Ferrous Oxide Activity in $\text{FeO-TiO}_2\text{-CaO-Al}_2\text{O}_3$ System

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Ferrous oxide activity has been determined in molten synthetic slag mixtures of the quaternary system $\text{FeO-TiO}_2\text{-CaO-Al}_2\text{O}_3$ at constant levels of Al_2O_3 . Furthermore, in the course of determining the FeO activity in this quaternary system, the ternary system $\text{FeO-CaO-Al}_2\text{O}_3$ was also investigated at 1450°C.

The technique used to measure the ferrous oxide activity in the investigated systems was the well established one of gas-slag-metal equilibration in which molten slags contained in armco iron crucibles are exposed to a flowing gas mixture with a known oxygen potential until equilibrium has been attained. After equilibration, the final chemical analysis of the slags give compositions having a particular ferrous oxide activity corresponding to the oxygen potential of the gas mixture.

The effect of Al_2O_3 additions on the FeO activity was determined. The results are presented as a series of iso-activity curves on pseudo-ternary diagrams. The interdependence between the ferrous oxide activities and slag composition was also studied.

KEY WORDS: ferrous oxide activity; $\text{FeO-CaO-Al}_2\text{O}_3$ system; $\text{FeO-TiO}_2\text{-CaO-Al}_2\text{O}_3$ system; steelmaking slags.

1. Introduction

The high affinity of titanium for both nitrogen and carbon has attracted attention of metallurgists to carry out many studies for using titanium in stabilizing of nitrogen, grain coarsening inhibiting at high temperatures, grain refinement and precipitation strengthening of the matrix.

Although the very attractive results obtained when using titanium addition,¹⁻²⁵⁾ the growth and acceptance of the production of titanium-microalloyed steels is still relatively limited. This limitation is mainly due to the very strong affinity of titanium for oxygen and therefore poor titanium recoveries are experienced.

Hence, for the effective use of titanium to produce titanium-microalloyed steels, the oxidation of titanium should be minimized. This aim can be realized if the concentration of oxygen, hence the activity of oxygen in metal, is kept as low as possible. The oxygen activity in the metal is directly related to the square root of the oxygen partial pressure.²⁶⁾ Thus, if the activity of oxygen in the slag is kept as low as possible, then so also will be the activity of oxygen in metal.

The oxidizing power of slag is reported in terms of its iron oxide activity, a_{FeO} , as iron oxide has a far higher oxygen pressure than any of the other constituents in the slag. This clarifies the prime importance of controlling the FeO activity to minimize the oxidation of titanium.

In addition, the ferrititanium added usually contains a considerable amount of aluminium due to its production

by alumino-thermic process, and consequently the slag formed when making these types of steels is expected to contain Al_2O_3 and TiO_2 . Furthermore, the necessity of lime addition for desulphurization and dephosphorization results in higher content of CaO in the formed slag.

The aim of this study is to investigate the ferrous oxide activity in the quaternary system $\text{FeO-TiO}_2\text{-CaO-Al}_2\text{O}_3$ at 1450°C. In the course of determining the effect of additions of FeO activity, the ternary system $\text{FeO-CaO-Al}_2\text{O}_3$ was also investigated at 1450°C.

2. Experimental

The technique used to measure the ferrous oxide activity in the investigated slag systems was the well established one of gas-slag-metal equilibration in which molten slags contained in armco iron crucibles are exposed to a flowing gas mixture with a known oxygen potential until equilibrium has been attained.

The gas mixtures contained 50% argon by volume, while the proportion of CO_2 and H_2 were varied so as to generate different oxygen potentials to give the desired values of a_{FeO} .

The molten slags were held in armco iron crucibles to react with the oxygen of the gas mixture and oxidize the iron from the crucibles according to the following reaction:

Consequently, the ferrous oxide content of the slags increased with time and their starting compositions changed until chemical equilibrium was attained. The final compositions of the slags were then determined by chemical analysis.

The quaternary system $\text{FeO-TiO}_2\text{-CaO-Al}_2\text{O}_3$ was investigated in this study, in order to investigate the iso-activity curves in this quaternary system at constant levels of Al_2O_3 . The slags of the basic ternary $\text{FeO-TiO}_2\text{-CaO}$ containing the same initial Al_2O_3 was equilibrated with different gas mixtures. After equilibration, the Al_2O_3 contents of these slags were decreased. The average of the final Al_2O_3 contents, of all the slags, which were determined by chemical analysis, was calculated and was considered the Al_2O_3 content of these slags.

