Activity of Titanium Oxide in CaO-SiO$_2$-Ti$_3$O$_5$ Slags at 1600°C.

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Abstract

Activity of titanium oxide was determined in CaO-SiO$_2$-Ti$_3$O$_5$ slags in the composition range 25-44% CaO, 30-46% SiO$_2$, 10-39% TiO$_{1.67}$ at 1600°C using electromotive force method.
In the experiments, slags with different titanium oxide contents were equilibrated with liquid iron at 1873K. Oxygen activity in the iron melt was measured and used with the titanium content in the metal to calculate titanium oxide activity in the slag. According to the results, it was concluded that the activity coefficient of titanium oxide ($\gamma_{TiO_{1.67}}$) is in the range of 0.39 to 1.68 depending on the titanium oxide content and slag basicity. It was evident from the experiments that the activity coefficient increases with the increase in basicity and tends to decrease with increasing SiO$_2$.

Introduction

Titanium has high affinity to non-metals like oxygen, nitrogen and carbon[1]. When added into steel it forms inclusions, oxides, nitrides, carbides or carbonitrides. "Stabilisation" of stainless steels is based on binding carbon with titanium. In micro-alloyed steel titanium can be used to form nitride and carbonitride precipitates, which have beneficial effects on mechanical properties. Titanium is also generally used in boron steels to protect boron from reacting with nitrogen or eventually with oxygen thus assuring the hardenability effect of boron[2]. A further potential application might be so-called "oxide metallurgy" [3]. Accordingly, a.o. Ti- or Zr- oxides if formed during casting are precipitated as very fine inclusions. These inclusions act as nuclei for other inclusions (sulphides, carbides) as well as for ferrite formation thus resulting in fine grain structure and improved mechanical properties. Ti-oxide inclusions also favour acicular ferrite formation e.g. in welding thus improving weld ductility [4].

The examples above show useful effects of titanium in steel. In these applications, the aim in steelmaking is to get high and reproducible yield of titanium. In some cases however, titanium is harmful, typical example being bearing steels in which Ti-content is limited to very low values (e.g. max 0.002%). In this case, the aim is to remove Ti effectively by oxidising it into the slag. The common feature for all the applications is that distribution of Ti between the steel melt and the slag should be strictly controlled. The solution thermodynamics of titanium in liquid steel is properly established [5]. On the contrary, the available information on thermodynamics of titanium in slags seems to be quite scanty as discussed later. Most of the studies concern slags outside the scope of ladle metallurgy. The present paper is a first approach to the problems of Ti-containing slags. It concentrates on the determination of the activity coefficient of titanium oxide ($\gamma_{TiO_{1.67}}$) in CaO-SiO_2-Ti_3O_5 slags using electromotive force (EMF) method. The work presented here was conducted in the Laboratory of Metallurgy, Helsinki University of Technology, Finland.

Experimental

1.   Apparatus

The experimental system consisted of a high temperature furnace equipped with an argon purification line, electromotive force measuring and recording instruments, oxygen probe and a crucible assembly.

The experimental apparatus is shown in Figure 1. A vertical resistance furnace heated by $LaCrO_3$ heating elements and fitted with water-cooled brass end caps to isolate the atmosphere inside the alumina tube.

A 15 mole percent MgO stabilised ZrO_2 crucible with inner diameter 28mm, outer diameter 32mm and height 50mm was used as the working crucible. The crucible was charged with 50g Fe-O alloy and 10g CaO-SiO_2-Ti_3O_5 slag and placed in an alumina protection crucible. The crucible assembly was then placed in a molybdenum holder fixed to the top of the thermocouple. The solid electrolyte, oxygen probe, consisted of 9 mole percent MgO partially stabilised zirconia tube closed at one end. The iso-statically pressed and sintered oxygen probes with inner diameter 5mm, outer diameter 8mm and height 50mm were supplied by Nippon Kagaku Tokyo Co. Ltd. The reference electrode was made up of a mixture of 80 weight percent Cr and 20 weight percent Cr_2O_3. The electrical circuit of the cell

was completed by Fe-Ti-O melt in equilibrium with CaO-SiO$_2$-Ti$_3$O$_5$ slag and a molybdenum wire welded to a ZrO$_2$-Mo cermet.

The whole system was protected by purified argon gas with a flow rate of 6 litres per hour. A purification train for the argon gas (99.998%) consisted of potassium hydroxide to remove carbon dioxide, silica gel and phosphorus pentoxide to remove moisture, and titanium turnings kept at 850°C in a resistance furnace to reduce oxygen partial pressure.

