The Thermodynamics of Titanium in CaO-MgO-Al_2O_3-SiO_2-TiO_x Slags

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ABSTRACT

The thermodynamics of titanium in CaO-SiO_2-TiO_x melts with additions of MgO or Al_2O_3 was investigated using a gas-slag equilibrium technique. The equilibrium experiments were carried out at temperatures between 1783 and 1903 K, under flowing CO-CO_2-Ar gas atmosphere. The effects of oxygen potential (10^{-12} to 10^{-7} atm), CaO/SiO_2 ratios (0.55 to 1.25) and titanium oxide content (7 to 21 wt%) on the titanium partitioning between different valency states and on the ratio of the activity coefficients of $TiO_{1.5}$ and TiO_2 were determined. The results obtained show that at a given temperature, the Ti^{3+}/Ti^{4+} ratio decreases with increasing CaO/SiO_2 ratio and/or oxygen potential. The additions of MgO to the slags resulted in a further decrease in the Ti^{3+}/Ti^{4+} ratio. The dependence of Ti^{3+}/Ti^{4+} on the oxygen potential showed departure from the ideal behaviour with the Ti^{3+}/Ti^{4+} ratio being proportional to the oxygen potential raised to the power of 0.21 ± 0.01. Temperature was found to have a significant effect on the on the redox equilibria, with an associated enthalpy of about 152 ± 25 kJ/mole.

1. INTRODUCTION

Information on the properties of titanium containing silicate melts is rather limited. Publications on experimentally determined thermodynamic properties of titanium oxides cover the CaO-TiO_2-Ti_2O_3 system with high (7-80 wt%) TiO_x concentrations[1,2], the complex CaO-SiO_2-MgO-Al_2O_3-TiO_x system at very low TiO_x (~ 1 wt%) concentration[3] and a blast furnace slag containing up to 14 wt% TiO_x[4]. The composition dependence of activity of TiO_2 in the binary FeO_x-TiO_2 and MnO-TiO_2 systems and the ternary FeO-TiO_2-SiO_2, CaO-MnO-TiO_2 and SiO_2-MnO-TiO_2 systems have been determined[5-7] using the Gibbs-Duhem equation.

The distribution of titanium between liquid metal and slag, as well as the partitioning between the Ti^{4+}, Ti^{3+} and Ti^{2+} valency states in the slag, depends on the oxygen partial pressure, slag composition and temperature. Oxides containing Ti^{4+} cations are expected to demonstrate amphoteric properties while titanium oxides of the reduced Ti^{2+} and Ti^{3+} states, are expected to behave like bases[8-10]. As such, slags containing titanium in different valency states will exhibit different physical and thermodynamic properties. This highlights the importance of accurate prediction of titanium partitioning between valency states.

Studies of the CaO-MgO-SiO_2-Al_2O_3-TiO_x system and sub-systems[1,2,11], have indicated that the Ti^{3+} - Ti^{4+} equilibria is described by the O-type redox reaction, which is common to a number of transition metals:

$$(TiO_4^{4-}) = (Ti^{3+}) + 7/2\,(O^{2-}) + 1/4\,O_2(g) \quad ..\ [1]$$

The present work was undertaken as part of an investigation into the redox behaviour of titanium in the CaO-SiO_2-TiO_x-MgO-Al_2O_3 system over a range of slag basicities, titanium oxide concentrations, oxygen partial pressures and temperatures. The results obtained to date and presented here are for CaO-SiO_2-TiO_x melts with and without additions of Al_2O_3 or MgO.

2. EXPERIMENTAL

Titanium distribution between different valency states in calcium silicate based melts containing up to 21 wt% TiO_x was investigated by gas-slag equilibrium experiments. Master slags were prepared from high purity (>99.8%) CaO, SiO_2, TiO_2, Al_2O_3 and MgO by repeated melting and grinding. Twelve master slags with different CaO/SiO_2 ratios (0.55, 0.7, 1.0 and 1.25) and three levels of TiO_2 (7, 14 and 21 wt%) were prepared by melting appropriate amounts of reagents in platinum crucible at temperatures above their liquidus. Four other master slags (with 14 wt% TiO_2 and a CaO/SiO_2 ratio of about 0.7) containing Al_2O_3 or MgO content of 5 or 15 wt% were also prepared. The master slags were analysed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) prior to the experiments.