The results of quaternary system $\text{FeO-TiO}_2\text{-CaO-Al}_2\text{O}_3$ are presented as a series of iso-activity curves on pseudo-ternary diagrams each corresponding to a constant mol% of Al_2O_3 .

2.1. Materials

The various slag components were of the highest purity which could be obtained or prepared. Ferrous oxide was prepared by decomposition of ferrous oxalate followed by quenching, crushing and analysis. The purest form of titania was used after calcination at 1000°C and chemically analysed to check its titanium content. The lime was obtained by calcination of analar calcium carbonate, stored in a sealed container and recalced occasionally to decompose any carbonate or hydroxide which may have formed. The purest form of alumina was used. Armco iron was used to make the iron crucibles with the dimensions 10 mm in inner diameter and 12 mm in height.

2.2. Experimental Apparatus

The experimental apparatus used in this study consists mainly of two parts, gas mixing unit and horizontal tube furnace. The gas mixing unit consists mainly of three calibrated flowmeters. Each flowmeter was used to adjust the flow rate of one of the three gases CO_2 , H_2 and argon. Argon was passed over copper powder preheated to 550°C to remove any oxygen contamination. Each of these gases was dried by passage through drying tower prior to measurement of their separate flow rates. Each gas mixture contained 50% argon by volume and the ratio of CO_2/H_2 was varied according to the ferrous oxide activity desired.^{27,28)} The total flow rate used was $400\text{ cm}^3\cdot\text{min}^{-1}$. The gases were intimately mixed in a tube filled with small glass beads and further dried just before entering the reaction tube by passing through a tower containing magnesium perchlorate. A bubbler situated after the reaction tube provided a visual record of the flowing gas.

A horizontal tube furnace was used in these experiments. It has an alumina tube and a hot zone of 6 cm which can contain four crucibles. A Pt-Pt-13%Rh thermocouple was inserted inside the reaction tube and in the center of hot zone.

2.3. Experimental Procedure

An alumina tray carrying four crucibles, each of which containing intimately mixed slag with certain composition, was placed in the hot zone of the furnace and the argon gas was passed about five minutes to exhaust the air from the furnace tube. The furnace was then switched on, the temperature of the furnace was raised gradually over a period of five hours until the temperature reached 1450°C which is the working temperature. During this period argon gas was passing continuously at a flow rate $200\text{ cm}^3\cdot\text{min}^{-1}$.

The slag was left half an hour after the temperature reached 1450°C to ensure complete melting and homogeneity of slag mixtures. The hydrogen and carbon dioxide gases were allowed to pass by certain ratio to give a certain oxygen potential corresponding to a certain ferrous oxide activity. The slags were remained under this condition three hours which were sufficient to establish equilibrium as it has been shown by preliminary investigations. After equilibrium time, hydrogen and carbon dioxide were turned off and the furnace was cooled to room temperature while argon continued to flow through the reaction tube.

After cooling to room temperature, the alumina tray was withdrawn from the furnace tube and each crucible was compressed to break away the slag. Each slag was ground to -170 mesh by an agate mortar demagnetized and stored in sealed container ready for chemical analysis.

2.4. Chemical Analysis of Slag

The slags studied contained a fair proportion of titania. Thus, fusion was necessary to render all the constituents soluble in acid. Fusion was accomplished using a 2:1 mixture of sodium carbonate and sodium tetraborate, and the cake was dissolved in 1:4 analar hydrochloric acid.

Ferrous oxide was determined by 1,10-phenanthroline method, where iron was reduced to the ferrous state by hydroxylamine and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The absorbance of the coloured solution was measured by spectrophotometer at 510 nm .²⁹⁾

Titania, calcium oxide, and alumina oxide were each obtained by atomic absorption spectrophotometry analyzer (2380 PERKIN), using previously determined calibration curves.

3. Results and Discussion

In this study, the standard state for the activities of FeO was FeO in equilibrium with solid δ -iron at 1450°C , which has the formula $\text{Fe}_{0.978}\text{O}$. It is this, rather than stoichiometric FeO, which is referred in all discussion.

The activity of FeO in the quaternary system $\text{FeO-TiO}_2\text{-CaO-Al}_2\text{O}_3$ was determined at constant levels of Al_2O_3 and at 1450°C . The Al_2O_3 investigated levels are 9.7, 13 and 18 mol%. The final chemical analysis of the slag equilibrated with the different gas mixtures in the investigated system are given in **Table 1**. The activ-

Table 1. Final chemical analysis of the slag equilibrated with the different gas mixtures in the investigated FeO–TiO₂–CaO–Al₂O₃ system at 1450°C.