The temperature of the hot zone (6cm) was measured by a Pt-6%Rh/Pt-30%Rh thermocouple and controlled within ±2K by a PID program. Electromotive force values were recorded by a Keithley 195A digital multimeter with an input impedance of 1 GΩ and accuracy of 0.01mV, connected to a SE 130 chart recorder as well as to a microcomputer equipped with a data acquisition card to continuously record the data.

2.   Raw Materials

Laboratory reagent grade chemicals – CaCO$_3$, SiO$_2$, and Ti$_3$O$_5$ powder were used. Electrolytic iron granules (99.99%), ferro-titanium, titanium wire (99.99%) and ferro-silicon were also used. The slag components were ground, mechanically mixed, and then stored in a desiccator ready for use.

3.   Principles

The traditional equilibration technique for measuring activities in liquid melts requires considerable time and its application to corrosive slags can be practically impossible.

Electromotive force (EMF) method makes it possible not only to study oxygen equilibrium at 1873K but also to measure activity changes in a wide temperature range in liquid and solid metal. EMF method was therefore adopted for the determination of the actual oxygen activity in the melt in the present work.

The following galvanic cell was used:

(+)Mo ‖ Cr,Cr$_2$O$_3$ ‖ ZrO$_2$(9mol%MgO) ‖ ((CaO-SiO$_2$-Ti$_3$O$_5$ slag),[Fe-Ti-O melt]) ‖ Mo(-)
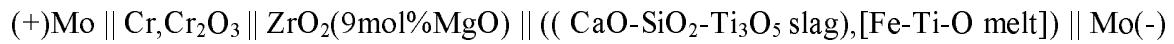
Considering the influence of electronic conduction in the above electrolyte at high temperature, the electromotive force can be expressed by the following equation (Nernst Equation):

$$E = \frac{R \cdot T}{F} \cdot \ln \frac{P_{O_2,ref}^{1/4} + P_e^{1/4}}{P_{O_2,melt}^{1/4} + P_e^{1/4}} \tag{1}$$

where,

E, the EMF value in volts;

R=8.314 $\dfrac{J}{K \cdot mol}$, gas constant;

F=96500 $\dfrac{J}{V \cdot mol}$, Faraday's constant;

T, the temperature in Kelvin;

$P_{O_2,melt}$, the oxygen partial pressure in the Fe-Ti-O melt, atm;

$P_{O_2,ref}$, the oxygen partial pressure in equilibrium between Cr and Cr2O3 in reference electrode, atm;

P_e, the characteristic oxygen partial pressure at which ionic and n-type electronic conductivities are equal for the $ZrO_2(9mol\%MgO)$ electrolyte, which is a function of temperature as defined below:

$$\log(P_e) = -\frac{64500}{T} + 20.40 \, [6]$$ (2)

4. Procedures

The procedure consisted mainly of the following consecutive steps:
1. Preparing metal and slag, heating up the furnace to the required temperature, raising the crucible assembly to the hot zone.
2. Measuring the open-circuit EMF of the solid electrolyte cell after equilibrium.
3. Taking metal and slag samples before changing composition or withdrawing the crucible assembly.

A certain amount of the required powders was mixed, homogenised and then placed into the crucible assembly. The furnace was then heated at a reasonable rate to the experimental temperature under deoxidised argon gas. After obtaining a stable temperature in the furnace, the crucible assembly was slowly and carefully raised to the hot zone of the furnace. After waiting for some time usually 30 minutes for equilibrium, the oxygen probe was inserted through a rubber stopper for sealing the furnace tube on the top of the water-cooled brass flange. A stable EMF value was achieved within a few seconds after immersion. The EMF values were measured by a digital voltmeter and recorded on a microcomputer as well as on a chart recorder. Stable reversible readings were sometimes obtained for as long as 30 minutes before removing the cells from the melt. Analytical samples were taken by controlled suction into an alumina tube of inner diameter 5mm and quickly quenched in ice water. The slag and metal compositions were altered by the addition of ferro-titanium, silicon and titanium oxide pellets respectively. A typical EMF reading is shown in Figure 2. Care was taking in the handling and preparation of the samples for analysis. All the metal samples were sound and upon close examination showed no oxide entrapment. The samples were cleaned by controlled machining of the surface. During machining, the surface was kept cool with acetone in order to avoid surface oxidation. Only the middle of the metal samples were used for analysis.

