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Chromium distribution between slag and non-carbon saturated metal phases under changing partial pressure of carbon monoxide

X. PAN and R.H. ERIC

School of Process and Materials Engineering, University of the Witwatersrand, Johannesburg, South Africa

Slag-metal equilibrium experiments were conducted at 1500ºC and 1580ºC under 0.03 atm, 0.05 atm and 0.83 atm CO partial pressures using silica and Cr-oxide crucibles. The complex slags belonged to SiO_2-CaO-Al_2O_3-MgO-FeO_x-CrO_x and the metal phase to the Cr-Fe-C-Si-(S) systems. The carbon saturation of the metal phase was avoided using oxide crucibles and thus the results are pertinent to ferrochromium refining slags and processes. From equilibrium data and thermodynamic calculations the CrO /(CrO+Cr_2O_3) ratio in the slag was determined as 0.75, 0.80 and 0.86 under 0.83 atm and 0.05 atm of CO pressure at 1500ºC and 0.03 atm and CO pressure at 1580ºC respectively. The results clearly demonstrated that a higher chromium content of the metal results in higher Cr in the slag, and chromium in slag decreases with increasing SiO_2. The results were also sensitive to the crucibles used as these oxide crucibles saturated the slag either with respect to SiO_2 or Cr-oxides. It was also demonstrated that the relative amount of CrO in the slag was higher when SiO_2 crucibles were used in accord with thermodynamic calculations. Iso-concentration curves for carbon and chromium of the metal phase in equilibrium with the slag were drawn on pseudo ternary SiO_2–(Al_2O_3+CaO+MgO)–(Cr_2O_3+Fe_2O_3) diagram. The activity coefficients and activities of carbon and chromium of the metal phase were also calculated from the experimental data and available thermodynamics information and were plotted as iso-activity curves in the same pseudo ternary diagram.

Keywords: Chromium, slag, equilibrium

Introduction

The demand for refined medium carbon ferrochromium alloys by the industry is likely to increase, due to the problem associated with the use of high carbon ferrochromium in stainless steelmaking, such as longer refining times for decarburization, high slag volumes, higher refractory corrosion/erosion and high consumption of oxygen. Moreover, the high grade chromite reserves are declining rapidly world wide, and from lower grade chromites only lower grade ferrochromium alloys can be produced with less Cr content than around 58%, but with above 6% C and 2% Si. Lower grade chromites cannot be converted to low or medium carbon (up to 4%) alloys by the conventional processes under economically feasible conditions[1]. Thus, decarburization of such lower grade ferrochromium alloys by oxygen blowing processes may suggest a production path to lower carbon, lower silicon containing high quality alloys, which could be utilized more efficiently by steelmakers.

The knowledge on the slag-metal-gas equilibrium without carbon saturation of the metal phase is of fundamental importance to understanding the pyrometallurgical processes of ferrochromium refining (and stainless steelmaking). Under refining conditions data on equilibrium distribution of chromium between the metal and the slag phases as CO partial pressure changes is essential to maximize chromium recovery and to run the process efficiently. Significant amounts of literature are available on the system Cr-Fe-Si-Ca-Mg-Al-C-O in terms of thermodynamic properties and equilibrium distribution with respect to the metal and slag phases, but almost all of them are under carbon saturated cases pertinent to ferrochromium smelting. The information on the above complex system relevant to ferrochromium refining is extremely limited. This work was initiated to fill this gap.

Experimental procedure

The slag samples were prepared as homogeneous mixtures from pre-melted master slags made from analytical grade pure oxides. Chromium oxide and iron oxide were added when necessary to these homogenized samples prior to experiments. The initial slag compositions were as follows: MgO: 6–25%, CaO: 1–5%, SiO_2: 35–65%, Al_2O_3: 10–35%, Cr_2O_3: 0–25%, Fe_2O_3: 0–5%.

The metal samples were also prepared as homogeneous mixtures made from analytical grade pure components. The starting metal compositions ranged as follows: Cr: 50–70%, Fe: 18–35%, Si: 0.1–5%,C: 3–9%, S: 0.01–1%.

