SULPHUR BEHAVIOUR UNDER CHANGING PARTIAL PRESSURE OF CO IN REFINING OF FeCr ALLOY

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ABSTRACT

The equilibrium distribution of sulphur between slag and metal phases encountered in refining of FeCr alloys has been investigated at 0.034, 0.05 and 0.83 atm of partial pressure of CO at 1773 and 1853K. It is shown that sulphur transfer from metal to slag phase increases with decreasing partial pressure of CO, increasing MgO content of the slag phase, and decreasing silica, alumina and chromium oxide content of the slag phase. It is also demonstrated that sulphur transfer from metal to slag phase increases with increasing carbon and decreasing chromium, and silicon (in the range; 0.005 to 0.02 mole fraction of Si) content of the metal phase, particularly when the partial pressure of CO decreases. The relations between MgO and sulphur capacity, the effect of silicon on the activity coefficients and activities of silicon and sulphur and the effects of silicon, carbon and chromium on the activity coefficients of sulphur and carbon have been discussed and used to interpret the experimental results.

1. INTRODUCTION

With the increase in demand for low-sulphur steels, the requirement on ferrochromium of low-sulphur content is on the increase as well. High carbon ferrochromium (HCFeCr) is the dominant alloy used in the steel, especially stainless steel industry and great efforts have been made to reduce its sulphur content. Coke or coal used in smelting is the greatest source of sulphur. From an economic point of view, desulphurization during smelting may be more important than choosing low-sulphur coke or coal which are in fact obtained from quite limited reserves.

It is known that there are certain relations among sulphur content and composition of both slag and metal phases. The studies[1,2] have demonstrated that when silicon and/or carbon in the metal phase or CaO into the slag phase increases, sulphur content of the alloy decreases. However, sulphur fluctuates in most cases and it is not easy to control the carbon content unless a suitable chromite ore is available for smelting. For certain applications, low silicon (which is unfavourable for lowering sulphur content) and low-sulphur containing FeCr alloy is required. In the smelting of this grade alloy and/or in the refining of HCFeCr to reduce carbon and silicon, utilization of other parameters is vital. When refining FeCr alloys by means of oxygen-blowing processes, the oxygen blown into the metal bath reacts with carbon to produce carbon monoxide extremely fast due to favourable kinetic and mass transfer conditions at high temperature. Therefore it can be regarded that carbon monoxide is the major component that influences the slag-metal-gas equilibrium.

In this study, the effects of the partial pressure of carbon monoxide, metal and slag compositions to the sulphur behaviour in refining of FeCr alloy have been investigated in terms of slag-metal-gas equilibrium at 1500° and 1580°C.

2. EXPERIMENTAL PROCEDURE

The slags were prepared as homogeneous mixtures from premelted 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; 6-20%, CaO; 1-5%, SiO_2; 40 - 65%, Al_2O_3; 10-30%, Cr_2O_3; 0-25%. The metal samples were also prepared as homogeneous mixtures made from analytical-grade pure components. The starting metal compositions ranged as the following : 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 Argon gases utilizing calibrated capillary flowmeters. Samples of 2g of metal and 4g of slag were placed in a chromium oxide or silica crucible and heated within the 30mm 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 equilibration, the crucibles were quenched by being dropped into water. The equilibration time was determined after a series of gas-slag-metal equilibrium runs, which were 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 seven components of the slag phase, 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 13 hours.

After equilibration and quenching, the distinct slag and metal phases were separated, cleaned when necessary and sent for analysis to Council for Mineral Technology (Mintek) of South Africa. The carbon and sulphur contents of the alloy were analyzed by means of a Leco apparatus, the other constituents of the metal by the ICP method. The iron an chromium in the slag were analyzed 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 slag/crucible interface to detect the crucible behaviour.

Three series of experiments were undertaken : (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; (iii) in silica crucibles at 1580°C and P_{CO} - 0.034 atm.

3. 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 of 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 alumia to hold the chromium crucibles.