The metal samples were analysed for titanium, oxygen, silicon and molybdenum by emission spectroscopy method in the State Technical Research Centre of Finland (VTT) as well as by QES4460 and Leco TC136 analysers in Fundia Kovenhar, Finland. The KCST slag samples were analysed by x-ray fluorescence in Fundia Kovenhar, Finland. Small slag samples trapped in between the crucible walls and on the top of the oxygen probes (SCST) were analysed by the scanning electron microscopy (SEM-EDS) method in the Laboratory of Metallurgy, Helsinki University of Technology, Finland.

Experimental Results

The aim of this study was to measure the activity coefficient $\gamma_{TiO_{1.67}}$ of titanium oxide in CaO-SiO_2-Ti_3O_5 slags.
For the calculation of the activity of oxygen from EMF values, there is need to calculate the free energy of formation of chromium oxide of the reference electrode.

$$2Cr(s) + 3/2O_2(g) = Cr_2O_3(s) \tag{3}$$

$$\Delta G^o(3) = -1077682 + 232.49*T(J) \text{ [7]} \tag{4}$$

Assuming that $a_{Cr_2O_3} = 1$ and $a_{Cr} = 1$, the oxygen partial pressure corresponding to the oxygen activity in the melt can be calculated as;

$$P_{O_2(melt)} = \left\{ \frac{P_{O_2(ref)}^{\frac{1}{4}} + P_e^{\frac{1}{4}}}{\exp\left(\dfrac{E \cdot F}{R \cdot T}\right)} - P_e^{\frac{1}{4}} \right\}^4 \tag{5}$$

By measuring the electromotive force E with the oxygen probe, we can calculate oxygen partial pressure $P_{O_2(melt)}$ respective to the dissolved oxygen activity in the melt according to the following relationships.

$$\frac{1}{2}O_2(g) = [\%O]_{Fe} \tag{6}$$

$$\Delta G^o(6) = -12900 - 2.09*T(J) \text{ [8]} \tag{7}$$

When the concentration range of titanium in liquid iron is less than 0.01 percent, the deoxidation product was stated to be TiO_x (x=1.70-1.87) and when it is from 0.013 to 0.25 percent it was assumed to be Ti_3O_5 [9].

Preliminary experiments were performed to equilibrate Fe-Ti-O liquid metal with $CaO-SiO_2-Ti_3O_5$ slag. However, it was difficult to attain any stable equilibrium value. Therefore, another approach was taken to use silicon to reduce titanium from the slag. The equilibria was therefore assumed to correspond to both [Ti]-[O]/(Ti$_3$O$_5$) and [Si] – [O]/(SiO$_2$) systems.
The experimental results are shown in Table 1.
In the table there is a comparison between the calculated oxygen activity from EMF readings, $\log a_{[\%O](emf)}$, and the oxygen activity calculated from the silicon content in the iron melt, $\log a_{[\%O](Si)}$.
Considering the reduction of titanium by silicon, the following equations are essential.

$$3[\%Ti] + 5[\%O] = Ti_3O_5(s) \tag{8}$$

$$\Delta G^o(8) = -1667000 + 557.939*T(J) \text{ [10]} \tag{9}$$

$$[\%Si] + 2[\%O] = (SiO_2) \tag{10}$$

$$\Delta G^o(10) = -576440 + 218.2*T(J) \text{ [10]} \tag{11}$$

The equation of the reduction reaction can be expressed as,

$$5[\%Si] + 2(Ti_3O_5) = 6[\%Ti] + 5(SiO_2) \tag{12}$$

and the standard free energy of formation,

$$\Delta G^o(12) = 451800 - 24.878*T(J) \tag{13}$$

Alternatively the titanium-oxygen reaction can be presented as,

$$[Ti] + 5/3[O] = (TiO_{1.67}) \tag{14}$$

and the free energy of formation,

$$\Delta G^o(14) = 1/3* \ \Delta G^o(9) = -555666.67 + 185.98*T(J) \tag{15}$$

The activity of titanium, oxygen and titanium oxide can therefore be calculated from the following equations.

$$\log a_{Ti} \quad = \quad e_{Ti}^{Ti}[\%Ti] + e_{Ti}^{Si}[\%Si] + e_{Ti}^{O}[\%O] + \log[\%Ti] \tag{16}$$

$$\log a_{O} \quad = \quad e_{O}^{O}[\%O] + e_{O}^{Si}[\%Si] + e_{O}^{Ti}[\%Ti] + \log[\%O] \tag{17}$$