The partial pressure of CO was controlled by mixing CO and Ar gases utilizing calibrated capillary flowmeters. Samples of 4 g metal and 6 to 8 g of slag were placed in a chromium oxide or silica crucible and heated within the 50 mm hot zone of a vertical molybdenum-wound resistance furnace, which maintained constant temperature within ±

1°C at 1500°C through a digital temperature controller activated by a Pt-6%Rh / Pt-30%Rh thermocouple. Sample temperatures were measured by another thermocouple of the same type. At the end of equilibrium runs, the crucibles were quenched by dropping them into water. The equilibration time was determined after a series of runs conducted at 1500°C at times varying up to 15 hours with the same initial compositions under CO atmosphere.

The approach to equilibrium was established by analysis of all the components of the slag phases namely: Al_2O_3, CaO, MgO, SiO_2, Cr_2O_3, Fe_2O_3 and S. After about 12 hours no significant change in compositions were observed and all the experiments, both at 1500°C and 1580°C, were run for 15 hours. After equilibration and quenching, the distinct slag and metal phases were separated, cleaned when necessary and sent for analysis.

The carbon and sulphur contents of the alloy were analysed by a Leco apparatus, the other constituents of the metal by the ICP method. The iron and chromium in the slag were analysed by the o-phenanthroline colorimetric and f-diphenylcarbazide colorimetric methods respectively, and the other contents of the slag by X-ray fluorescence. In addition, some X-ray diffraction analyses and metallographic examinations were conducted on the slag/crucible interface to detect the crucible behaviour. Three series of experiments were conducted: (i) in chromium oxide crucibles at 1500°C and P_{CO} = 0.05 atm, (ii) in chromium oxide crucibles at 1500°C and P_{CO} = 0.83 atm, and (iii) in silica crucibles at 1580°C and P_{CO} = 0.03 atm.

Results and discussion

About 120 successful experiments were conducted. The failure of some of the experiments were due to the cracking of the chromium oxide crucibles. Efforts to reduce cracking was one of the major challenges during the test work and included preheating the crucibles to 1400°C in a muffle furnace (prior to experiments), winding Mo wire around the crucibles to form a basket, and utilizing external crucibles such as molybdenum, zirconia or alumina (with Cr_2O_3 powder between the internal and external crucibles) to hold the chromium oxide crucibles. The results on sulphur partition were covered in an earlier publication[2] and thus will not be repeated here. Under the specified conditions of the present work, the partial pressure of oxygen can be calculated by using the following equilibrium and its free energy.

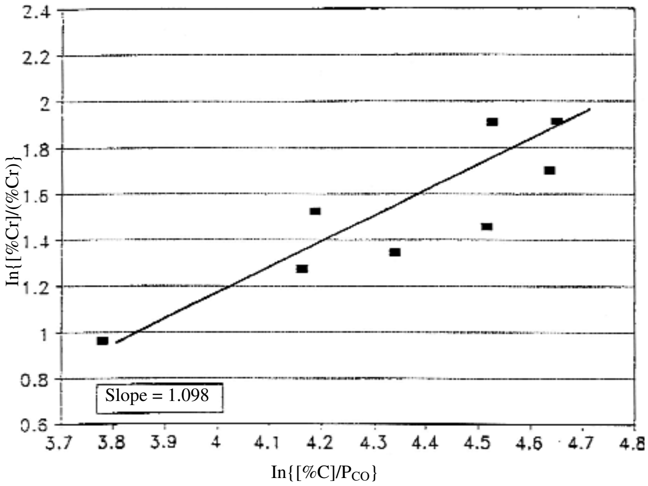

Figure 1. Variation of the partition ratio of chromium with ln[%C/P_{CO}] at 1500°C (Cr-oxide crucible)

$$\underline{C} + \tfrac{1}{2}O_2(g) = CO(g) \qquad [1]$$

$$P_{O_2} = \left(P_{CO} / a_C.K_1\right)^2 \qquad [2]$$

In this investigation P_{CO} changed from 0.03 atm to 0.83 atm, and the activity of carbon in the metal phase from 0.025 to 0.117 depending upon the composition of the equilibrium metal phase as calculated by using activity coefficients and relevant interaction parameters. Thus the calculated P_{O_2} range would fall in the 3.01 x 10^{-17} to 5.05 x 10^{-13} atm bracket. Thus the chromium oxide must exist only in the forms of CrO and CrO_{1-5} according to the work of Marston and Argent[3]. A slag-metal reaction can be written between carbon and chromium oxides:

