

Phase diagram of the system Ca–Ti–O at 1200 K

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Abstract. Phase relations in the system Ca–Ti–O have been established by equilibration of several samples at 1200 K for prolonged periods and identification of phases in quenched samples by optical and scanning electron microscopy, XRD and EDS. Samples representing 20 compositions in the ternary system were analyzed. There was negligible solid solubility of Ca in the phases along the binary Ti–O, and of Ti in CaO. Four ternary oxides were identified: CaTiO_3 , $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ and $\text{Ca}_3\text{Ti}_2\text{O}_7$ containing tetravalent titanium, and CaTi_2O_4 containing trivalent titanium. Tie-lines link calcium titanite (CaTi_2O_4) with the three calcium titanates (CaTiO_3 , $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ and $\text{Ca}_3\text{Ti}_2\text{O}_7$), CaO, oxygen excess $\text{TiO}_{1+\delta}$ and stoichiometric TiO. Tie-lines connect CaTiO_3 with TiO_{2-x} , Magneli phases $\text{Ti}_n\text{O}_{2n-1}$ ($28 \geq n \geq 4$), Ti_3O_5 , Ti_2O_3 and $\text{TiO}_{1+\delta}$. CaO was found to coexist with TiO, and Ti–O solid solutions α and β . The phase diagram is useful for understanding the mechanisms and kinetics of direct calciothermic reduction of TiO_2 to metal and electrochemical reduction of TiO_2 using graphite anode and molten CaCl_2 electrolyte.

Keywords. Phase diagram; system Ca–Ti–O; calciothermic reduction of TiO_2 ; reaction pathway.

1. Introduction

Although titanium and its alloys have excellent properties such as high strength, low density and very good corrosion resistance, their use is restricted by high cost. Titanium occurs in nature in the form of oxides, mainly as rutile and ilmenite. Pure titanium dioxide (TiO_2), extracted from the ores, is converted to titanium tetrachloride (TiCl_4) by carbo-chlorination. Titanium metal is commercially produced by the Kroll process in which titanium tetrachloride is reduced by magnesium to form titanium sponge and magnesium chloride. The process is batch type and labor intensive. The cost of titanium metal can be considerably lowered if TiO_2 can be directly reduced either chemically or electrochemically to metal, eliminating the chlorination step. In the reduction process several lower oxides of titanium and Ti–O solid solutions are encountered. Calcium, a more powerful reductant than magnesium, is required for the reduction of TiO_2 to metal. An alternative to direct reduction is electrodeoxidation where TiO_2 is made the cathode, graphite is used as the anode and CaCl_2 is used as the electrolyte (Oki and Inoue 1967; Deura *et al* 1992; Chen *et al* 2000). By applying a voltage below the decomposition potential of the salt at temperatures in the vicinity of 1200 K, the oxide is reduced to metal through several intermediate steps, and oxides of carbon are released at the anode. When using calcium metal for direct reduction or CaCl_2

as the fused electrolyte in the electrochemical reduction, mixed oxides of calcium and titanium can also form as intermediate products. Phase diagram for the ternary system Ca–Ti–O is useful for understanding the reaction mechanism.