The gas atmosphere in the tube furnace was controlled by Ar-CO-CO_2 gas mixtures flowing at about 1 l/min. For each experiment the required gas mixture was prepared by mixing appropriate amounts of purified Ar, CO and CO_2 in a column of glass beads before delivering the gas mixture to the furnace. The gases were purified by passing them through oxygen getter furnace, containing copper turning or titanium granules, and silica gel for removing moisture. In the case of Ar and CO, they were also also passed through Ascarite to remove CO_2. The flow rates of gases were controlled using pre-calibrated mass flow meters. For the preparation of mixtures with high CO/CO_2 ratios, a pre-mixed bottle of Ar-3%CO_2 was used instead of pure CO_2 and the composition of the final mixture was checked using a mass spectrometer. The flowing Ar-CO-CO_2 gas mixture was delivered onto the surface of the slag sample by an alumina tube.

The equilibrium experiments were carried out in a vertical $MoSi_2$ furnace fitted with water cooled brass end caps to isolate the atmosphere inside the alumina work tube. The temperature of the hot zone was measured by a Pt-6%Rh/Pt-30%Rh thermocouple touching the bottom of the crucible containing the slag. The accuracy of the temperature measurements was estimated to be within 5 K. At oxygen partial pressures between 10^{-7} and 10^{-9} atm, a platinum crucible was used to contain the slag. At oxygen potentials of 10^{-10} atm (CO/CO_2 ratio of about 34 and higher at 1843 K) and lower thick walled molybdenum crucibles were used, as the platinum crucible became brittle.

For each experiment about 4 g of the slag was placed in a crucible which was lowered into the hot zone of the furnace as the reducing gases were turned on. After the desired reaction period, the sample was quickly withdrawn from the furnace and quenched by immersing the bottom portion of the crucible into water. Care was taken to avoid direct contact between the slag and water.

The quenched slag sample was then analysed by ICP-AES for major components. The total amount of reduced titanium (Ti^{3+} and Ti^{2+}) in the slags was determined by a modified version of an indirect potentiometric redox titration method[12]. This scheme involved dissolution of the slag in HF-HCl-H_2O solution with excess Fe^{3+}, under an argon atmosphere. The reduced titanium is oxidised by the ferric ions through the reaction:

$$xTi^{3+} + yTi^{2+} + (x+2y)Fe^{3+} = (x+y)Ti^{4+} + (x+2y)Fe^{2+} \quad ..[2]$$

Following dissolution, the resulting Fe^{2+} solution was titrated with standardised 0.005M ceric sulphate solution, using ferrous 1,10-phenanthroline (ferroin) as a buffer. This method has a detection limit of approximately 10^{-6} moles of reduced titanium and an absolute error of ±5% of the detected amount. The quantity of titanium in the Ti^{4+} valency state was calculated as the difference between total and reduced titanium. Since under the present experimental conditions, the concentration of Ti^{2+} is likely to be relatively low in comparison with the Ti^{3+}, all reduced titanium is reported as Ti^{3+}.

Two series of kinetic experiments were carried out to determine the time required for approaching equilibrium between gas and slag. In one of these series a master slag with CaO/SiO_2 ratio of 0.55 and 21 wt% TiO_2 was reacted with Ar-CO-CO_2 ($CO/CO_2 \simeq 10.7$) at about 1843 K for 4, 6 and 11 hrs. In the second series the same slag was reduced by a more reducing gas mixture ($CO/CO_2 \simeq 456$) for 4, 6 and 18 hrs at 1843 K. The results from the first series showed that equilibrium was approached after 4 hrs. For the second series, it was found that 6 hrs was sufficient to approach equilibrium at 10^{-12} atm. On the basis of these results an equilibration time of 6 hrs was used for oxygen potentials of 10^{-10} to 10^{-7} atm and 8 hrs for 10^{-12} atm.