CO ₂ /H ₂	a_{FeO}	Chemical Composition, Mole %			
		FeO	TiO ₂	CaO	Al ₂ O ₃
0.263	0.4	72.5	0	17.8	
		66.3	2.4	21.6	
		61.7	8.0	20.6	9.7
		62.9	10.9	16.5	
0.320	0.5	77.1	0	13.2	
		71.9	1.4	17.0	
		67.0	4.0	19.3	9.7
		66.8	7.5	16.0	
0.370	0.6	86.0	0	4.3	
		79.0	4.1	7.2	
		77.0	6.0	7.3	9.7
		76.1	12.6	1.6	
0.263	0.4	72.0	0	15.0	
		69.0	1.5	16.5	
		67.0	4.5	15.5	
		63.8	8.2	15.0	13.0
		64.0	11.5	11.5	
		66.0	12.4	8.6	
0.320	0.5	77.5	0	9.5	
		74.5	2.0	10.5	
		73.0	3.5	10.5	
		70.8	8.3	7.9	13.0
		73.0	8.6	5.4	
		81.0	0	6.0	
0.370	0.6	80.0	1.0	6.0	
		78.0	2.5	6.5	
		76.5	4.0	6.5	13.0
		78.0	5.1	3.9	
		71.0	0	11.0	
		68.0	2.0	12.0	
0.263	0.4	66.0	6.0	10.0	
		63.0	8.0	11.0	18.0
		64.0	9.5	8.5	
		67.0	9.0	6.0	
		76.0	0	6.0	
		74.0	2.0	6.0	
0.320	0.5	75.0	3.0	4.0	
		73.0	5.0	4.0	18.0
		74.0	5.0	3.0	
		79.0	0	3.0	
		78.8	1.0	2.2	
		78.0	1.5	2.5	18.0
0.370	0.6	79.0	2.2	0.8	

ity of ferrous oxide for each mole percent of Al₂O₃ is shown in Figs. 1–3. The plot in each case is a pseudo-ternary of constant $N_{\text{Al}_2\text{O}_3}$.

All the investigated mixtures gave molten slags at the temperature of investigation, 1450°C. On the ternary side FeO–CaO–Al₂O₃ of the quaternary, the activity values of ferrous oxide were obtained experimentally at 1450°C. The high TiO₂ contents of the ternary system FeO–TiO₂–Al₂O₃ which cause the creep of these slags from the crucible were a handicap to the determination of a_{FeO} at FeO–TiO₂–Al₂O₃ side of the pseudo-ternary.

To investigate the effect of Al₂O₃ on the activity of ferrous oxide in the ternary system FeO–CaO–Al₂O₃, the change of a_{FeO} with N_{FeO} at different mole fraction of Al₂O₃, $N_{\text{Al}_2\text{O}_3}$, are plotted in Fig. 4. This figure clarifies the increasing of ferrous oxide activity by increasing both FeO and Al₂O₃. The effect of Al₂O₃ additions in increasing the activity coefficient of FeO at constant N_{FeO} is clearly illustrated in Fig. 5. It is evident that replacement of CaO by Al₂O₃, within the range investigated, results in increasing the activity of ferrous oxide.

By comparing the values of interaction energy between cations of major components in steelmaking slags given by Ban-Ya,³⁰⁾ it can be concluded that the interaction between Al₂O₃ and CaO is stronger than that between either FeO and CaO or Al₂O₃ and FeO. This explains the increase of the activity of FeO by the continuous

Fig. 1. FeO iso-activity curves in the system FeO–TiO₂–CaO–Al₂O₃ at 1450°C and 9.7 mol% Al₂O₃.

Fig. 2. FeO iso-activity curves in the system FeO–TiO₂–CaO–Al₂O₃ at 1450°C and 13 mol% Al₂O₃.

Fig. 3. FeO iso-activity curves in the system FeO–TiO₂–CaO–Al₂O₃ at 1450°C and 18 mol% Al₂O₃.

replacement of CaO by Al₂O₃ (within the range investigated) in the ternary system FeO–CaO–Al₂O₃.

On the contrary, in the quaternary system FeO–TiO₂–CaO–Al₂O₃, Figs. 1–3 indicate a continuous decrease in the activity of FeO with increasing Al₂O₃ content in the

Fig. 4. Activity of ferrous oxide as a function of N_{FeO} at different levels of Al_2O_3 in the ternary system $\text{FeO}-\text{CaO}-\text{Al}_2\text{O}_3$.