Ye and Rosenqvist (1991) investigated phase relations in the system Ti– TiO_2 –CaO at 1673 and 1873 K. Two oxide solid solution series, designated as CaTiO_{1+x} ($0.8 \leq x \leq 2$) and $\text{Ca}_4\text{Ti}_3\text{O}_{4+3x}$ ($1 \leq x \leq 2$), were identified. Since these solid solutions originate from the two calcium titanates, CaTiO_3 and $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, and extend into the ternary with constant ratio of cations and reduction in oxygen content, they are probably better designated as $\text{CaTiO}_{3-\delta}$ and $\text{Ca}_4\text{Ti}_3\text{O}_{10-\delta}$. The two solid solutions are connected by tie-lines. The oxides phases along the binary Ti– TiO_2 were found to coexist with the solid solution, $\text{CaTiO}_{3-\delta}$ ($0 \leq \delta \leq 1.003$), at 1673 K. A liquid phase region was found to separate the binary oxides of titanium from the $\text{CaTiO}_{3-\delta}$ solid solution at 1873 K. There are several points of concern regarding the phase diagram proposed by Ye and Rosenqvist (1991). They report only two calcium titanates along the binary join CaO– TiO_2 . Phase equilibria and thermodynamic properties of the system CaO– TiO_2 have been studied extensively and the existence of three stable ternary oxides, CaTiO_3 , $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, and $\text{Ca}_3\text{Ti}_2\text{O}_7$, has been established in the literature (Roth 1958; Jongejan and Wilkins 1970; Jacob and Abraham 2009). The three inter-oxide compounds can be visualized as members of the Ruddlesden–Popper series having the general formula, $\text{Ca}_{n+1}\text{Ti}_n\text{O}_{3n+1}$, with $n = 2$ for $\text{Ca}_3\text{Ti}_2\text{O}_7$, $n = 3$ for $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, and $n = \infty$ for

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CaTiO_3 . The orthorhombic structure of CaTiO_3 (space group, $Pcmm$) results from the tilting of TiO_6 octahedra with respect to the cubic perovskite axes. In $\text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, excess Ca cations are structurally accommodated by regular insertion of distorted NaCl-type layers between perovskite blocks; structure of $\text{Ca}_3\text{Ti}_2\text{O}_7$ consists of double perovskite layers interleaved with CaO, while $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ has triple perovskite layers interleaved with CaO. The two solid solutions with constant cationic ratios and very large oxygen deficiency suggested by Ye and Rosenqvist (1991) are inconsistent with crystal chemistry of the end member calcium titanates.

Single crystals of the ternary oxide, CaTi_2O_4 , containing trivalent titanium ions were grown by Rogge *et al* (1998) by reduction of CaTiO_3 with Ti metal powder in a CaCl_2 flux under nitrogen at 1273 K. The structure of CaTi_2O_4 is pseudo-brookite-type. CaTi_2O_4 crystallizes in the orthorhombic space group $Bbmm$; $a = 0.9718$ nm, $b = 0.9960$ nm and $c = 0.3140$ nm with four formula units per unit cell (Rogge *et al* 1998). The structure is built up from edge-sharing chains of TiO_6 octahedra that condense to form one-dimensional tunnels in which the calcium atoms are located. This compound does not appear on the phase diagram of Ye and Rosenqvist (1991). Hence the phase diagram for the system Ca–Ti–O was revisited at 1200 K.

2. Experimental

2.1 Materials

The starting materials for the preparation of calcium titanates, CaTiO_3 , $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, and $\text{Ca}_3\text{Ti}_2\text{O}_7$ were CaCO_3 and TiO_2 (rutile type) of purity >99.99%. A reactive form of CaO, obtained by decomposition of CaCO_3 in vacuum ($p \approx 10$ Pa) at 1100 K, was used in the preparation of ternary oxides. The CaO was handled carefully to prevent the adsorption of CO_2 and H_2O from ambient air. The rutile form of TiO_2 was dried at 573 K before use. Calcium titanates were prepared by heating mixtures of CaO and TiO_2 in the appropriate molar ratio contained in platinum crucibles at 1773 K for 160 ks in air with three intermediate grindings. The mixtures of component oxides were pelletized at 100 MPa using a steel die before heating. Completion of the reaction was confirmed by powder X-ray diffraction (XRD) analysis of the product. All the three titanates had the orthorhombic structure: CaTiO_3 with cell parameters $a = 0.5441$ nm, $b = 0.7642$ nm, and $c = 0.5380$ nm; $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ with cell parameters $a = 0.5408$ nm, $b = 2.7143$ nm, and $c = 0.5434$ nm; $\text{Ca}_3\text{Ti}_2\text{O}_7$ with cell parameters $a = 0.5417$ nm, $b = 1.9517$ nm, and $c = 0.5423$ nm.

