ARIYO, C., GONZALEZ, P., and HOLAPPA, L. Oxidation state of titanium in CaO-SiO$_2$-TiOx slags at 1873K. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

Oxidation state of titanium in CaO-SiO$_2$-TiOx slags at 1873K

C. ARIYO*, P. GONZALEZ†, and L. HOLAPPA†
**CSC-Scientific Computing, Espoo, Finland*
†Laboratory of Metallurgy, Helsinki University, Espoo, Finland

Oxidation state of titanium was determined in CaO-SiO$_2$-TiO$_x$ slags in the composition range 25–53 per cent CaO, 27–46 per cent SiO$_2$, 10–55 per cent TiO$_x$ at 1873K using gas equilibration method.

In the experiments, slags with different titanium oxide contents were equilibrated with a known carbon monoxide and carbon dioxide ratio. The results were used to determine the Ti^{3+} and Ti^{4+} contents as well as the activity coefficient ratio of corresponding oxides in the slag.

The dependency of the activity coefficient ratio as a function of oxygen partial pressure was determined.

Keywords: titanium, titanium oxide, activity, activity coefficient, slag iron, carbon monoxide, carbon doixide, gas, equilibrium.

Introduction

In steelmaking operations, oxygen is an undesirable impurity since it forms oxide inclusions that reduce the mechanical properties of steel. It is, therefore, unavoidable but to find effective methods for the removal of oxygen. Titanium is one such strong oxide forming element which can be effectively used for deoxidation. Three basic characteristics of titanium contribute to its reaction with oxygen:

- Ti forms a number of oxides: TiO$_2$, Ti$_3$O$_5$, Ti$_2$O$_3$, TiO
- All oxides have very large negative free energy of formation
- Pure titanium exhibits high solubility for oxygen.

Titanium is also used for binding nitrogen, to form nitrides or carbonitrides, which is of great importance in the production of micro alloyed steels as well as boron steels.

Oxygen partial pressure, slag composition and temperature determine the distribution of titanium between liquid metal and slag, as well as portioning among different valency states (Ti^{4+}, Ti^{3+}, Ti^{2+}) in the slag. The oxides associated with the three valencies of titanium exhibit different properties, affecting both the physical and thermodynamic behaviour of slags containing these oxides. TiO$_2$ is generally classified as amphoteric while the reduced forms Ti$_2$O$_3$ and TiO behave more like basic oxides.

Despite the relative importance of titanium in steelmaking slags, there are ample uncertainties in the available thermodynamic properties.

Experimental procedure

The experimental apparatus consists of a vertical resistance furnace heated by LaCrO3 heating elements and equipped with mixing flow controllers and measuring instruments. The furnace was equipped with an alumina furnace tube, into which the crucible assembly is raised with the help of an alumina tube with the thermocouple for temperature measurements. The alumina tube is fitted with water-cooled brass end caps to seal the ends (Figure 1).

The temperature of an even hot zone in the furnace was measured by a B-type thermocouple (Pt-6%Rh/Pt-30%Rh) and controlled by a PID program to within ±3K. The partial pressure of the gas atmosphere in the furnace was controlled by CO-CO$_2$ gas mixtures. The gas mixtures were delivered by an alumina tube on to the surface of the slag. The individual gas flow rates were controlled using pre-calibrated mass flow controllers.

A molybdenum crucible 30 mm inner diameter, 36 mm outer diameter and 67 mm height was used as the working crucible.