3. RESULTS AND DISCUSSION

3.1 Effect of temperature

In silicate based melts, the enthalpy of reduction of redox reactions is generally within the range of 42-293 kJ/mol[13]. The reduction of TiO_2 is endothermic, and increasing the reaction temperature should stabilise the Ti^{3+} oxidation state. Figure 1 shows the typical variation of the log (Ti^{3+}/Ti^{4+}) with the reciprocal of temperature from this and other studies[2,11]. It is evident that for a given oxygen potential, increasing the temperature results in stabilisation of the lower oxidation state of titanium.

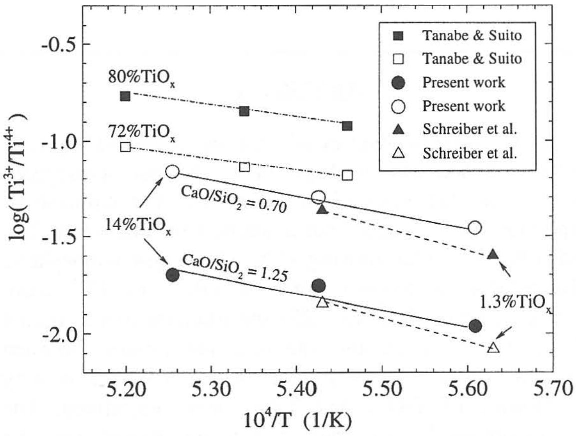

Figure 1. Variation of log (Ti^{3+}/Ti^{4+}) with reciprocal temperature in various titania containing slags at comparable oxygen potentials. (CaO-TiO_x; Tanabe and Suito[2], CaO-SiO_2-TiO_x; Present work, CaO-MgO-SiO_2-Al_2O_3-TiO_x; Schreiber *et al.*[11]).

For the reaction:

$$TiO_2(s) = TiO_{1.5}(s) + 0.25\ O_2\ (g) \quad .. [3]$$

$$\Delta G^\circ = 189\,954 - 48.5\ T \quad (J/mol) \quad .. [4]$$

and the enthalpy of reaction is about 190 kJ/mol[14]. Based on the above Gibbs free energy data and the experimental data on the redox equilibria, the ratio of activity coefficients ($\gamma_{TiO1.5}/\gamma_{TiO2}$) was calculated. These results showed only a small increase in the $\gamma_{TiO1.5}/\gamma_{TiO2}$ ratio with increasing temperature. Neglecting this small change and assuming that the $\gamma_{TiO1.5}/\gamma_{TiO2}$ ratio in these slags is not affected by temperature, then the enthalpy of the reaction [3] (ΔH) from the plot of log (Ti^{3+}/Ti^{4+}) against the reciprocal temperature can be deduced, i.e;

$$\log\frac{(Ti^{3+})}{(Ti^{4+})} = -\frac{\Delta H}{2.303R}\left(\frac{1}{T}\right) + C \qquad .. [4]$$

where; R is the gas constant, T is the absolute temperature, and C is a constant which is assumed to be independent of the temperature.

The reduction enthalpy calculated from the results of the present study is about 152 ± 25 kJ/mole and appears to be independent of the slag basicity. This value lies between those determined by Tanabe and Suito[2] (104 ±12 kJ/mol) and Schreiber *et al.*[11] (293 ± 96 kJ/mol). The differences between the experimentally determined ΔH values may be attributed to differences in the $\gamma_{TiO1.5}/\gamma_{TiO2}$ ratio for different slag compositions, as discussed by Mysen[15]. It is interesting to note that the enthalpy of reduction appears to increase as the concentration of TiO_x in the slag decreases.