The Ti metal powder used in this study was of 99.99% purity while Ca metal was of 99.8% purity. The lower oxides of titanium, TiO and Ti_2O_3 , were prepared by

heating compacted powder mixtures Ti and TiO_2 in the appropriate ratio under flowing argon gas. Argon gas of 99.999% purity was further dried by passing through columns of anhydrous silica gel, magnesium perchlorate and diphosphorus pentoxide and deoxidized by passage through titanium sponge at 1123 K prior to use.

2.2 Equilibration experiments

The phase relations in the system Ca–Ti–O were explored by equilibrating 22 samples representing 20 predetermined compositions at 1200 K, followed by quenching in liquid nitrogen or chilled Hg and phase identification. Different compositions were equilibrated for a total period of ~14 days. The samples were quenched, ground to –325 mesh, and repelletized thrice during this period. The phase compositions of the samples were found to be unaltered by further heat treatments. The overall compositions of the samples used are listed in table 1 and shown by cross (X) marks in figure 1(a). In some cases samples of the same overall composition were made using different starting materials.

For equilibrating the samples, two configurations were used. Mixtures containing CaO and TiO_2 were equilibrated at 1200 K in pure oxygen at standard pressure $p_{\text{O}_2}/p^\circ = 1$ using an apparatus described earlier (Jacob and Mathews 1991). The samples were held in platinum crucibles. The pellets were kept on a sacrificial disk of the same composition to avoid contamination by the crucible. The mass of each pellet was determined before and after equilibration. Mixtures containing metals or oxides containing titanium in lower valence states were equilibrated in closed iron crucibles. The mixtures were prepared in an inert atmosphere glove box. In samples containing metallic Ca, tiny pieces of the metal were buried in the pellet. Because of the significant vapour pressure of Ca at 1200 K, the metal equilibrates with other materials in the pellet via the gas phase. The iron crucibles were suspended in an alumina tube closed at both ends and heated under flowing high purity Ar gas. Titanium internal getters were placed in the path of Ar gas flowing at 6 ml/s to scavenge residual oxygen and oxygen-bearing species that desorbed from the alumina tube during heating. The oxygen partial pressure in the inert gas was less than $p_{\text{O}_2}/p^\circ = 10^{-17}$. After equilibration at 1200 K, the samples were quenched. There was no interaction between the iron crucibles and the various oxides phases. However, there was some evidence of localized reaction between Ti metal particles in the sacrificial pellet and the crucible material. To avoid possible effects of this reaction on phase relations in the ternary system Ca–Ti–O, a thin layer was removed from the outer surface of the pellets before examination. The phases present in the quenched samples were identified by optical and scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and

Table 1. Starting materials, average composition of the sample and phase identified after equilibration in the system Ca–Ti–O at 1200 K.