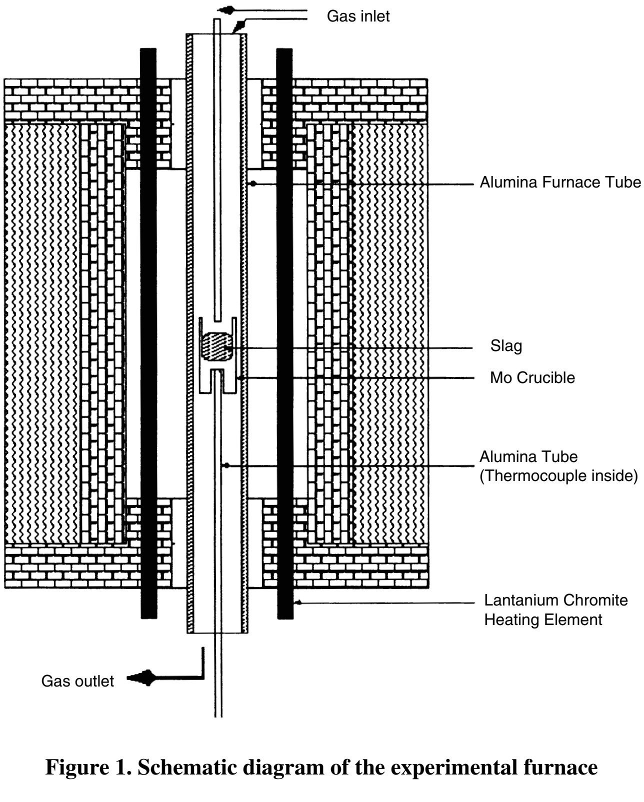

Figure 1. Schematic diagram of the experimental furnace

The furnace was heated to the desired temperature 1873K. The crucible with the thermocouple was placed at the bottom of the furnace and sealed. Carbon dioxide was then supplied to flush the system of oxygen for a few minutes, after which it was changed to include carbon monoxide. The crucible was then slowly raised into the hot zone. The crucible was left in the hot zone for a period of 8 hours, which was previously determined to be long enough for equilibrating the system.

The reaction involving the gas equilibrium can be expressed as follows:

$$CO(g) + 1/2O_2(g) = CO_2(g) \qquad [1]$$

$$\Delta G^O = -281144 - 85.29 \bullet T\ (J/mol)^1 \qquad [2]$$

Raw materials

Laboratory reagent grade oxides were used ($CaCO_3$, SiO_2, and Ti_3O_5 pellets). A master slag containing 51.5 per cent SiO_2 and 48.5 per cent CaO was used. Electrolytic iron granules (99.99 per cent), ferro-titanium, titanium wire (99.99 per cent) and ferro-silicon were also used. The master slag was pre-melted in a carbon crucible in vacuum at temperatures above the liquidus. It was then quenched in water, ground, analysed and then stored in a desiccator ready for use.

Slag analysis

The contents of Ca, Si and Ti in slags were determined using ICP-AES analyser (Varian Liberty) after dissolution with HNO_3, HF and HCl.

The total amount of reduced titanium (Ti^{2+} and Ti^{3+}) was determined by a modified version of an indirect potentiometric redox titration method[2]. Under the present conditions, the concentration of Ti^{2+} should be low in comparison to Ti^{3+} and therefore all reduced titanium was reported as Ti^{3+}.

The reduced Ti^{3+} is oxidized by ferric ion through the following reaction

$$Fe^{3+} + Ti^{3+} = Fe^{2+} + Ti^{4+} \qquad [3]$$

Following the dissolution, the resulting Fe^{2+} was titrated with standardized 0.02N potassium dichromate in a glove box. The quantity of titanium in the Ti^{4+} valency state was calculated as the difference between total and reduced titanium (Ti^{3+}).

Results and discussion

The aim of this research was to determine the activity and the activity coefficients of titanium in the slag.

The reduction reaction of TiO_2 to $TiO_{1.5}$ may be presented as

$$TiO_2(s) \Leftrightarrow TiO_{1.5}(s) + \tfrac{1}{4}O_2(g) \qquad [4]$$

$$\Delta G^O = 189954 - 48.5 \bullet T\ (J/mol)^1 \qquad [5]$$

Based on the standard Gibbs free energy for reaction (4) and the experimental data on the redox equilibria, the activity coefficient ratio of the oxides was calculated.

The experimental results are shown in Table I.

Figure 2 shows the slag compositions in the ternary diagram. Figure 3 shows the variation of $\frac{Ti^{3+}}{Ti^{4+}}$ as a function of TiO_x at an oxygen partial pressure of about $4*10^{-12}$.