3.2 Effects of oxygen potential and slag chemistry

According to reaction [3], if the $\gamma_{TiO1.5}/\gamma_{TiO2}$ is not affected by oxygen potential (p_{O_2}), then a plot of log (Ti^{3+}/Ti^{4+}) versus log (p_{O_2}) should yield a straight line with a slope of -0.25. This relationship has been experimentally investigated by a number of researchers[1,2,11] and the slope has been found to lie between -0.25 and -0.20. The results from the present study, for the $CaO\text{-}SiO_2$-14wt% TiO_x system at p_{O_2} in the range 10^{-12} to 10^{-7} atm, are illustrated in Figure 2. The Ti^{3+}/Ti^{4+} ratios for $p_{O_2} = 10^{-12}$ atm were determined at 1873 K and re-calculated at 1843 K, using the experimentally determined reduction enthalpy. In Figure 2 all lines, which are plotted for different CaO/SiO_2 ratios, have slopes close to -0.21. The deviation from the slope of -0.25 indicates that the $\gamma_{TiO1.5}/\gamma_{TiO2}$ ratio is affected by the Ti^{3+}/Ti^{4+} partitioning which, in turn, is determined by the oxygen potential.

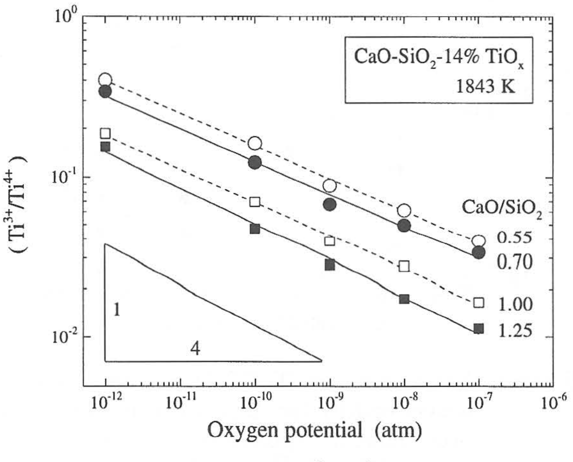

Figure 2. Variation of the Ti^{3+}/Ti^{4+} ratio with oxygen potential in $CaO\text{-}SiO_2\text{-}TiO_x$ melts at 1843 K.

Although this departure from ideal behaviour has been observed in other systems containing transition metal oxides such as FeO_x and MnO_x[16-18], it is of interest to examine the variation of the $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ with oxidation state of the slag or in particular the concentration of the $TiO_{1.5}$. In Figure 3, the calculated values of $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ over a narrow temperature range (1843 to 1873 K) are plotted against the concentration of $TiO_{1.5}$. It is evident that when the concentration of $TiO_{1.5}$ is greater than 2 wt%, the $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ ratio is virtually independent of the concentration of $TiO_{1.5}$ or the oxidation state of melts. However, the dependence on the $TiO_{1.5}$ concentration appears to become more pronounced at lower $TiO_{1.5}$ contents and higher slag basicity. This apparent dependence is likely to be influenced by the analytical errors in the determination of very low concentrations of Ti^{3+}. Ignoring the apparent sharper dependence at very low $TiO_{1.5}$ content, then the relatively mild dependence is not unreasonable, specially when the small effect of temperature differences is taken into consideration.

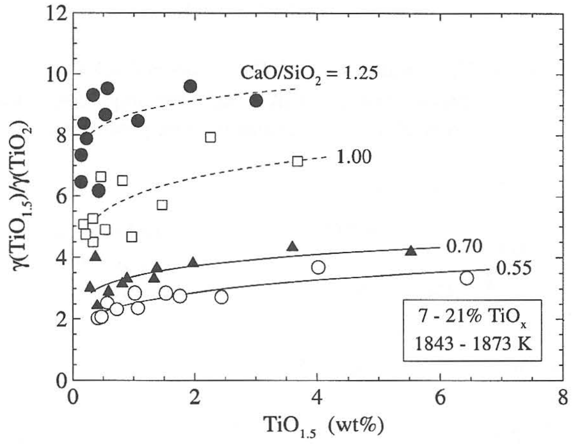

Figure 3. Variation of $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ ratio with concentration of $TiO_{1.5}$ in $CaO\text{-}SiO_2\text{-}TiO_x$ slags at 1843 to 1873 K.