Sample number	Starting materials	Average composition of samples			Phases identified	Techniques used
		X_{Ca}	X_{Ti}	X_O		
1	Ca + Ti ₂ O ₃	0.50	0.20	0.30	Ca + Ti(β) + CaO	XRD, SEM, EDS
2	Ca + TiO	0.40	0.30	0.30	Ca + Ti(β) + CaO	XRD, SEM, EDS
3	Ca + Ti + Ti ₂ O ₃	0.30	0.40	0.30	Ti(β) + CaO	XRD
4	Ca + Ti + Ti ₂ O ₃	0.28	0.42	0.30	Ti(β) + CaO	XRD
5	Ca + Ti + Ti ₂ O ₃	0.20	0.50	0.30	Ti(β) + Ti(α) + CaO	XRD, SEM, EDS
6	Ca + Ti + Ti ₂ O ₃	0.20	0.40	0.40	Ti(α) + CaO	XRD
7	Ca + Ti + Ti ₂ O ₃	0.16	0.40	0.44	Ti(α) + TiO + CaO	XRD, SEM, EDS
8	CaO + Ti + TiO ₂	0.30	0.20	0.50	TiO + CaO	XRD, SEM, EDS
9	CaO + Ti + Ti ₂ O ₃	0.30	0.20	0.50	TiO + CaO	XRD, SEM, EDS
10	CaO + Ti + TiO ₂	0.20	0.27	0.53	TiO + CaO + CaTi ₂ O ₄	XRD, SEM, EDS
11	CaO + TiO ₂	0.35	0.10	0.55	CaO + Ca ₃ Ti ₂ O ₇	XRD
12	CaO + Ti + TiO ₂	0.29	0.16	0.55	CaO + Ca ₃ Ti ₂ O ₇ + CaTi ₂ O ₄	XRD, SEM, EDS
13	CaO + Ti + TiO ₂	0.25	0.20	0.55	CaO + CaTi ₂ O ₄	XRD
14	CaO + Ti + TiO ₂	0.10	0.35	0.55	CaTi ₂ O ₄ + TiO	XRD, SEM, EDS
15	CaO + Ti + TiO ₂	0.13	0.30	0.57	CaTi ₂ O ₄ + TiO _{1+x}	XRD, SEM, EDS
16	CaO + Ti + TiO ₂	0.10	0.33	0.57	CaTi ₂ O ₄ + TiO _{1+x} + CaTiO ₃	XRD, SEM, EDS
17	CaO + Ti + TiO ₂	0.21	0.21	0.58	Ca ₃ Ti ₂ O ₇ + Ca ₄ Ti ₃ O ₁₀ + CaTi ₂ O ₄	XRD, SEM, EDS
18	CaO + Ti + TiO ₂	0.21	0.20	0.59	Ca ₄ Ti ₃ O ₁₀ + CaTiO ₃ + CaTi ₂ O ₄	XRD, SEM, EDS
19	CaO + Ti + TiO ₂	0.10	0.30	0.60	CaTiO ₃ + Ti ₂ O ₃	XRD, SEM, EDS
20	CaO + Ti + TiO ₂	0.10	0.29	0.61	CaTiO ₃ + Ti ₂ O ₃ + Ti ₃ O ₅	XRD, SEM, EDS
21	CaO + TiO ₂	0.125	0.25	0.625	CaTiO ₃ + TiO ₂	XRD
22	TiO ₂ + Ca ₄ Ti ₃ O ₁₀	0.125	0.25	0.625	CaTiO ₃ + TiO ₂	XRD

energy dispersive spectroscopy (EDS). Pure TiO₂ and CaTiO₃ were used as standards for EDS.

To determine the limit of deoxidation of Ti metal by calcium, a thin foil of Ti containing 0.35 atom percent O fixed to a iron frame was inserted into liquid calcium and equilibrated at 1200 K for 3 days. The foil was withdrawn after equilibration and analysed for oxygen using inert gas fusion–infrared absorption spectroscopy (LECO).

3. Results

The starting chemicals used in the preparation of the samples, their average composition, and phases identified after equilibration at 1200 K are listed in table 1. An isothermal section of the phase diagram for the system Ca–Ti–O composed from the results of this study is shown in figure 1(a). An expanded view of the diagram between $X_O = 0.5$ and $X_O = 0.73$ is displayed in figure 1(b). The average composition of the samples examined in this study is shown by cross (X) marks on the figure. Four ternary oxides without detectable range were identified: CaTiO₃, Ca₄Ti₃O₁₀ and Ca₃Ti₂O₇ containing tetravalent titanium, and CaTi₂O₄ containing trivalent titanium. There was no evidence of CaTiO_{3- δ} and Ca₄Ti₃O_{10- δ} solid solutions suggested by Ye and Rosenqvist (1991). Oxygen vacancies are common in perovskite oxides. When the vacancy concentration is large, vacancy ordering is expected. The best known example of perovskite oxide

with ordered anion vacancies is the brownmillerite structure (space group *Pnma*) exhibited by Ca₂Fe₂O₅ (Smyth 1993). One-sixth of the oxygen ions are absent and the oxygen vacancies are ordered in alternate (001) FeO₂ planes of the cubic structure such that alternate [110] rows of oxide ions are missing. A small oxygen deficiency may exist in CaTiO₃, but it was below the detection limit of the characterization techniques used in this study. Certainly oxygen deficiency of the order suggested by Ye and Rosenqvist (1991), CaTiO_{3- δ} ($0 \leq \delta \leq 1.2$), does not exist. Perovskite structure would be destabilized at the high oxygen vacancy concentrations.