The value of interaction parameters used in this work are shown in Table 2.
The activity of titanium oxide in the slag can then be calculated as follows,

$$\log a_{TiO_{1.67}} \quad = \quad \log K(14) + \log a_{Ti} + \frac{5}{3} \cdot \log a_{O} \tag{18}$$

The experimental results are presented accordingly in Figure 3. Equilibrium lines at six different $a_{TiO_{1.67}}$ values (from 1 to 0.1) are drawn in the figure as well.
The activity coefficient of titanium oxide for every slag composition can be estimated from activity and mole fractions of titanium oxide in the slag.

$$\log \gamma_{TiO_{1.67}} \quad = \quad \log a_{TiO_{1.67}} - \log X_{TiO_{1.67}} \tag{19}$$

Figure 4 shows the dependence of activity of titanium oxide on the slag composition.
In spite of quite big scatter, it can be seen that $\gamma_{TiO_{1.67}}$ has highest values at compositions corresponding to the highest slag basicity.

Discussion and Conclusions

The activity of titanium oxide in $CaO\text{-}SiO_2\text{-}Ti_3O_5$ slags were extensively studied using EMF method.
Titanium exists in different oxidation states, Ti^{2+}, Ti^{3+} and Ti^{4+}. The corresponding oxide forms are for example TiO, Ti_2O_3, Ti_3O_5 and TiO_2. These oxides can be more or less non-stoichiometric. This makes it exceedingly difficult to determine its thermodynamic properties in the slag. However, the form Ti_3O_5 is generally accepted as a deoxidation product in iron melt at concentrations 0.013-0.25%Ti[9]. Although in these experiments Ti-contents were mostly below this range, titanium was assumed to be as Ti_3O_5 ($TiO_{1.67}$) in the slags. This is because the titanium oxide contents in the slags were far below unity ($X_{TiO_{1.67}} = 0.08 \dots 0.35$),

hence the ambient a_O values in the system were in accordance with the mentioned titanium contents in iron melt in equilibrium with pure titanium oxide.

There are no publications in the literature where the activity or activity coefficient of Ti_3O_5 were determined in the slag corresponding to this study. Therefore, it is very difficult to find any reliable comparison. It is worth to note that the activity coefficient of titanium oxide depends very much on the temperature and slag composition. An attempt though was made in Table 3 to compare the activity coefficient from this work to related previous works.

Having a closer look at the results in Table 1, it can be seen that the oxygen activity calculations based on EMF are very close to the oxygen activity calculated from the analysed silicon from the melt [%Si]. This confirmed that there was equilibrium between oxygen and silicon, respectively oxygen and titanium in the melt during measurements. However, the experimental results with high silicon content [%Si] > 1 seem less reliable. It is questionable if the final equilibrium content of titanium was attained in the experiments. Further, it is uncertain if the silicon-silicon interaction parameter given in the literature is still valid at this high concentration (SCST10). For these reasons the run SCST10 was neglected in the final results. The effect of basicity is shown in Figure 4. Due to the amphoteric nature of titanium oxides, it may be difficult to see the dependency clearly. This can be explained further by presenting $TiO_{1.67}$ with the following equation.

$$3TiO_{1.67} = TiO_2 + 2TiO_{1.5} \tag{20}$$

$$\Delta G^o (20) = 833.33 - 3*T(J) \, [10] \tag{21}$$

$$[Ti] + 2[O] = TiO_2 \tag{22}$$

$$\Delta G^o (22) = -646500 + 224.555*T(J) \, [10] \tag{23}$$

$$[Ti] + 3/2[O] = TiO_{1.5} \tag{24}$$

$$\Delta G^o (24) = -1023000 + 342.581*T(J) \, [10] \tag{25}$$

Based on the above equations an attempt was made to calculate the activities of TiO_2 and $TiO_{1.5}$. The calculated values are shown in Table 1.

According to Morizane et al. [10] an increase in $TiO_{1.5}$ increases the activity coefficient of $TiO_{1.67}$ while an increase in TiO_2 decreases the activity coefficient in the slag. This implies that $TiO_{1.5}$ may act more basic than TiO_2, which may act a little acidic in the melt. Therefore, the sequence of basicity in the present work can be presented as CaO, $TiO_{1.5}$, TiO_2, and SiO_2.

In conclusions, the activity coefficient of titanium oxide for 25-44% CaO, 30-46% SiO_2, 10-39% $TiO_{1.67}$ slags at 1600^oC was determined to be 0.39-1.68.

