture of oxides is used as the cathode, the metals form an alloy of uniform composition.<sup>8</sup> This article assesses the thermodynamic limit of reduction titanium oxides by calcium metal and the residual dissolved oxygen in the final product in a pictorial fashion. Similar modified oxygen potential diagrams involving solution phases have been used earlier in the analysis of refining and deoxidation of liquid copper.<sup>9,10</sup>

## CONSTRUCTION OF OXYGEN POTENTIAL DIAGRAM

The chemical potential of oxygen ( $\Delta\mu_{O_2} = RT \ln P_{O_2}$ ) is plotted in Figure 1 as a function of temperature in the range of 800 K to 1,400 K for different single- and two-phase regions of the system Ti-O. An enlarged view of the low oxygen potential region is shown in Figure 2a. The data required for construction of the diagrams are obtained from the literature. Older thermodynamic data for compounds and solid solutions in the system Ti-O have been assessed by O. Kubaschewski et al.<sup>11</sup> New information on Magneli phases ( $Ti_nO_{2n-1}$ ,  $28 \geq n \geq 4$ ) and thermodynamics of nonstoichiometric  $TiO_{2-x}$  is provided by K.T. Jacob et al.<sup>12</sup> Assessed thermodynamic data for several oxides of titanium are given in the NIST-JANAF Thermochemical

### How would you...

#### ...describe the overall significance of this paper?

*Direct reduction of titania provides a resource and cost-effective route for the production of titanium metal. This paper examines the limit of deoxidation that can be achieved using different deoxidants as a function of temperature. Calcium metal is the best reductant and can be produced in-situ by electrolysis of  $CaCl_2$ .*

#### ...describe this work to a materials science and engineering professional with no experience in your technical specialty?

*Diagrammatic representation of thermodynamic potentials is useful for comprehensive visualization of different process options. Presented in this paper is an oxygen potential diagram based on the best thermodynamic information now available. The diagram is useful for identifying the best conditions for calciothermic reduction of titania.*

#### ...describe this work to a layperson?

*The feasibility of new pyrometallurgical processes can be assessed by computation and modeling studies. The effect of process variables on product quality can be readily explored. Thermodynamics provides a useful tool for assessing the feasibility of new processes at high temperatures.*

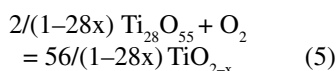
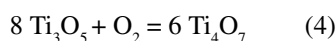
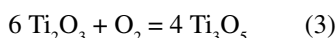
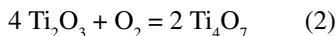
Tables.<sup>13</sup> More recently, M. Cancarevic et al.<sup>14</sup> have provided a thermodynamic assessment of the system Ti-O based on all available data using the CALPHAD method.

Single-phase compositions shown in the diagram correspond to Ti-O solid solutions with mole fractions of oxygen  $X_o = 0.0001, 0.001, 0.01, 0.1, 0.26,$  and  $0.5$  (TiO), and  $\text{TiO}_{1.999}$  (rutile). The chemical potentials of oxygen at constant compositions are plotted in the figure. The oxygen potential plots for  $X_o = 0.0001, 0.001$  and  $0.01$  show steps corresponding to  $\alpha \rightarrow \beta$  transformation. The oxygen potential in the  $\beta$ -solid solution phase is higher than in the  $\alpha$ -phase for the same oxygen concentration. The oxygen dissolution reaction can be written as:



where  $\underline{\text{O}}_{\text{Ti}}$  represents oxygen dissolved in titanium. The slope of the lines representing the oxygen potential of solid solution phases decreases with decreasing oxygen concentration because of the increasing partial entropy of oxygen.

The diagram also displays chemical potentials of two-phase fields  $\text{Ti}_2\text{O}_3 + \text{Ti}_4\text{O}_7$ ,  $\text{Ti}_2\text{O}_3 + \text{Ti}_3\text{O}_5$ ,  $\text{Ti}_3\text{O}_5 + \text{Ti}_4\text{O}_7$ , and  $\text{Ti}_n\text{O}_{2n-1}$  ( $\text{Ti}_{28}\text{O}_{54}$ ) +  $\text{TiO}_{2-x}$ . Magneli phases are represented by the general formula  $\text{Ti}_n\text{O}_{2n-1}$ . Jacob et al.<sup>12</sup> have estimated the highest value of  $n$  in the Magneli phases to be 28. Oxygen potentials of the two-phase regions are defined by the reactions:



Data for  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$ , and  $\text{Ti}_4\text{O}_7$  for Reactions 2 to 4 are taken from NIST-JANAF tables<sup>13</sup> and for Reaction 5 from Jacob et al.<sup>12</sup> Since  $\text{Ti}_3\text{O}_5$  is unstable below 910 K, the lines corresponding to  $\text{Ti}_2\text{O}_3 + \text{Ti}_3\text{O}_5$  and  $\text{Ti}_3\text{O}_5 + \text{Ti}_4\text{O}_7$  equilibria converge at this temperature;  $\text{Ti}_2\text{O}_3$  and  $\text{Ti}_4\text{O}_7$  become the stable phases in equilibrium at lower temperatures. Although there are several other two-phase fields in

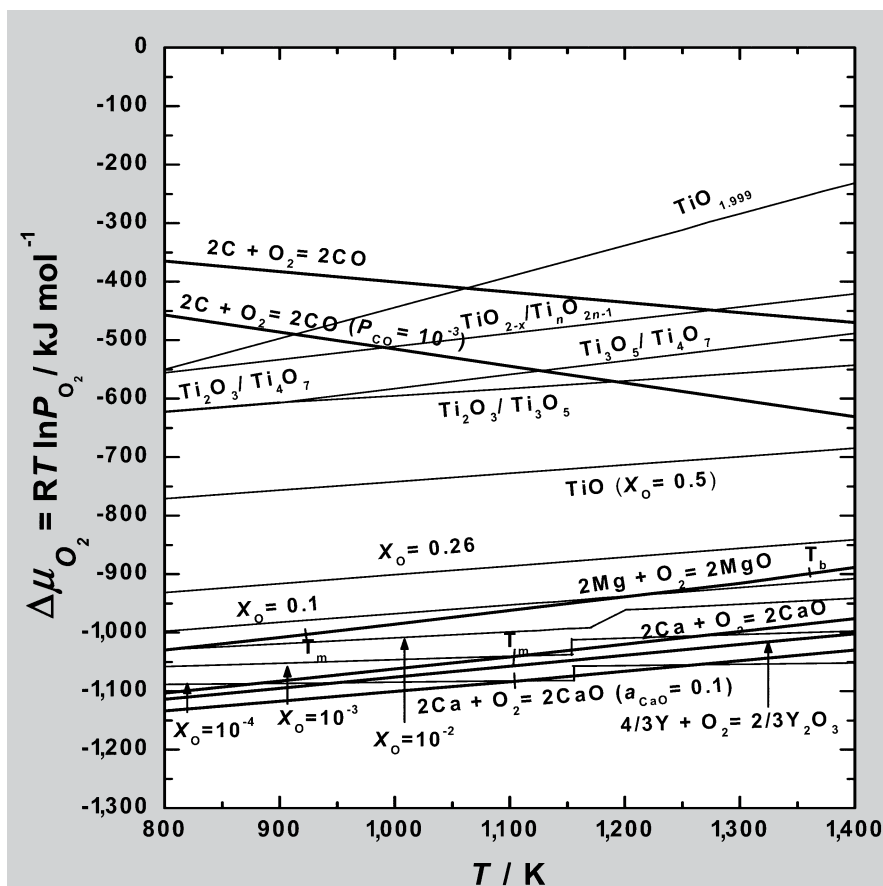
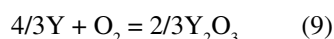
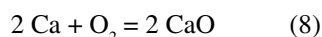
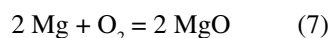
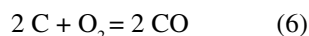


Figure 1. An oxygen potential diagram à la Ellingham–Richardson–Jeffes showing chemical potentials of interest to the calciothermic reduction of  $\text{TiO}_2$ .

the system Ti-O for which oxygen potentials are known, they are not shown in the diagram to avoid clutter. The representative lines shown in the figure indicate the wide oxygen potential range through which rutile passes during its reduction to metal.