The equilibrium constant for reaction (4) can be expressed:

$$K_4 = \frac{a_{TiO_{1.5}} . p_{O_2}^{\frac{1}{4}}}{a_{TiO_2}} \qquad [6]$$

Further;

$$K_4 = \frac{\gamma_{TiO_{1.5}} . \%TiO_{1.5} \cdot p_{O_2}^{\frac{1}{4}}}{\gamma_{TiO_2} \cdot \%TiO_2} \qquad [7]$$

Assuming that the $\frac{\gamma TiO_{1.5}}{\gamma TiO_2}$ ratio is not affected by the reduction of Ti^{4+} to Ti^{3+}, a plot of log $\frac{Ti^{3+}}{Ti^{4+}}$ against the $\log(P_{O_2})$ should yield a straight line with a slope of -0.25[3]. Figure 4 shows the ratio log $\frac{Ti^{3+}}{Ti^{4+}}$ as a function of the oxygen partial pressure and is in very good agreement with the work of Tranell *et. al.*[3].

Table II shows comparison between activity coefficients of titanium oxide in the present work and the most relevant studies in the literature. It is very difficult to make any direct comparison between the works because of the different temperatures as well as the basicities. The work of Tranell *et. al.*[3] can be said to be close to the present work considering the temperature differences as well as the basicity. This can also be seen clearly in Figure 3.

Table I
Experimental results

Exp.	$(\%CaO)$	$(\%SiO_2)$	$(\%TiO_{1.5})$	$(\%TiO_2)$	$(\%TiO_x)$ $\log(P_{O_2})$	$B=\frac{\%CaO}{\%SiO_2}$	X_{CaO}	X_{SiO_2}	$X_{TiO_{1.5}}$	X_{TiO_2}	$\log\frac{Ti^{3+}}{Ti^{4+}}$	$\log\left(\frac{\gamma_{TiO_{1.5}}}{\gamma_{TiO_2}}\right)$
1	52.62	36.77	0.79	9.83	-12.62	1.43	0.5571	0.3633	0.0065	0.0730	-1.05	1.44
2	46.64	31.06	4.57	17.74	-12.49	1.50	0.5090	0.3163	0.0389	0.1358	-0.54	0.90
3	40.68	26.43	2.50	30.39	-12.42	1.54	0.4590	0.2783	0.0220	0.2407	-1.04	1.38
4	32.88	20.17	4.04	42.91	-12.36	1.63	0.3869	0.2216	0.0370	0.3544	-0.98	1.31
5	27.40	17.25	7.52	47.84	-12.32	1.59	0.3303	0.1941	0.0707	0.4048	-0.78	1.07
6	36.21	34.38	4.34	25.07	-12.45	1.05	0.4055	0.3594	0.0379	0.1971	-0.72	1.06
7	36.06	29.20	6.26	28.48	-12.45	1.24	0.4089	0.3091	0.0554	0.2266	-0.61	0.96
8	42.53	28.83	1.61	27.03	-12.45	1.48	0.4744	0.3000	0.0140	0.2116	-1.18	1.53
9	44.13	28.11	1.46	26.31	-12.45	1.57	0.4905	0.2916	0.0126	0.2052	-1.21	1.56
10	48.70	23.29	0.60	27.41	-12.45	2.09	0.5402	0.2412	0.0052	0.2134	-1.61	1.96
11	48.32	34.76	0.91	16.02	-10.00	1.39	0.5220	0.3500	0.0069	0.1210	-1.33	0.94
12	48.13	34.81	1.07	15.98	-11.00	1.38	0.5200	0.3510	0.0081	0.1210	-1.13	1.11
13	48.07	34.38	1.07	16.48	-11.30	1.40	0.5200	0.3470	0.0081	0.1250	-1.05	1.20
14	47.21	34.78	1.67	16.35	-12.00	1.36	0.5110	0.3520	0.0127	0.1240	-0.95	1.18

Conclusions

The oxidation state of titanium was studied in CaO-SiO2-TiOx slags at 1873K using gas equilibration method with the following conclusions:

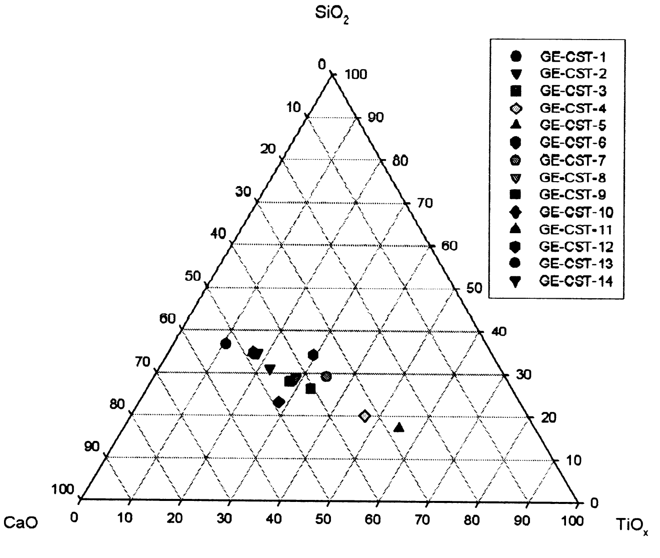

Figure 2. Ternary diagram showing the slag compositions

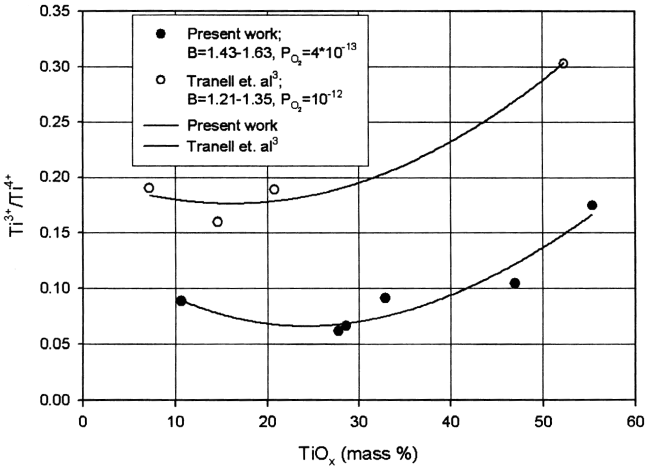

Figure 3. Variation of $\frac{Ti^{3+}}{Ti^{4+}}$ with concentration of TiO_x in the slag at 1873K

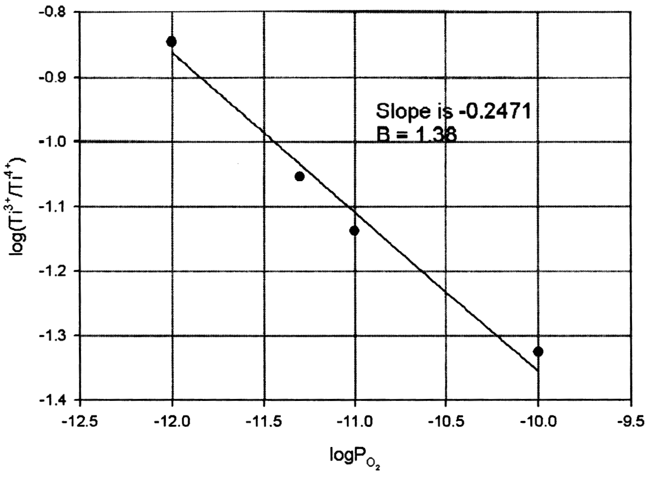

Figure 4. Variation of $\frac{Ti^{3+}}{Ti^{4+}}$ with concentration of TiO_x in the slag at 1873K

- The $\frac{Ti^{3+}}{Ti^{4+}}$ ratio decreases as the basicity increases.
- The $\frac{Ti^{3+}}{Ti^{4+}}$ ratio changes with the TiO_x content in the slag and reaches a minimum at about 25% TiO_x.
- The $\frac{Ti^{3+}}{Ti^{4+}}$ decreases with increasing oxygen partial pressure and have a slope of -0.25.