Metals Ca and Ti are immiscible. Metal Ca is liquid and β form of Ti metal with *bcc* structure is the stable phase at 1200 K. Increasing the oxygen content of the biphasic alloy results in the formation of CaO and generation of a three-phase region Ca(l) + Ti(β) + CaO. Application of the phase rule indicates that at constant temperature and pressure three-phase equilibrium in any ternary system is associated with zero degree of freedom. Consequently, activities of all components and species are constant in three-phase regions. Oxygen solubility in liquid Ca and β -Ti is limited at 1200 K. Dissolved oxygen stabilizes the low-temperature α phase of Ti. The stability range of α Ti–O solid solution is $0.04 \leq X_O \leq 0.33$, with negligible solubility of Ca. The α Ti–O solid solutions (α Ti_{ss}) are in equilibrium with CaO. The α + β two-phase field along the Ti–O binary extends from $X_O = 0.005$ to $X_O = 0.04$. The α and β phases in equilibrium with CaO generates a three-phase region α -Ti_{ss} + β -Ti_{ss} + CaO. The

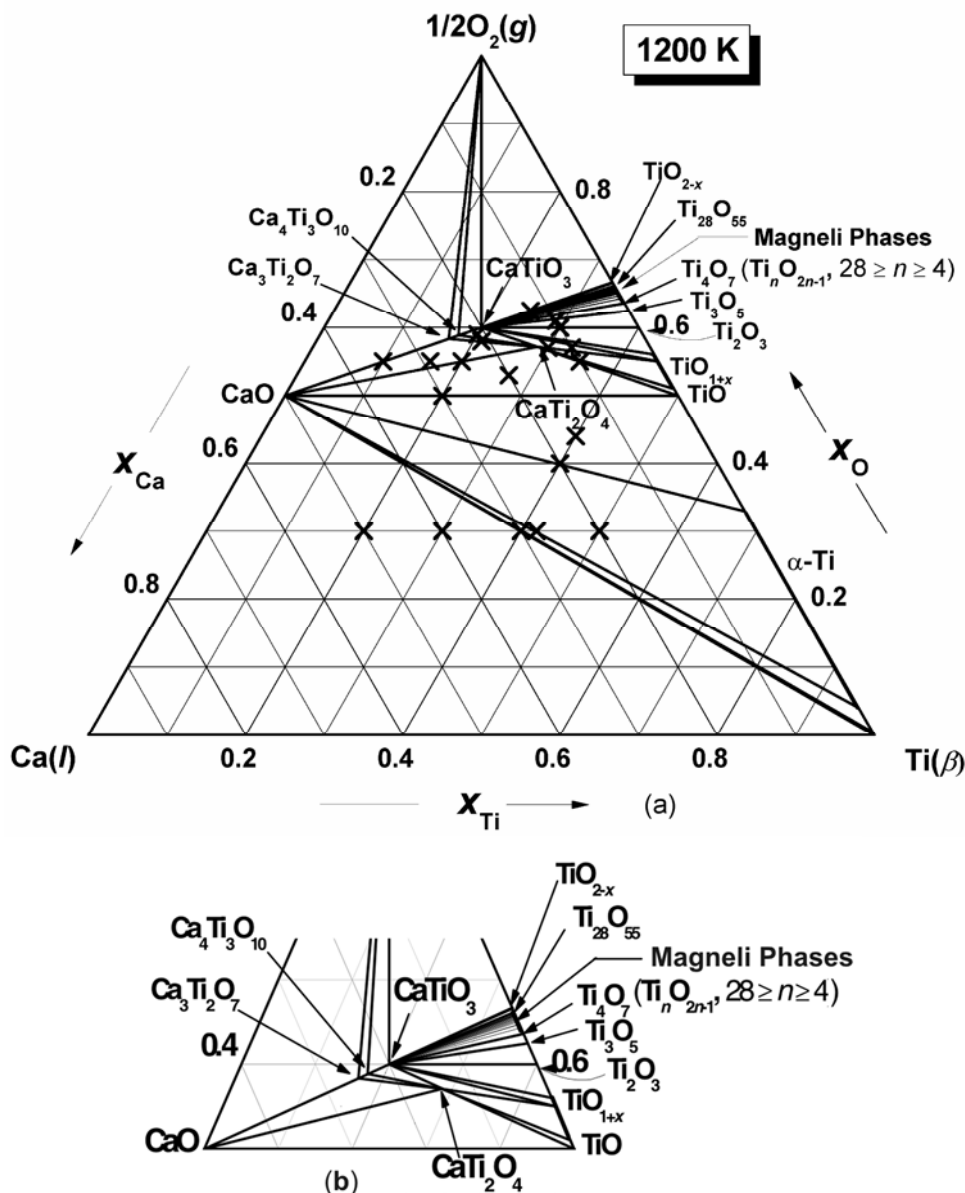


Figure 1. (a) An isothermal section of the phase diagram for the system Ca–Ti–O at 1200 K composed from the results of this study and (b) an expanded view of the diagram between $X_{\text{O}} = 0.5$ and $X_{\text{O}} = 0.73$.

titanium foil containing 0.35 atom percent O was deoxidized by calcium metal; the residual oxygen content was 0.084 (± 0.013). This represents the oxygen concentration of $\beta\text{-Ti}_{\text{ss}}$ in equilibrium with Ca and CaO. Measurements of Okabe *et al* (1991) suggest a slightly higher value of 0.11 atom percent oxygen in $\beta\text{-Ti}_{\text{ss}}$ in equilibrium with Ca and CaO.