$$(CrO_x) + x\underline{C} = \underline{Cr} + x\ \ CO(g) \qquad [3]$$

$$K_3 = \left(P_{CO}\right)^x a_{Cr} / a_{CrOx}.a^x{}_C \qquad [4]$$

Equation [4] can be altered to the following format using activity coefficients and concentrations and collecting all the conversion factors into a single constant:

$$\ln L_{Cr} = x\ln\left(\%C / P_{CO}\right) + C^1 \qquad [5]$$

Where L_{Cr} is the partition ratio of chromium defined as: L_{Cr} = (%Cr in metal) /(% Cr in slag), and C^1 is the constant mentioned above. Equation [5] is linear with slope x and intercept C^1. Using the experimental data gathered on equilibrium composition of the metal and slag phases, graphs were plotted for all three series of experiments to determine the slope x. Figure 1 shows a typical case: the experiments at 1500°C in a Cr-oxide crucible at P_{CO} = 0.05 atm. Despite some scatter in the data, good linear fits were achieved. The slopes are 1.125, 1.098 and 1.075 respectively for 1500°C, P_{CO} = 0.83 atm, Cr-oxide crucible data; 1500°C, P_{CO} = 0.05atm, Cr-oxide crucible data and 1580°C, P_{CO} = 0.03 atm, silica crucible data. These slopes represent that CrO in the slag phase is 75%, 80% and 86% of chromium oxides respectively. These results are consistent with the work of Xiao and Holappa[4] and Rankin and Biswas[5].

Considering the following reaction and its equilibrium constant between Cr-oxides and carbon:

$$\left(CrO_{1-5}\right) + \tfrac{1}{2}\underline{C} = (CrO) + \tfrac{1}{2}CO(g) \qquad [6]$$

$$K_6 = \left(a_{CrO} / a_{CrO1-5}\right)\left(P_{CO} / a_C\right)^{1/2} \qquad [7]$$

it becomes clear that the activity ratio of CrO to CrO_{1-5} is related to temperature (through K_6), partial pressure of CO, and activity of carbon in the metal phase. Moreover, the concentration ratio X_{CrO} to $X_{CrO1.5}$ will also be affected by slag composition through the activity coefficient of CrO and CrO_{1-5} in the slag. The activity of carbon in the metal phase will be strongly influenced by its own concentration as well as those of chromium, silicon and sulphur. A typical

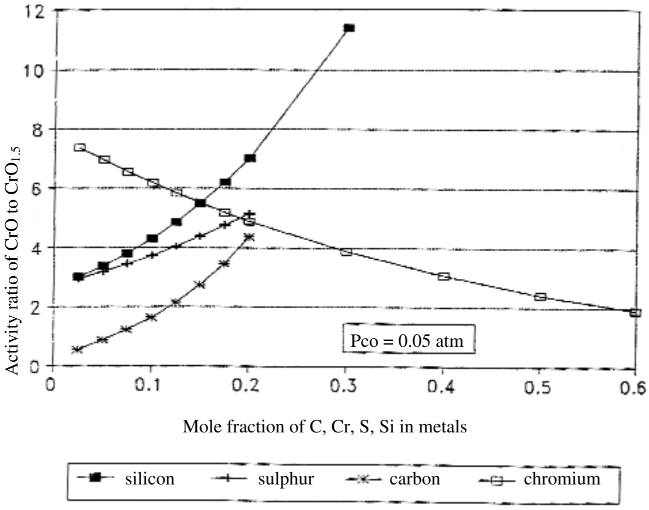

Figure 2. Influence of C, Cr, S and Si of the metal phase on the $(a_{CrO})/(a_{CrO1.5})$ ratio of the slag at 1500°C and P_{CO}=0.05 atm