Reduction potentials of C, Mg, Ca, and Y can be assessed by plotting the oxygen potentials corresponding to their oxidation according to the reactions:



Data for the four oxides are taken from compilations of thermodynamic data.<sup>13,15</sup> The line corresponding to C-CO equilibrium has negative slope because the gaseous oxide is associated with high entropy compared to solid oxides of magnesium, calcium, and yttrium. At any desired temperature

the residual oxygen content of titanium obtained by using a metallic reductant (M) can be estimated from the position of oxygen potential lines for the Ti-O solid solutions immediately above and below the line corresponding to the line for the reductant ( $\text{M} + \text{M}_m\text{O}_n$  equilibria). The interpolation between any two adjacent oxygen potential lines for Ti-O solid solutions is logarithmic. For very dilute solutions of oxygen in titanium, the activity coefficient of oxygen may be taken as a temperature-dependent constant for each phase. For interpolation of oxygen concentration between lines for dilute solutions of oxygen shown in Figure 2a, a nomogram is provided in Figure 2b. Distances for interpolation at the desired temperature can be transposed from Figure 2b to Figure 2a.

## RESULTS AND DISCUSSION

As shown in Figure 1, carbon is not a sufficiently powerful reductant for  $\text{TiO}_2$ . The reducing power of carbon increases with temperature and can be further enhanced by lowering the

partial pressure of CO in the reaction chamber. A line corresponding to partial pressure of CO,  $(P_{\text{CO}}/P^{\circ}) = 10^{-3}$ , is shown in Figure 1 for illustration. The standard atmospheric pressure is denoted by  $P^{\circ}$ . Carbon will combine with titanium to form TiC when reduction proceeds beyond  $\text{Ti}_2\text{O}_3$ . Hence carbon can at best be used only for partial reduction of  $\text{TiO}_2$  to  $\text{Ti}_2\text{O}_3$  (i.e. for the removal of 25% of oxygen present in  $\text{TiO}_2$ ). Partial reduction by carbon can reduce the quantity of expensive metallic reductant required, but the saving is offset by the cost of an additional process step.

Magnesium, calcium, and yttrium can reduce titanium dioxide to titanium. Although from a thermodynamic point of view yttrium appears to be the best reductant, it is not attractive from

a kinetic viewpoint. Because yttrium is a solid at reduction temperatures, modeling studies show that the reaction is limited by the small contact area between the reductant and  $\text{TiO}_2$ . The identification of yttria as the best mold face-coat material for titanium casting is based on the position of the oxygen potential line for  $\text{Y}/\text{Y}_2\text{O}_3$  equilibrium in Figure 2. Titanium metal will not pick up significant oxygen from yttria. Modeling studies show that the oxygen contamination on the surface of the casting is in the range of 10% to 16% of the equilibrium value because of the rapid cooling and short reaction time.

The oxygen content of titanium metal produced by Mg reduction is significantly higher than in the metal resulting from Ca and Y reduction. The standard Gibbs free energy of formation of CaO