On increasing the oxygen content along the binary Ti–O, the phase that formed after $\alpha\text{-Ti}_{\text{ss}}$ is an almost stoichiometric TiO. There was no evidence of the compound Ti_3O_2 reported in the literature. There was no solid solubility or compounds along the join CaO–TiO as indicated by the analysis of a sample on this join. A three-phase region $\alpha\text{-Ti}_{\text{ss}} + \text{TiO} + \text{CaO}$ was identified by

analysis of a sample in this triangle, just below CaO–TiO join.

On increasing the oxygen content beyond the compound TiO along the binary Ti–O, a nonstoichiometric TiO_{1+x} phase was observed between $X_{\text{O}} = 0.51$ and $X_{\text{O}} = 0.56$. The TiO_{1+x} phase in the composition range $0.51 \leq X_{\text{O}} \leq 0.55$ is in equilibrium with calcium titanite CaTi_2O_4 . Below this two-phase field lies the narrow three-phase region $\text{TiO} + \text{TiO}_{1+x} + \text{CaTi}_2\text{O}_4$ and the larger three-phase field $\text{TiO} + \text{CaO} + \text{CaTi}_2\text{O}_4$. The TiO_{1+x} phase in the composition range $0.55 \leq X_{\text{O}} \leq 0.56$ is in equilibrium with calcium titanate CaTiO_3 .

All the higher oxides of titanium, Ti_2O_3 , Ti_3O_5 , Magneli phases ($\text{Ti}_n\text{O}_{2n-1}$, $28 \geq n \geq 4$) (Jacob *et al* 2000) and TiO_{2-x}