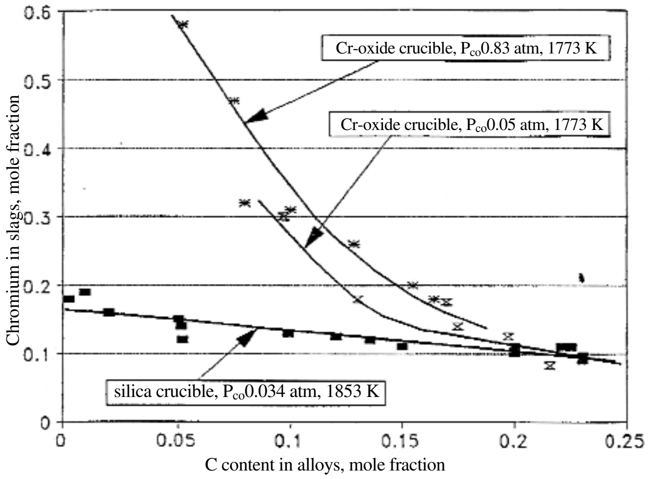

Figure 4. The relationship between Cr in the slag and C in the metal

plot on the effect of the metal constituents on a_{CrO} / $a_{CrO1.5}$ ratio is shown is Figure 2. An increase in the concentrations of silicon, sulphur and carbon in the metal phase increases the $a_{CrO}/a_{CrO1.5}$ ratio favouring the existence of Cr^{2+} ions in the slag. On the other hand, the ratio decreases with increasing Cr of the metal phase. These results are also in agreement with the results of Rankin and Biswas[5].

The direct relationship between the chromium contents of the metal and slag phases is illustrated in Figure 3. As expected, they are directly proportional to each other. At lower CO partial pressures, the chromium content of the slags is also lower, despite the fact that it again increases with increasing chromium levels in the metal.

The inverse relationship between the chromium content of the slag and carbon in the metal can be seen in Figure 4. The results obtained using Cr-oxide crucibles clearly show a sharp decline in chromium levels in the slag with increasing carbon content of the metal. Lowering the CO partial pressure also leads to lower chromium concentration in the slag. In silica crucibles, where the slag is saturated with respect to this oxide, chromium levels in the slag are low and decrease rather slowly with increasing carbon content of the metal. This finding agrees well with the results reported by Xiao and Holappa[4]. It is quite clear that reduction of chromium from slags is promoted by increased carbon and decreased chromium levels in the metal, as well as lower CO partial pressure in the gas. The obvious reasons for this behaviour can easily be analysed when the thermodynamics of the following reaction are considered.

$$\underline{C} + (CrO) = CO(g) + \underline{Cr} \qquad [8]$$

$$X_{CrO} = \gamma_{Cr} X_{Cr} P_{CO} / a_c \gamma_{CrO} K_8 \qquad [9]$$

In this context, Figure 5 is drawn to illustrate the variation of activity coefficients of Cr and C and the a_{Cr} / a_C ratio of the metal phase from a particular equilibrium run of this study.

The influence of MgO content of the slag on the chromium content of the slag from equilibrium experiments is summarized in Figure 6. In all the cases, as MgO increases, the chromium content of the slag initially decreases relatively quickly and thereafter the decrease