Figure 3 shows that there is a relatively strong effect of basicity expressed as CaO/SiO_2 ratio (on wt% basis) on the ratio of activity coefficients of titanium oxides. In Figures 4 and 5 the measured Ti^{3+}/Ti^{4+} ratios are plotted against the CaO/SiO_2 ratio in $CaO\text{-}SiO_2\text{-}TiO_x$ melts. These Figures show that at a given temperature and p_{O_2} the proportion of titanium in the lower oxidation state increases with decreasing CaO/SiO_2 ratios between 0.55 and 1.25. Figure 5 also shows an interesting behaviour with respect to the TiO_x content of the slags, i.e. increasing the TiO_x concentration from 7 to 14 wt% reduced the Ti^{3+}/Ti^{4+} ratio by increasing the $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ ratio. This trend implies that addition of up to 14% TiO_x makes the slag slightly more basic. This is in accord with sulphide capacity data by Brown *et al.*[18] on $CaO\text{-}SiO_2\text{-}TiO_x$ system. However, the results on titanium partitioning in slags containing 21 wt% TiO_x are not consistent with this trend. For these slags, the Ti^{3+}/Ti^{4+} ratio is close to, or slightly higher that the ratio for measured for 14 wt% TiO_x. A possible explanation for this non-linear dependence might be the formation of more complex anions at high TiO_x concentrations[20-23], such as $Ti_2O_7^{6-}$ and $Ti_2O_6^{4-}$ rather than TiO_4^{4-}.

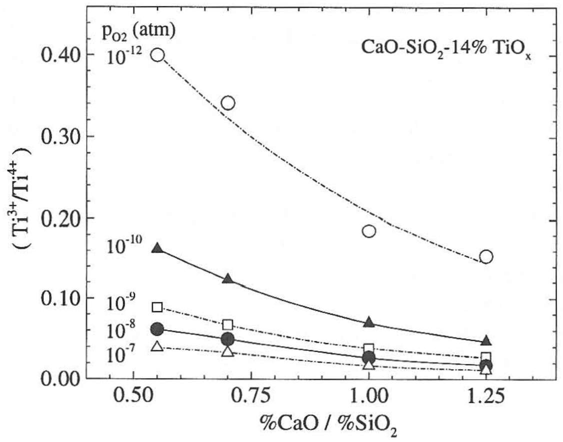

Figure 4. Variation of the Ti^{3+}/Ti^{4+} ratio in CaO-SiO_2-TiO_x melts with CaO/SiO_2 ratio for slags containing 14 wt% TiO_x at various oxygen potentials.

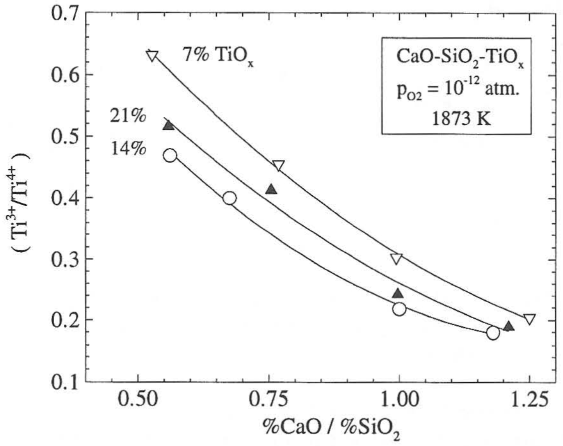

Figure 5. Variation of the Ti^{3+}/Ti^{4+} ratio in CaO-SiO_2-TiO_x melts with CaO/SiO_2 ratio for slags containing 7, 14 and 21 wt% TiO_x at an oxygen potential of 10^{-12} atm and 1873 K.