Acknowledgements

The financial support for this research from the Finnish Technology Development Foundation (TES) and Helsinki University of Technology (C.A.) as well as from the National Technology Agency (TEKES) (P.G.) is gratefully acknowledged.

References

1. TURKDOGAN, E.T. Physical Chemistry of High Temperature Technology, Academic Press Inc., New York, NY. 1980.
2. CLOSE, P.W. and TILLMAN, J.F. *Glass Technology*, 1969, vol. 10, pp. 134–146.
3. TRANELL, G., OSTROVSKI, O., and JAHANSHAHI, S. *Metallurgical and Materials Trans. B*, vol. 33B, Feb. 2002, pp. 61–67.

Table II
Comparison of the activity coefficient of Titanium oxides in slags

$\gamma_{TiO_{1.5}}$	$\gamma_{TiO_{1.67}}$	γ_{TiO_2}	$\frac{\gamma_{TiO_{1.5}}}{\gamma_{TiO_2}}$	Slag Composition	$B = \frac{(\%CaO)}{(\%SiO_2)}$	Temp. (K)	Author(s)
-	-	-	7.9–91.2	32–52%CaO, 20–37%SiO_2, 10-55%TiO_x	1.0–2.1	1873	Present work
-	-	-	2–11	24.5–51.6%CaO, 24.5–60.6%SiO_2, 7–50%TiO_x	0.55–1.35	1783, 1903	3
-	0.39–2.28	-		25–44%CaO, 29–47%SiO_2, 10–39%$TiO_{1.67}$	0.72-1.30	1873	4
2.3–8.8	-	0.1–0.3		35–50%CaO, 25–45%SiO_2, 7–22%Al_2O_3, 10%MgO, 4–7%TiO_x (x = 1.5,2)		1773	5
14.3–28	-	1.8–3.4		SiO_2-CaO-Al_2O_3-TiO_2	1	1773	6
59.6	-	0.97		CaO-SiO_2-Al_2O_3-MgO-TiO_x	0.42–1.3	1673–1823	7
-	-	0.11 $3.7 \cdot 10^{-4}$		38.29–46.62%CaO, 4.55–7.24%MgO, 33.06–40.6%SiO_2, 6.71–7.12%Al_2O_3, 0.53–14.87%TiO_2	1.09–1.16	1723–1823	8
0.3–1.5	-	0.5–2.3		CaO-SiO_2-30%Al_2O_3-MgO-TiOx and CaO-SiO_2-20%Al_2O_3-MgO-TiO_x			9

4. ARIYO, C. and HOLAPPA, L. Activity of Titanium Oxide in CaO-SiO_2-Ti_3O_5 Slags at 1600°C. *Scandinavian Journal of Metallurgy*, vol. 31 (2002) pp. 385–392.

5. MORIZANE, Y., OZTURK, B., and FRUEHAN, R.J. Thermodynamics of TiOx in Blast Furnace-Type Slags. *Metallurgical and Materials Trans.*, vol. 30B, February 1999, p. 29–43.

6. ITO, K., SATO, N., and MATSUENTA, Y. *Tetsu-to-Hagané,* vol. 65, no. 4, 1979. p. S5

7. ITO, K. and SANO, N. The Thermodynamics of Titanium in Molten Slags Equilibrated with Graphite. Tetsu-to-Hagané, vol. 67, 1981, pp. 2131–2137.

8. BENESCH, R., LEDZKI, A., KOPÉC, R., and STACHURA, R. Equilibrium of Reduction of Titanium Oxides from BlastFurnace-Type Slags of the CaO-MgO-SiO_2-Al_2O_3-TiO_2 System in Liquid Phases. *Thermochimica Acta*, 152. 1989 pp. 447–461

9. JUNG, S. and FRUEHAN, R.J. Thermodynamics of Titanium Oxide in Ladle Slags. *ISIJ International*, vol. 41, no. 12, 2001. p. 1447—1453