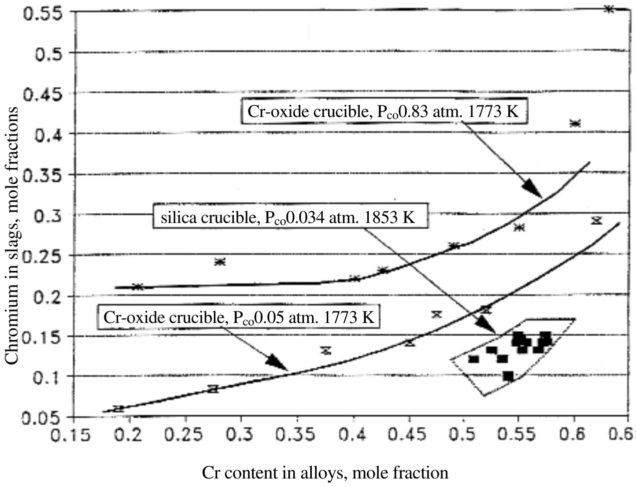

Figure 3. The relationship between Cr in the metal and Cr in the slag

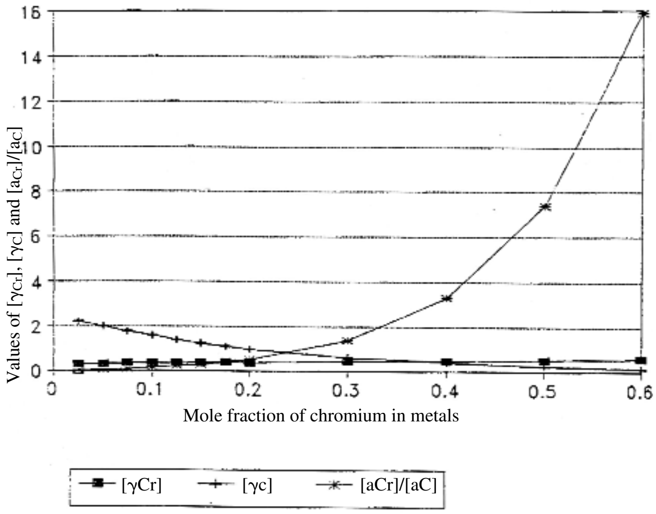

Figure 5. Relations between chromium in metal and $[\gamma_C]$, $[\gamma_{Cr}]$ and $[a_{Cr}]/[a_C]$ ratio at 1500°C

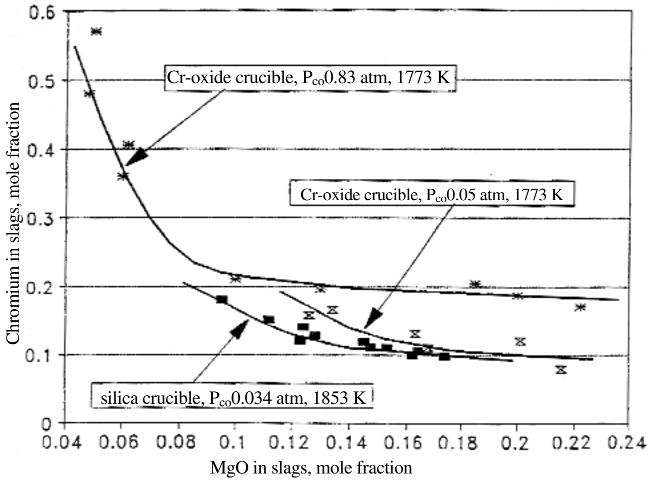

Figure 6. Effect of MgO on chromium content of slag

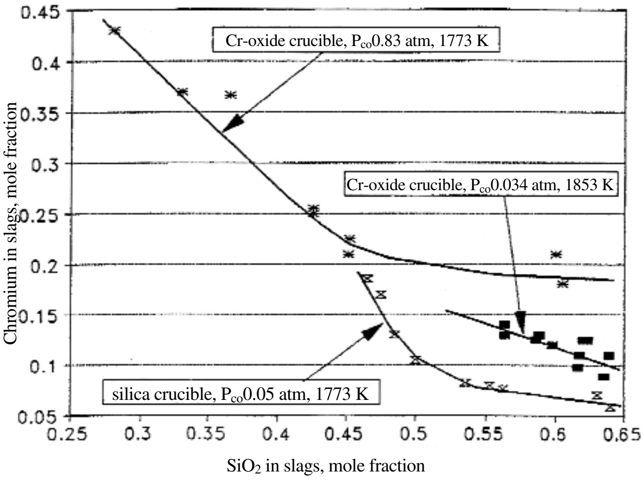

Figure 8. Effect of SiO_2 on chromium content of slag

slows down considerably. These findings are in good agreement with those of Xiao and Holappa[4] and Morita and Sano[6].

The typical relation between chromium content of the slag and its alumina is shown in Figure 7. The results clearly demonstrate the fact that when Al_2O_3 increases, the chromium in the slag decreases. Marita and Sano's[6] study has clearly showed that when Al_2O_3 was added to MgO-SiO_2-CaO melts the solubility of chromium oxides decreased rapidly and that the effect of CaO/SiO_2 ratio in solubilities was very small, both under atmospheric and reducing conditions.

The relationship between chromium and silica contents of the slag is illustrated in Figure 8. The chromium in the slag decreases with increasing SiO_2 and the lower the partial pressure of CO, the lower the chromium content in the slag. The study by Xiao and Holappa[4] has shown that the activities of both CrO and $CrO_{1\text{-}5}$ decrease with an increase of silica in SiO_2-CrO_x and CaO-SiO_2-CrO_x slags and that the CrO percentage of (CrO+$CrO_{1\text{-}5}$) of the slags can be enhanced by increasing the silica content of the slag.