It was shown in Figure 3 that the $\gamma_{TiO1.5}/\gamma_{TiO2}$ ratio increases with increasing slag basicity. This behaviour was observed at all TiO_x concentrations and CaO/SiO_2 ratios studied. This differ from the findings of Ito and Sano[3], where it was found that both TiO_2 and $TiO_{1.5}$ behave as bases in CaO-SiO_2-10%Al_2O_3-2%TiO_x melts with CaO/SiO_2 ratios below one. At CaO/SiO_2 ratios above one, $TiO_{1.5}$ still behaved as a base while TiO_2 acts as an acidic oxide. The $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ ratio was found to decrease with increasing slag basicity at a CaO/SiO_2 ratio below one and increase when the slag basicity was above one.

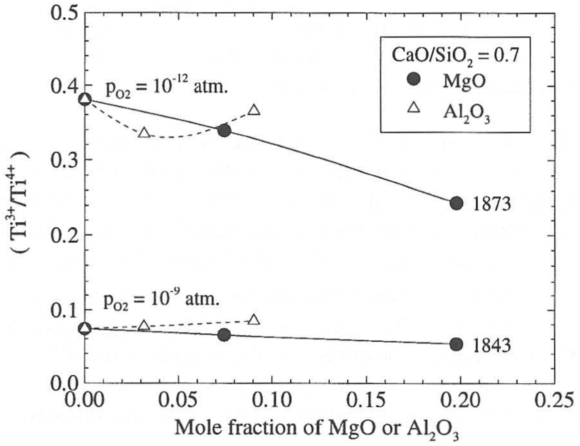

Figure 6. Dependence of Ti^{3+}/Ti^{4+} ratio on the additions of Al_2O_3 and MgO to CaO-SiO_2-14%TiO_x slag at different temperatures and oxygen potentials.

In Figure 6 the measured effects of MgO and Al_2O_3 to the CaO-SiO_2-14%TiO_x based slags are shown at two oxygen potentials and temperatures. Additions of MgO decreased the Ti^{3+}/Ti^{4+} ratio, indicating that introduction of MgO to the slag with CaO/SiO_2 ratio of 0.7 results in increased basicity of the slag and hence stabilising the higher oxidation state of titanium. The experimental results for Al_2O_3 additions are scattered; it may be suggested that the effect of Al_2O_3 on the Ti^{3+}/Ti^{4+} ratio is relatively small.

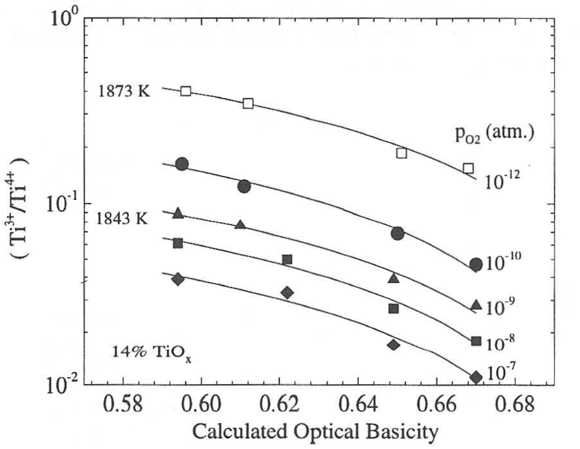

Figure 7. Variation of log (Ti^{3+}/Ti^{4+}) with the calculated optical basicity for slags containing 14% TiOx over a range of oxygen potentials (10^{-10} to 10^{-7} atm at 1843K; 10^{-12} atm at 1873 K).