ACKNOWLEDGEMENTS

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Figures
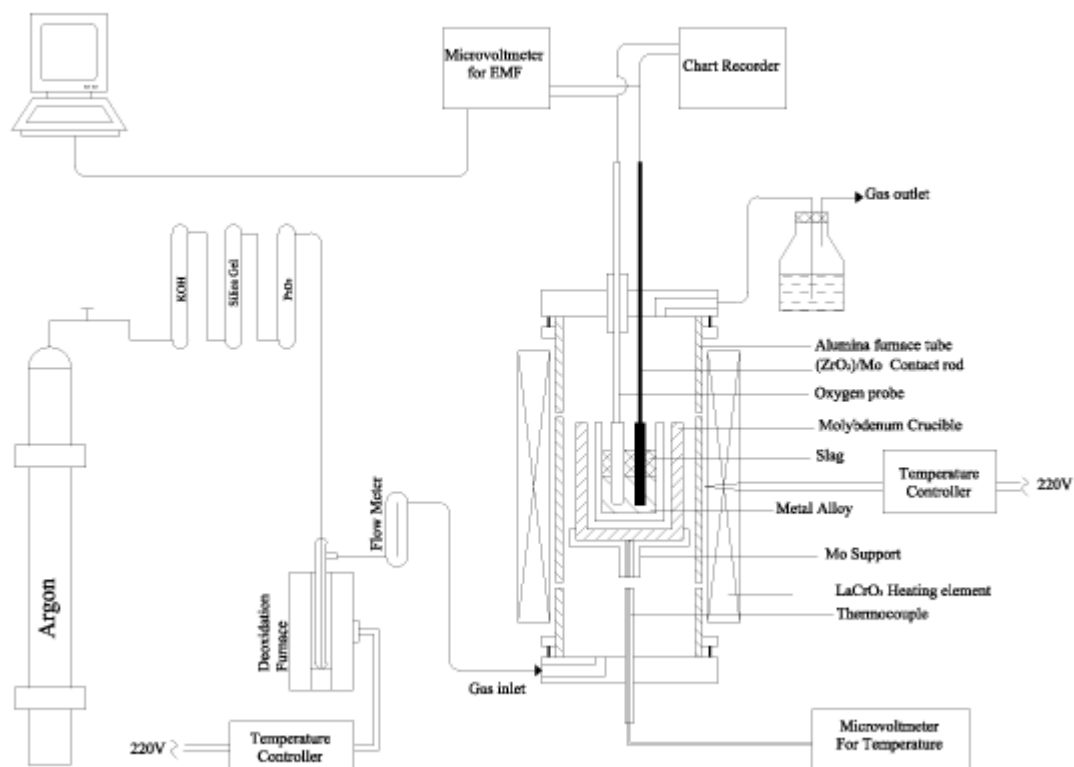
Figure 1. Schematic diagram of the experimental apparatus.
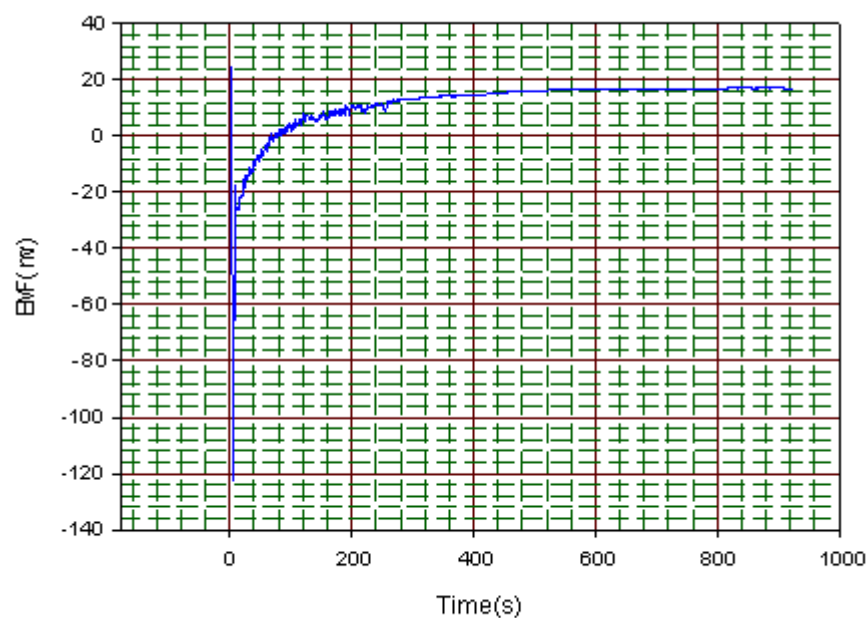