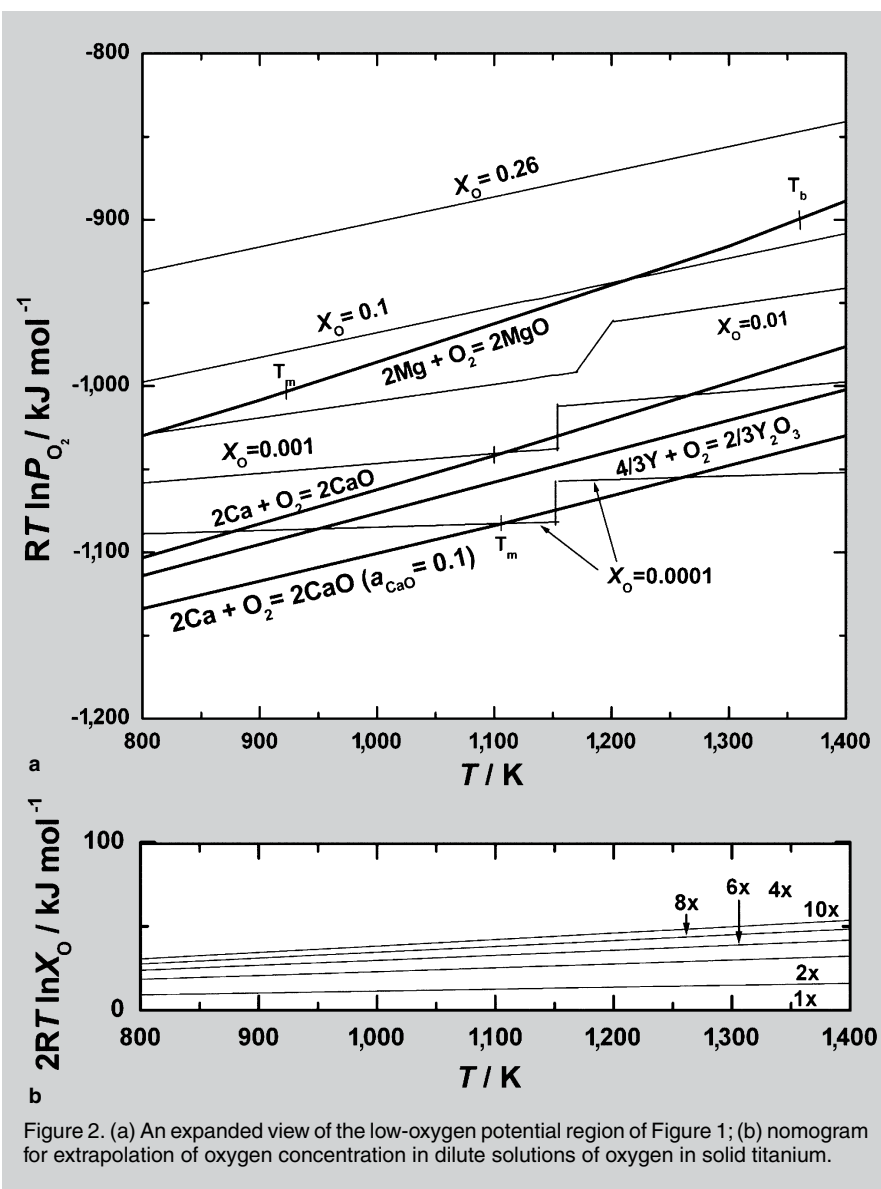
is more negative than that of MgO. Thus, Ca is the preferred reductant from a technical point of view. However, Mg can be used for preliminary reduction of  $\text{TiO}_2$  and Ca for the final reduction if economics dictates such a preference. Further complication with the use of Mg as the reductant is the solid solubility of Mg in Ti metal (2.4 at.% in  $\beta$ -Ti and 1.6 at.% in  $\alpha$ -Ti at 1,135 K), which necessitates further refining for the removal of Mg. In contrast, Ca has negligible solubility in Ti.

Even when Ca is used as the reductant, the oxygen content of Ti after reduction at 1,100 K would be around 1,000 at. ppm ( $\sim 330$  mass ppm) when the product CaO is present at unit activity. Because of the difference in slopes of the lines representing the oxygen potential of the solid solutions and the Ca + CaO line, deoxidation is less effective at higher temperatures for both  $\alpha$  and  $\beta$  solid solutions. However, the higher activity coefficient of oxygen in the  $\beta$  solid solution ensures more favorable deoxidation in the stability range of the  $\beta$  phase.

Lowering the concentration or activity of CaO in molten  $\text{CaCl}_2$  is an efficient method for removing more oxygen. For example by reducing the activity of CaO to 0.1 by dissolving it in a halide flux, almost an order of magnitude reduction in oxygen concentration can be achieved. This is the thermodynamic rationale for the electrochemical deoxidation of titanium wires containing 4,200 at. ppm oxygen to 300 at. ppm by T.H. Okabe et al.<sup>16</sup> at 1,223 K. Similarly, the calcium halide flux deoxidation method suggested by T.H. Okabe et al.<sup>17</sup> is also based on this principle. Oxygen was removed from titanium up to 60 to 180 at. ppm by calcium metal dissolved in  $\text{CaCl}_2$ .<sup>17</sup> The oxide formed also dissolves in the fused salt. By using a large concentration of fused salt in comparison to the amount of oxygen to be removed from titanium, the activity of CaO can be maintained at a very low value. This facilitates effective deoxidation.

## CONCLUSION

Oxygen chemical potentials associated with reduction of titanium oxides and deoxidation of titanium metal are displayed diagrammatically as a func-



tion of temperature. The degree of de-oxidation that can be achieved by using different metallic reductants under different conditions can be quantitatively assessed using the diagram.

Recently proposed single-stage electroreduction processes for reducing  $\text{TiO}_2$  to metal essentially involve calciothermic reduction of  $\text{TiO}_2$  at the cathode. The reductant Ca may be present at low activity as dissolved species in  $\text{CaCl}_2$  melt or as a separate phase depending upon the voltage employed for electrolysis. Hence the diagram presented is useful for analyzing both direct metallothermic reduction of  $\text{TiO}_2$  as well as electroreduction of  $\text{TiO}_2$  using the fused salt process.

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