To analyse the effect of slag composition on the titanium Ti^{3+} - Ti^{4+} partitioning, the Ti^{3+} /Ti^{4+} ratio was examined as a function of slag optical basicity, Λ. The optical basicities for various slags were calculated using Λ values for the individual oxides recommended by Young *et al.*[24] The optical basicity for Ti_2O_3 is unknown; based on the calculation of the electronegativity of oxygen in Ti_2O_3 [24,25] it was estimated to be about 0.76. The same approach for TiO_2 gave an optical basicity of 0.60, compared to the 0.65 value recommended by Young *et al.*[24]

In Figure 7, typical variations of log (Ti^{3+}/Ti^{4+}) with the calculated optical basicity are presented for slags at different oxygen potentials. While the variation of log (Ti^{3+}/Ti^{4+}) with the calculated Λ for these slags does not appear to follow a linear dependence, as an approximation a value of about -6.2 may be taken to represent the average slope. Combining this with the measured dependence of Ti^{3+}/Ti^{4+} ratio on oxygen potential and temperature, the following correlation was obtained for calculation of the titanium distribution between Ti^{3+} and Ti^{4+} valency states:

$$\log(Ti^{3+}/Ti^{4+}) = 5.17 - 0.21\log(p_{O_2}) - 7940/T - 6.2\Lambda \qquad .. [5]$$

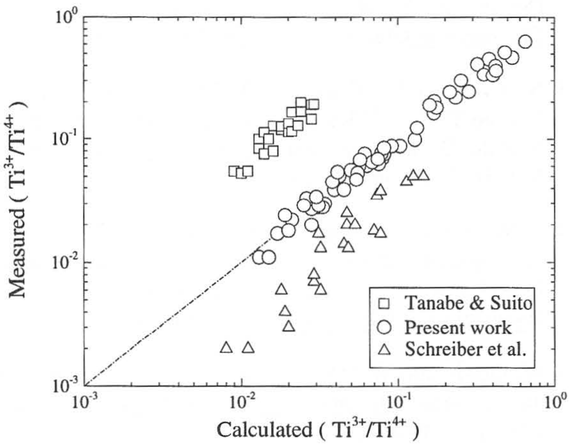

Figure 8. Comparison of the measure and calculated values of Ti^{3+}/Ti^{4+} ratios.

As shown in Figure 8, equation [5], gives a reasonably good representation of the data obtained in the present study. Experimental results obtained by Schreiber *et al.*[11] and Tanabe and Suito[2] show some deviation from the calculated data. These deviations are partly due to the differences in the measured effect of temperature on the Ti^{3+}/Ti^{4+} ratio, as shown in Figure 1 and discussed in section 3.1.

CONCLUSIONS

Equilibrium data on the Ti^{3+}-Ti^{4+} redox reaction in CaO-SiO_2-TiO_x melts containing up to 21 wt% TiO_x shows that the Ti^{3+}/Ti^{4+} ratio increases with decreasing oxygen potential and CaO/SiO_2 ratio. Over the temperature range of 1783 to 1903 K, the apparent enthalpy of the reduction reaction for slags containing 14% TiO_x was found to be about 152 ± 25 kJ/mole and independent of slag basicity.

The dependence of the Ti^{3+}/Ti^{4+} on the oxygen potential showed some deviation from ideal behaviour in slags containing 7 to 21 wt% TiO_x and CaO/SiO_2 ratios in the range 0.55 to 1.25. This small departure resulted in mild variation of the $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ ratio with oxygen potential. The $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ ratio increased from about 3 to 10 as the CaO/SiO_2 ratio was increased from 0.55 to 1.25.

Increasing the TiO_x content from 7 to 14% resulted in a reduction in the Ti^{3+}/Ti^{4+} ratio, while further addition of TiO_x (21 wt%) did not follow the same trend. This behaviour suggests the possibility of formation of more complex titania anions such as $Ti_2O_6^{4-}$ in high titania slags.

While additions of up to 15 wt% MgO to the slags with CaO/SiO_2 ratio of 0.7, resulted in a reduction in the Ti^{3+}/Ti^{4+} ratio at a given temperature and oxygen potential, addition of Al_2O_3 did not show a significant effect.

The measured effects of slag chemistry on the titanium partitioning between different valency states could be reasonably well correlated with the calculated optical basicity of slags.

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