Figure 2. Typical response curve during EMF measurement
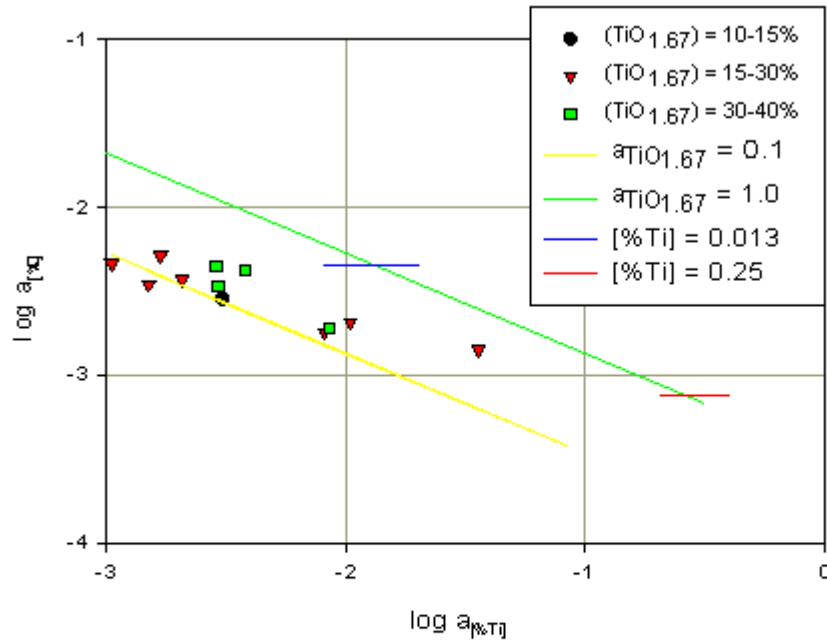
Figure 3.   Titanium deoxidation in liquid iron in the presence of CaO-SiO$_2$-TiO$_{1.67}$ **slag; calculated lines with different activities of** TiO$_{1.67}$ are shown for comparison. Deoxidation product is Ti$_3$O$_5$ between 0.013 - 0.25%Ti.
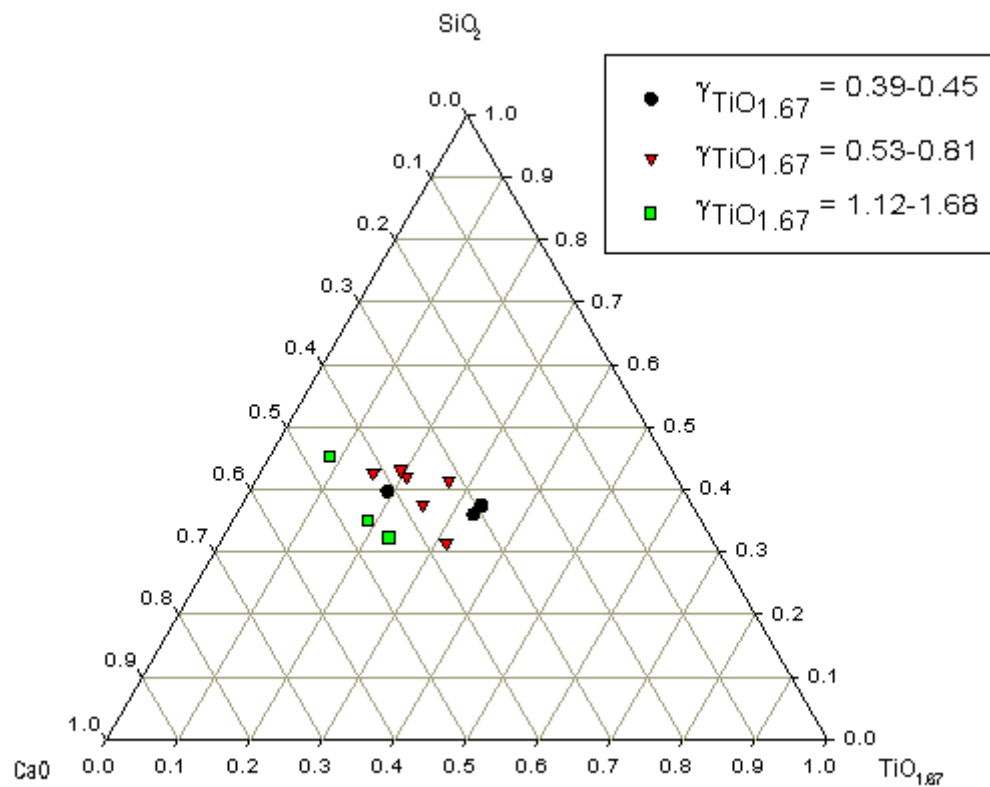

Figure 4.   **Activity coefficients for titanium oxide (**γTiO$_{1.67}$**).**

Tables

Table 1.   Experimental Results for the CaO-SiO$_2$-TiO$_{1.67}$ Slag at 1600°C.