When silica increases in slags, the equilibrium silicon content of the metal also increases[7], which decreases the activity coefficient of chromium in the metal slightly but enhances the activity coefficient of carbon considerably. The increased activity of carbon then imposes a higher reducing potential to the system and thus reduces chromium from the slag phase, thereby reducing its concentration.

The results obtained in this investigation at 1500°C and 0.83 atm of CO partial pressure using Cr-oxide crucibles are also shown in pseudo-ternary SiO_2—(Al_2O_3 + CaO + MgO)—(Cr_2O_3 + Fe_2O_3) diagram in the form of iso-concentration, iso-activity coefficient and iso-activity curves for carbon and chromium. The activity coefficients and activities of carbon and chromium were calculated based upon the data generated in this work for the alloy and slag phases in equilibrium with each other. Three typical plots: Figures 9, 10 and 11, illustrate the iso-concentrations for Cr, iso-activity coefficients for Cr and iso-activities for C respectively.

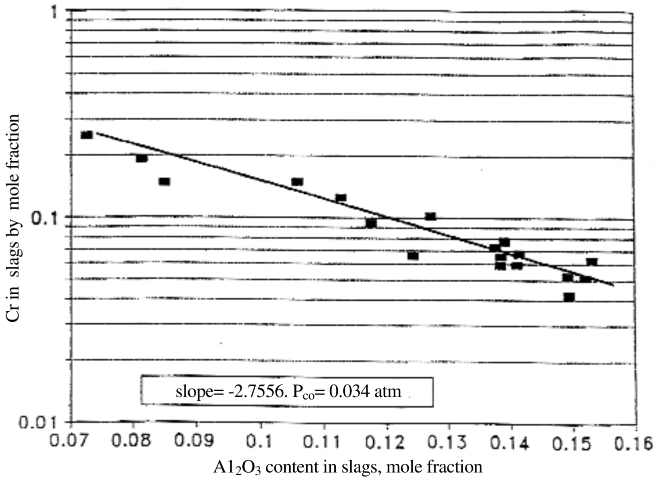

Figure 7. Effect of Al_2O_3 on chromium content of slag at 1580°C

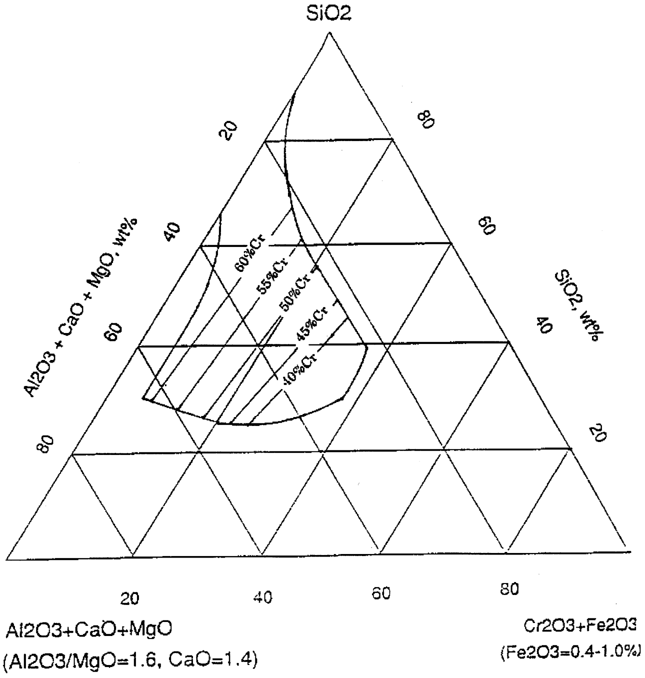

Figure 9. Chromium iso-concentration curves of the metal phase in equilibrium with slags at 1500°C and P_{CO}=0.83 atm

