Note

Equilibria between Silica Saturated MnO–SiO₂–TiO_x Slag and Mn–Si–Ti Melt

1. Introduction

Oxide metallurgy that has recently been developed¹⁾ is a process for enhancing steel strength by dispersing fine oxide particles in a metal matrix and by controlling physical and chemical properties of these particles. Oxide particles that form in different stages during solidification can act as nucleation sites for other precipitates such as carbides, nitrides and sulfides. These available inclusions can influence iron transformations by providing nucleation sites in the metal matrix or restraining grain growth in the subsequent thermo-mechanical treatments.

Some researches have been conducted to investigate the equilibrium reactions relating to oxide metallurgy. Mizoguchi *et al.*^{2,3)} has used a model to evaluate the composition of the inclusions in liquid steel as a function of mass of the deoxidizing agent added. The results are calculated for deoxidization of steel with Zr, Ti and Al at 1570°C. The equilibrium composition of liquid steel and MnO–TiO_{1.5} inclusions during deoxidization with manganese and titanium were also measured by Morioka *et al.*⁴⁾ However, lack of thermodynamic information at lower temperatures limits these studies to liquid steel.

This study is focused on the thermodynamic properties of MnO–SiO₂–TiO_x inclusions formed during solidification of Ti-deoxidized steels. Good thermo-mechanical properties of this group of steels are supposed to be a result of their finely dispersed inclusions. In the present study the equilibria between MnO–SiO₂–TiO_x slag and Mn–Si–Ti metal were investigated using a silica crucible at 1300 and 1400°C.

2. Experimental Procedure

MnO–SiO₂–TiO₂ master slags were prepared from mixtures of reagents in a graphite crucible in an argon atmosphere. Semiconductor grade silicon, electrolytic manganese and reagent grade titanium were premelted in a silica crucible by an induction furnace.

Six grams of master slag and four grams of master alloy were placed in a silica crucible, which was then placed in a porous alumina holder and put into a vertical resistance furnace. A TiO₂ pellet pressed under 980 MPa and sintered at 1500°C was used in the case of SiO₂–TiO₂ doubly saturation composition. Temperature was kept constant by a PID controller connected to a Pt–Rd thermocouple inside the furnace. Experiments were carried out in a dehumidified argon atmosphere. Primary experimental results had shown that 30 h are enough to establish the equilibrium so the experimental time was selected between 30 and 40 h.

After the experiment, the molten sample was cooled by argon flushing. Metal and slag were carefully separated and cleaned and samples of both phases were subjected to chemical analyses after fusing with alkaline. Manganese in metal and slag was analyzed by atomic absorption photometry and titanium in metal and slag by colorimetry using diantipyrylmethane. Although silica content of some slag samples was confirmed by gravimetric method, it was calculated as the remainder of slag after subtracting TiO_{1.5}, TiO₂ and MnO contents in all cases. The same was performed for the silicon content of metal by using the analysis results of titanium and manganese. Oxygen was analyzed by fusion technique in a helium atmosphere detected by infrared absorption. For measuring Ti³⁺, slag samples were dissolved in HCl solution and Ti³⁺ ions were converted to Ti⁴⁺ using Fe³⁺ solution. The content of converted Fe²⁺ in solution was finally determined by titration with potassium dichromate. Ti⁴⁺ content of slag was calculated by subtracting Ti³⁺ content from total titanium content of slag.

3. Results and Discussion

The following equations were in equilibrium in these experiments:

This system has two degrees of freedom at constant temperature and pressure. Hence the degree of freedom becomes unity by saturating the system with SiO₂.

Experiments were started from the MnO–SiO₂ binary system. After finding the equilibrium composition of the Mn–Si metal phase, titanium and titanium oxide were gradually added to the metal and slag. Final compositions of metal and slag for all experiments are listed in **Table 1**. Titanium distribution between metal and silica saturated slag is shown in **Fig. 1**. There is a linear

Table 1. Final compositions of metal and slag.