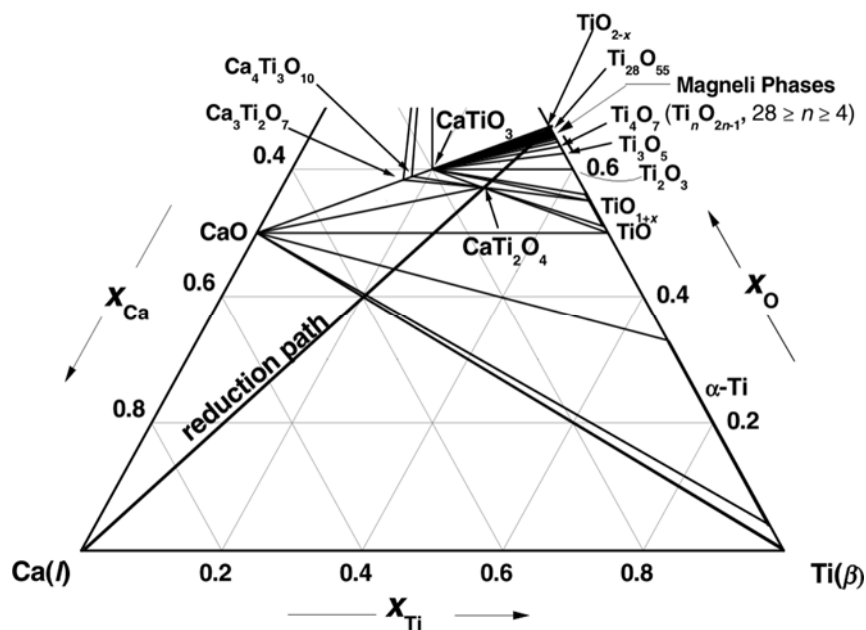


Figure 2. Reaction pathway for the reduction of TiO_2 with calcium metal superimposed on the phase diagram.

Table 2. Sequence of phase formation during reduction of TiO_2 by Ca under equilibrium conditions.

Stage	Phases formed
1	$\text{TiO}_{2-x} + \text{CaTiO}_3$
2	$\text{Ti}_n\text{O}_{2n-1} + \text{CaTiO}_3$ ($28 \geq n \geq 4$)
3	$\text{Ti}_3\text{O}_5 + \text{CaTiO}_3$
4	$\text{Ti}_2\text{O}_3 + \text{CaTiO}_3$
5	$\text{TiO}_{1+x} + \text{CaTiO}_3$
6	CaTi_2O_4
7	$\text{TiO} + \text{CaO}$
8	$\alpha\text{-Ti}_{\text{ss}} + \text{CaO}$
9	$\beta\text{-Ti}_{\text{ss}} + \text{CaO}$

were in equilibrium with CaTiO_3 , generating several three-phase regions in between. Any two of these adjacent three-phase regions are separated by a very narrow two-phase field, represented by the tie-line that defines the shared side between the two triangles. The compound CaTi_2O_4 was found to coexist with CaTiO_3 , $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, $\text{Ca}_3\text{Ti}_2\text{O}_7$ and CaO . Three-phase fields $\text{CaTi}_2\text{O}_4 + \text{CaTiO}_3 + \text{Ca}_4\text{Ti}_3\text{O}_{10}$, $\text{CaTi}_2\text{O}_4 + \text{Ca}_4\text{Ti}_3\text{O}_{10} + \text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{CaTi}_2\text{O}_4 + \text{Ca}_3\text{Ti}_2\text{O}_7 + \text{CaO}$ were identified. The phase relations along the Ti–O binary at 1200 K shown in figure 1(a) is reasonably consistent with the phase diagrams for the binary system given in the compilation by Massalski *et al* (1986) and those suggested by Cancarevic *et al* (2007) and Okamoto (2001).

Figure 1(a) provides the first available complete experimentally determined isothermal section of the system Ca–Ti–O. In principle, it would be possible to compute the phase diagram from thermodynamic data for various

phases present. Accurate data on Gibbs free energies of formation of calcium titanates (CaTiO_3 , $\text{Ca}_4\text{Ti}_3\text{O}_{10}$, and $\text{Ca}_3\text{Ti}_2\text{O}_7$) have been measured recently (Jacob and Abraham 2009). Considerable thermodynamic data on phases present along the Ti–O binary are available in the literature (Kubaschewski 1983; Chase Jr 1998; Jacob *et al* 2000; Cancarevic *et al* 2007). Although some of the data are not of high accuracy, it can nevertheless be used for the first iteration in a Gibbs energy minimization code. However, there is no thermodynamic data for the compound CaTi_2O_4 . When this data becomes available, it would be possible to check the experimental results obtained in this study by thermodynamic computation.