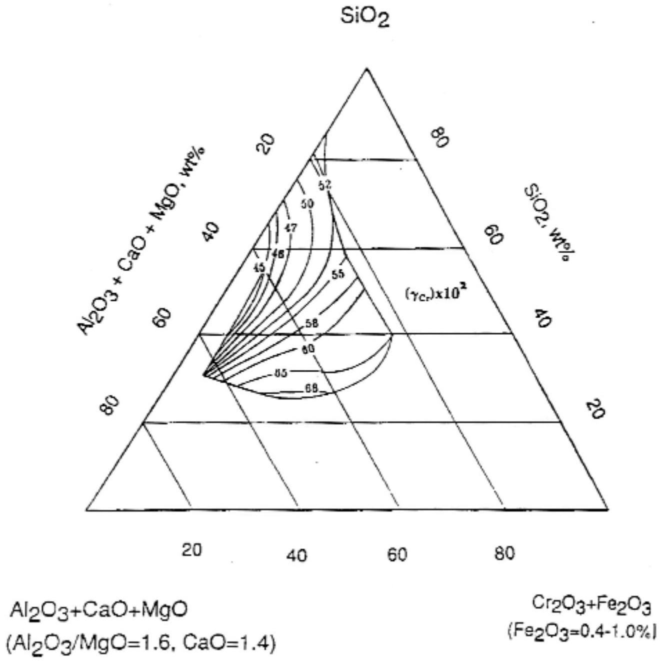

Figure 10. Iso-activity coefficient curves for chromium of the metal phase in equilibrium with slags at 1500°C and P_{CO}=0.83 atm

Summary and conclusions

Slag-metal equilibrium experiments were conducted at 1500°C and 1580°C under 0.03 atm, 0.05 atm and 0.83 atm CO partial pressures using silica and Cr-oxide crucibles avoiding carbon saturation of the metal phase. Thus the results are applicable to ferrochromium refining and stainless steel making processes. SiO_2-$A1_2O_3$-MgO-CaO-FeO_x-CrO_x slags were equilibrated with Cr-Fe-C-Si-(S) alloys, and equilibrium compositions were determined. From the gathered data and thermodynamic calculations the CrO / (CrO+CrO_{1-5}) ratios in the slag were determined as 0.75 under 0.83 atm CO pressure, 0.80 under 0.05 atm CO pressure both at 1500°C, and 0.86 under 0.03 atm CO pressure at 1580°C. The results also indicated that the concentration of CrO in the slag increases as silica concentration of the slag increases.

The chromium concentration in the slag decreases with factors such as increases in carbon and silicon contents of the metal and decrease in CO partial pressure. The effect of carbon on the chromium concentration in the slag is higher when the metal contains less chromium.

The chromium concentration of the slag decreases when MgO or SiO_2 concentration of the slag increases, where as when the metal phase contains low levels of chromium, the chromium content of the slag also decreases with an increase in $A1_2O_3$ concentration. In conclusion, a careful adjustment of slag composition mainly by optimizing the MgO and SiO_2 concentrations and, to a lesser extent, $A1_2O_3$ concentration and adjusting the level of CO partial pressure together with optimized Si and C concentration in the metal phase, ferrochromium refining can be achieved efficiently.

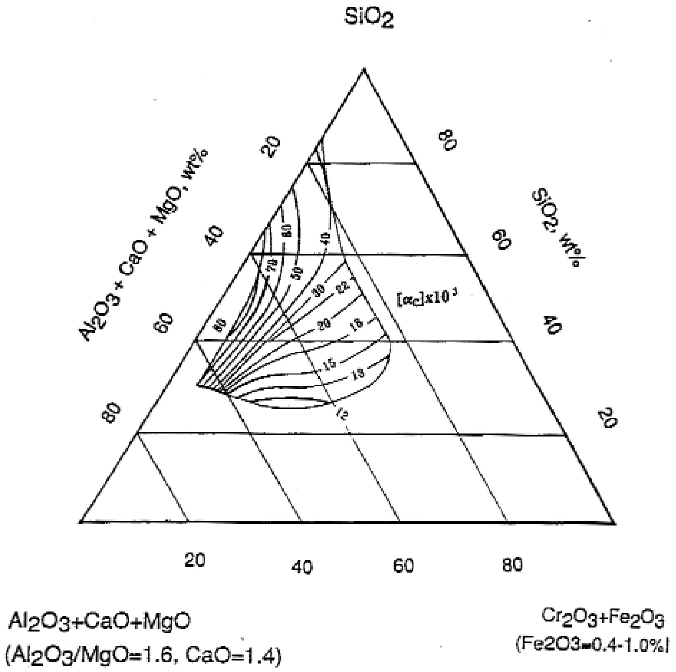

Figure 11. Iso-activity curves for carbon of the metal phase in equilibrium with slags at 1500°C and P_{CO} = 0.83 atm.

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