NO.	(%CaO)	(%SiO2)	(%TiO$_{1.67}$)	$X_{(CaO)}$	$X_{(SiO_2)}$	$X_{(TiO_{1.67})}$	[%Ti]	$\log L_{Ti} = \dfrac{(\%Ti)}{[\%Ti]}$	$\log L_{Ti} = \dfrac{(\%Si)}{[\%Si]}$	[%Si]	[%O](an)
KCST1	38.4	42.3	19.3	0.416	0.427	0.157	0.0011	4.07	2.29	0.1005	0.00445
KCST2	33.6	36.2	30.2	0.374	0.375	0.252	0.0012	4.06	2.13	0.1267	0.00540
KCST3	34.0	40.9	25.1	0.373	0.420	0.207	0.0021	3.89	2.02	0.1811	0.00415
KCST4	28.5	39.8	31.7	0.319	0.415	0.267	0.0028	3.86	1.82	0.2805	0.00455
KCST5	27.4	34.0	38.6	0.311	0.360	0.329	0.0028	3.94	1.70	0.3163	0.00360
KCST6	25.8	35.3	38.9	0.293	0.375	0.333	0.0073	3.54	1.16	1.1412	0.00240
KCST7	37.7	39.0	23.3	0.411	0.398	0.191	0.0015	4.00	2.14	0.1315	0.00395
KCST8	33.0	30.0	37.0	0.372	0.315	0.314	0.0037	3.81	1.63	0.3247	0.00490
SCST9	34.3	42.2	23.5	0.376	0.431	0.193	0.0068	3.35	1.17	1.3343	0.00267
SCST10	42.4	47.0	10.6	0.450	0.465	0.084	0.0471	2.16	0.76	3.8321	0.00660
SCST11	43.7	45.8	10.5	0.463	0.453	0.084	0.0029	3.37	1.60	0.5395	0.00410
SCST12	42.5	34.5	23.0	0.462	0.350	0.188	0.0084	3.25	1.03	1.5037	0.00447
SCST13	40.7	31.4	27.89	0.447	0.323	0.230	0.0258	2.84	0.82	2.2128	0.00290

[%O](an), Oxygen analysis in the melt.

Table 1. Experimental Results for the CaO-SiO$_2$-TiO$_{1.67}$ Slag at 1600°C cont.

NO.	[%O](e)	$\log a_{[\%Ti]}$	$\log a_{[\%Si]}$	$\log a_{[\%O](emf)}$	$\log a_{[\%O](Si)}$	$\log a_{(TiO_{1.67})}$	$\log a_{(SiO_2)}$	$\log a_{(TiO_2)}$	$\log a_{(TiO_{1.5})}$	$\gamma_{TiO_{1.67}}$	$B = \dfrac{X_{(\%CaO)}}{X_{(\%SiO_2)}}$
KCST1	0.00480	-2.976	-0.988	-2.334	-2.122	-1.083	-0.977	-1.350	-0.881	0.53	0.97
KCST2	0.00540	-2.768	-0.884	-2.287	-2.198	-0.797	-0.780	-1.049	-0.603	0.63	0.99
KCST3	0.00396	-2.678	-0.723	-2.429	-2.199	-0.943	-0.903	-1.242	-0.726	0.55	0.89
KCST4	0.00494	-2.539	-0.522	-2.347	-2.208	-0.668	-0.539	-0.940	-0.464	0.81	0.77
KCST5	0.00377	-2.529	-0.466	-2.469	-2.305	-0.862	-0.726	-1.174	-0.637	0.42	0.86
KCST6	0.00275	-2.068	0.182	-2.723	-2.581	-0.823	-0.584	-1.219	-0.556	0.45	0.78
KCST7	0.00366	-2.818	-0.867	-2.457	-2.234	-1.130	-1.102	-1.438	-0.908	0.39	1.03
KCST8	0.00470	-2.417	-0.454	-2.376	-2.510	-0.594	-0.527	-0.875	-0.385	0.81	1.18
SCST9	0.00278	-2.087	0.272	-2.745	-2.697	-0.880	-0.540	-1.284	-0.609	0.68	0.87
SCST10	0.00199	-1.081	1.006	-3.250	-3.240	-0.715	-0.816	-1.288	-0.361	2.28	0.97
SCST11	0.00342	-2.513	-0.209	-2.543	-2.563	-0.969	-0.617	-1.305	-0.732	1.28	1.02
SCST12	0.00336	-1.983	0.342	-2.687	-2.971	-0.678	-0.353	-1.063	-0.418	1.12	1.32
SCST13	0.00295	-1.448	0.589	-2.848	-3.133	-0.412	-0.429	-0.850	-0.124	1.68	1.39