4. Sequence of phase formation during calciothermic reduction of TiO_2

From the phase diagram, sequence of phase formation during calciothermic reduction of TiO_2 under equilibrium conditions can be identified. The reduction path is superimposed on the phase diagram in figure 2. The reduction path follows the line joining Ca metal to TiO_2 . The sequence of phase formation during the reduction of TiO_2 by Ca is listed in table 2.

In the initial phase of reduction, TiO_2 becomes oxygen deficient (TiO_{2-x}) and then the Magneli phases $\text{Ti}_n\text{O}_{2n-1}$ ($28 \geq n \geq 4$) are formed in sequence with decreasing value of n . Subsequent reduction will result in the formation of Ti_3O_5 and Ti_2O_3 . The oxygen from titanium oxides is mopped up by Ca to form CaO , which in turn reacts with TiO_2 to produce CaTiO_3 . The activity of TiO_2 decreases with decreasing oxygen content along the

binary Ti–O. For example, the activity of TiO₂ in the two-phase region involving Ti₂O₃ and Ti₃O₅ is 0.358 at 1200 K based on Gibbs free energy data for titanium oxides from NIST-JANAF thermochemical tables (Chase Jr 1998). This activity is sufficient for the formation of CaTiO₃ (Jacob and Abraham 2009). Oxygen-rich TiO_{1+x} solid solution is the lowest oxide of titanium that can coexist with CaTiO₃. Unfortunately accurate data for the solid solution TiO_{1+x} does not exist. Up to this point of reduction, two oxide phases are present simultaneously, a titanium oxide phase and CaTiO₃.

Further reduction by Ca results in the formation of single phase CaTi₂O₄ with all titanium in trivalent state. This marks a critical step in reduction. In the next step of reduction, CaO oxide appears as the product for the first time along with stoichiometric TiO. Thus the single phase CaTi₂O₄ on reduction produces two oxide phases. Further reaction results in the formation of α -Ti_{ss} and β -Ti_{ss} solid solutions containing dissolved oxygen, but with no detectable calcium. These solid solutions coexist with CaO. The limit of deoxidation of β -Ti_{ss} by Ca forming CaO as the product is 0.084 atom percent oxygen at 1200 K. This limit can be lowered by dissolving CaO in a molten salt and thereby reducing the activity of CaO.

The formation of single phase CaTi₂O₄ from a mixture of TiO_{1+x} and CaTiO₃, and its subsequent decomposition to TiO and CaO on further reduction with calcium metal may act as a kinetic constriction in the calciothermic reduction of TiO₂.

5. Conclusions

An isothermal section of the phase diagram for the system Ca–Ti–O at 1200 K is composed based on phase analysis of 20 compositions after equilibration at high temperature and subsequent quenching to room temperature. The phases present in the quenched samples were identified by optical and scanning electron microscopy (OM, SEM), powder X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Four ternary oxides without detectable range were identified: CaTiO₃, Ca₄Ti₃O₁₀ and Ca₃Ti₂O₇ containing tetravalent titanium, and CaTi₂O₄ containing trivalent titanium. There was no detectable presence of calcium in the oxide and solid solution phases along the Ti–O binary.

From the phase diagram, the reduction pathway and the sequence of phase formation during calciothermic reduction of TiO₂ under equilibrium conditions was identified. In the initial stages, reduced titanium oxides (TiO_{2-x},

Ti_nO_{2n-1} ($28 \geq n \geq 4$), Ti₃O₅, Ti₂O₃ and TiO_{1+x}) form along with CaTiO₃. At the intermediate stage a single phase product, calcium titanite (CaTi₂O₄), is obtained. Subsequent reduction results in the formation of two products: TiO, α -Ti_{ss} and β -Ti_{ss} containing dissolved oxygen on one side, and pure CaO on the other.

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