Fig. 5. Effect of Al_2O_3 additions on the activity coefficient of FeO at constant N_{FeO} in the ternary system $\text{FeO}-\text{CaO}-\text{Al}_2\text{O}_3$.

melt. This fact is further clarified in Fig. 6 which shows the change in the activity of FeO with N_{FeO} at constant ratio of $N_{\text{TiO}_2} : N_{\text{CaO}}$ and different contents of Al_2O_3 . At constant $N_{\text{TiO}_2} : N_{\text{CaO}}$ ratio, the activity of FeO increases by increasing N_{FeO} and decreasing $N_{\text{Al}_2\text{O}_3}$. Figure 7 also clarifies the decrease of the activity coefficient of FeO by increasing Al_2O_3 at constant N_{FeO} and $N_{\text{TiO}_2} : N_{\text{CaO}}$ ratio.

The opposite behaviour of Al_2O_3 on the activity of FeO in both ternary and quaternary $\text{FeO}-\text{CaO}-\text{Al}_2\text{O}_3$, $\text{FeO}-\text{TiO}_2-\text{CaO}-\text{Al}_2\text{O}_3$ systems could be attributed to the presence of TiO_2 in the quaternary system. In the quaternary system containing the four oxides FeO , CaO , TiO_2 and Al_2O_3 in the molten state, TiO_2 and Al_2O_3 are anion formers and so there is no attraction between them. On the other hand, FeO can form association with TiO_2 , CaO and Al_2O_3 . However, the values of interaction energy³⁰⁾ indicate that the interaction between FeO and

Fig. 6. Activity of ferrous oxide as a function of N_{FeO} at constant $N_{\text{TiO}_2} : N_{\text{CaO}}$ ratio and different levels of Al_2O_3 in the quaternary system $\text{FeO}-\text{TiO}_2-\text{CaO}-\text{Al}_2\text{O}_3$.

Fig. 7. Effect of Al_2O_3 additions on the activity coefficient of FeO at constant $N_{\text{FeO}}=0.7$ and constant ratios of $N_{\text{TiO}_2} : N_{\text{CaO}}$.

Al_2O_3 in the liquid state is stronger than that between FeO and both CaO and TiO_2 . Thus FeO reacts preferentially with Al_2O_3 resulting in a decrease of its ac-

Fig. 8. Changes of the activity coefficient of FeO with $N_{TiO_2} : N_{CaO}$ ratio at constant $N_{FeO} = 0.7$ and different levels of Al_2O_3 in the quaternary system FeO–TiO₂–CaO–Al₂O₃.

tivity with increasing Al_2O_3 content. Due to the higher attraction between Al_2O_3 and CaO,³⁰⁾ the more pronounced effect of Al_2O_3 in decreasing the activity of FeO is attained at higher Al_2O_3 content.

In the quaternary system FeO–TiO₂–CaO–Al₂O₃, at constant N_{FeO} and constant Al_2O_3 content, a maximum activity coefficient of FeO, γ_{FeO} , is attained at $N_{TiO_2} : N_{CaO}$ mole ratio equals 1, Fig. 8, confirming that CaO–TiO₂ is the most stable of the calcium titanates. The introduction of Al_2O_3 in the form of AlO_3^{3-} anion in the melt containing the anion TiO_4^{4-} would result in a repulsion between the two anions. In melts containing higher TiO₂ than the stoichiometric of the most stable calcium titanate, CaO·TiO₂, ($N_{TiO_2} : N_{CaO} > 1$), the excess TiO_4^{4-} and AlO_3^{3-} anions will attract Fe^{2+} cations with the result of decreasing the FeO activity. By increasing the content of Al_2O_3 , more AlO_3^{3-} anions are introduced into the melt and the activity of FeO is decreased even more.

4. Conclusions

In the ternary system FeO–CaO–Al₂O₃, replacement of CaO by Al_2O_3 , within the range investigated, results in increasing the activity of FeO. On the contrary, in the quaternary system FeO–TiO₂–CaO–Al₂O₃, increasing Al_2O_3 additions from 9.7 to 18 mol% is found to decrease the FeO activity at constant N_{FeO} and $N_{TiO_2} : N_{CaO}$ ratio. In this quaternary system, at constant N_{FeO} and Al_2O_3 content, a maximum γ_{FeO} is attained at $N_{TiO_2} : N_{CaO}$ mole ratio equals 1.

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