[%O](e), Oxygen values calculated from $a_{[\%O]}$ from the EMF readings.

$\log a_{[\%O](emf)}$, activity values calculated from the EMF readings.

$\log a_{[\%O](Si)}$, activity values calculated from the analyzed [%Si] in the melt.

Table 2. Interaction parameter values used in the present work.

e_x^y	Values	Concentration	Temperature (K)	Author(s)
e_o^o	-0.20		$-\dfrac{1750}{T}+0.734$	[11]
e_o^{Si}	-0.14	Si < 3		[12]
e_O^{Ti}	-0.30		$\log(\varepsilon_O^{Ti})=\dfrac{4848}{T}-0.817$	[13]
e_{Si}^{Si}	0.11		$\dfrac{34.5}{T}+0.089$	[14]
e_{Si}^{Ti}	0.041		1873	[15]
e_{Ti}^{Ti}	0.048		1873	[16, 17]

Table 3. **Comparison of the activity coefficient of titanium oxides in slags.**

$\gamma_{TiO_{1.5}}$	$\gamma_{TiO_{1.67}}$	γ_{TiO_2}	Slag Composition	$B = \dfrac{(\%CaO)}{(\%SiO_2)}$	Temp. (K)	Author(s)
-	0.39-2.28	-	25-44%CaO, 29-47%SiO$_2$, 10-39%TiO$_{1.67}$	0.72-1.30	1873	present work
2.3-8.8	-	0.1-0.3	CaO-MgO-Al$_2$O$_3$-SiO$_2$-TiO$_x$	0.8-2.2	1773	[10]
14.3-28	-	1.8-3.4	SiO$_2$-CaO-Al$_2$O$_3$-TiO$_2$	1	1773	[18]
59.6	-	0.97	CaO-SiO$_2$-Al$_2$O$_3$-MgO-TiO$_x$	0.42-1.3	1673-1823	[19]
9-30	-	2.0-2.6	30-34%CaO, 56-59%Al$_2$O$_3$, 1-4%TiO$_{1.5}$, 6-9%TiO$_2$, 0.1-4%Cr$_2$O$_3$		1873	[20]
-	-	0.8-1.1	0.07-3.91%V$_2$O$_5$, 4.59-25.30%TiO$_2$, 9.7-24.92%CaO, 6-36.7%MgO, 0.53-2.2%MnO, 4.3-46.09%Al$_2$O$_3$		1873	[21]
>100	-	10	3%VO$_x$, 3%NbO, 3%MnO, 0-4%Na$_2$O, 0.8%TiO$_2$ CaO:CaF$_2$:SiO$_2$=65:22:13	5	1573	[22]
0.48	-	0.13	31-35%CaO, 56-59%Al$_2$O$_3$, 9-10%TiO$_x$		1873	[23]
14.8	-	2.28	13-15%CaO, 24-31%Al$_2$O$_3$, 55-63%TiO$_x$		1873	[23]
-	-	0.108-3.77.10^{-4}	38.29-46.62%CaO, 4.55-7.24%MgO, 33.06-40.6%SiO$_2$, 6.71-7.12%Al$_2$O$_3$, 0.53-14.87%TiO$_2$	1.09-1.16	1723-1823	[24]
4.7-26	-	0.36-2.5	31-34%CaO, 56-59%Al$_2$O$_3$, 5-9%TiO$_2$, 2-4%TiO$_{1.5}$ 12-14%CaO, 28-34%Al$_2$O$_3$, 24-40%TiO$_2$, 13-32%TiO$_{1.5}$ 24-30%CaO, 49-60%TiO$_2$, 9-22%TiO$_{1.5}$			[25]