Sample No.	Metal (mass %)			Slag (mass %)		
	Ti	Mn	O	Ti	Mn	Ti ³⁺
101	-----	74.41	0.019	-----	40.03	-----
102	0.55	70.97	0.131	1.07	37.86	0.97
103	1.31	60.71	0.012	2.67	37.21	0.93
104	1.95	61.31	0.042	2.82	37.87	1.64
105	4.79	37.41	0.031	7.25	34.36	2.53
106	7.32	21.74	0.051	11.79	34.77	5.41
107	8.93	13.31	0.052	13.34	32.64	3.32
108	10.64	1.51	0.307	28.26	24.21	11.71
109	10.64	2.26	0.157	18.36	29.17	8.51
110	12.52	2.19	0.291	33.27	20.09	14.35
111	12.15	1.84	0.247	33.4	20.85	n.d.

n.d. not detected

Fig. 1. Titanium distribution between Mn-Si-Ti metal and MnO-SiO₂(sat.)-TiO_x slag at 1400°C.

Fig. 2. Silicon, manganese and oxygen content of metal vs. the titanium content.

relationship between them up to 10 mass% Ti and then TiO_x content of slag drastically increases with increasing titanium content of the metal. TiO_x in this graph is the sum of TiO₂ and TiO_{1.5}. In Fig. 2 change in silicon, manganese and oxygen contents of metal with increasing titanium content of the metal can be seen. Silicon and oxygen contents increase with titanium while manganese decreases. Oxygen content of the metal increases with increasing titanium content probably due to the strong affinity of titanium for oxygen.

The silica saturation line in the MnO-SiO₂-TiO_x ternary system at 1400°C is shown in Fig. 3 together with some points of silica saturation composition at 1300°C. The line starts from the MnO-SiO₂ binary system and ends at the SiO₂-TiO₂ doubly saturated composition. The results of this study are reasonably in agreement with those of Amitani *et al.*⁵⁾ for MnO-SiO₂-TiO₂ system at 1500°C as shown at the same graph.

Empirical linear relationships between MnO, SiO₂ and TiO_x contents are expressed as follows:

$$\text{mass\% SiO}_2 = 1.24 \times (\text{mass\% MnO}) - 14.2 \quad \text{.....(4)}$$

$$\text{mass\% TiO}_x = -2.24 \times (\text{mass\% MnO}) + 114.2 \quad \text{....(5)}$$

Fig. 3. Silica saturation line in the MnO-SiO₂-TiO_x slag system. Broken line shows the results of Amitani⁵⁾ for MnO-SiO₂-TiO₂ system at 1500°C.

Fig. 4. Ti³⁺ and Ti⁴⁺ of slag as a function of total Ti in slag.

Fig. 5. Metal composition in equilibrium with silica saturation line at 1400°C.

Although some experiments were carried out at 1300°C, composition range of the metals was limited because the solid metal phase is stable at high titanium content.

The results of valence analysis are shown in Fig. 4. Although the amount of TiO_2 is larger than $\text{TiO}_{1.5}$, the ratio of $\text{Ti}^{4+}/\text{Ti}^{3+}$ does not change significantly with slag composition except when TiO_2 is saturated.

Metal composition in equilibrium with the slag on the silica saturation line is shown in Fig. 5. Increase in silicon content with increasing titanium in metal is significant.

4. Conclusion

Equilibria between $\text{MnO-SiO}_2\text{-TiO}_x$ slag and Mn-Si-Ti have been investigated and the distribution ratios of elements between metal and slag are shown in this study. These results can be used to calculate the activities of slag components and evaluate the precipitation of inclusions in steel matrix provided the activities in the Mn-Si-Ti system are available. The silica solubility line at 1400°C was determined and the liquid region was compared with the $\text{MnO-SiO}_2\text{-TiO}_2$ slag system. The Ti^{4+} content of silica saturated slags is higher than that of Ti^{3+} , $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio being almost constant, except when TiO_2 is saturated.

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