3.1 Influence of slag composition on sulphur distribution

The relationship between the sulphur distribution-expressed as the ratio of molar fraction of sulphur in the slag to that in the metal; $(X_s)/[X_s]$ - and the molar fractions of all the constituents in the slag phase were investigated under different P_{CO} in equilibrium with Cr-Fe-Si-C-S alloys. The slag composition range was as follows : 0-0.1%S, 0-25%Cr_2O_3, 40-60%SiO_2, 10-30%Al_2O_3, 1-5% CaO, 6 - 20% MgO, and about 0.5% Fe (in mass %). In the metal phase the compositional range was 45-65% Cr, 0-9%C, 0-5% Si, 0-0.05% S and balance Fe by mass.

As shown in figure 1, with the increase of MgO content of the slag, its desulphurization capability increases both in Cr_2O_3 and SiO_2 crucibles at 1500°C and 1580°C. The sulphur distribution in Cr_2O_3 crucible is higher than under silica saturation even though the silica saturation data is at the higher temperature of 1580°C. This clearly implies the stronger power of chromium oxide in reducing the sulphur content of the metal. The results at 1500°C in Cr_2O_3 crucibles indicate that the sulphur distribution ratio increases when P_{CO} decreases when the MgO content of the slag is the range from 0.17 to 0.35 by molar fraction. The slag-metal equilibrium in terms of sulphur and oxygen species can be written as :

$$[S] + (O^{2-}) = (S^{2-}) + [O] \tag{1}$$

where square and round brackets indicate the metal and slag phases respectively. MgO in the slag will dissociate according to :

$$(MgO) = (Mg^{2+}) + (O^{2-}) \tag{2}$$

Thus an increase in MgO content of the slag will increase free O^{2-} anions in the slag resulting in an increase of the activity of O^{2-} anions which in turn will help to shift reaction (1) to the right, in turn assisting sulphur removal from the metal.

The sulphide capacity; Cs of the slag has been defined by Sharma and Richardson[3] from the following equilibrium :

$$\frac{1}{2}S_2(g) + (O^{2-}) = (S^{2-}) + \frac{1}{2}O_2(g) \tag{3}$$

$$Cs = (\%S)\,(Po_2/Ps_2)^{\frac{1}{2}} \tag{4}$$

Cs is a function of several variable such as temperature and slag composition, but mainly temperature and basicity of the slag. From the work of Martin et al[4], the following equation was obtained :

$$\log C_s = B/A + 2.28 - 13300/T \tag{5}$$

where A and B are defined as :

$$A = \%CaO + 1.391\%\ MgO + 1.867\%\ SiO_2 + 1.65\%\ Al_2O_3 \tag{6}$$

$$B = 5.623\%\ CaO + 4.15\%\ MgO - 1.152\%\ SiO_2 + 1.457\%\ Al_2O_3 \tag{7}$$

An increase in MgO content of the slag will increase the B/A ratio and thus Cs will increase. The relationship between Cs, B/A ratio and % MgO is depicted in Figure 2, for a slag containing 5% CaO, 20% Al_2O_3, 45% SiO_2, 0.5% Fe_2O_3, 5-25% MgO and balance Cr_2O_3.

The explicit effect of Cr_2O_3 in the slag on sulphur distribution is shown in Figure 3. In general when chromium content decreases sulphur transfer from metal to slag increases. This indicates that Cr_2O_3 in the slags behaves like an acidic oxide consuming free O^{2-} ions. This result is in agreement with Xiao and Hollappa's[5] work in silicate slags containing chromium oxides. The higher the chromium oxide in the slag, the lower the divalent chromium fraction and the higher the trivalent chromium. The results show that the slags contain more sulphur in Cr_2O_3 crucibles at 1500°C then under SiO_2 saturation at 1580°C. This again clearly demonstrates the highly acidic nature of SiO_2. Thus a slag high in Cr_2O_3 will increase its desulphurization ability. Moreover, conditions become more favourable for sulphur removal from metal at lower P_{CO} values.

The effect of Al_2O_3 on the partition ratio of sulphur is illustrated in Figure 4. The partition ratio decreases slightly with

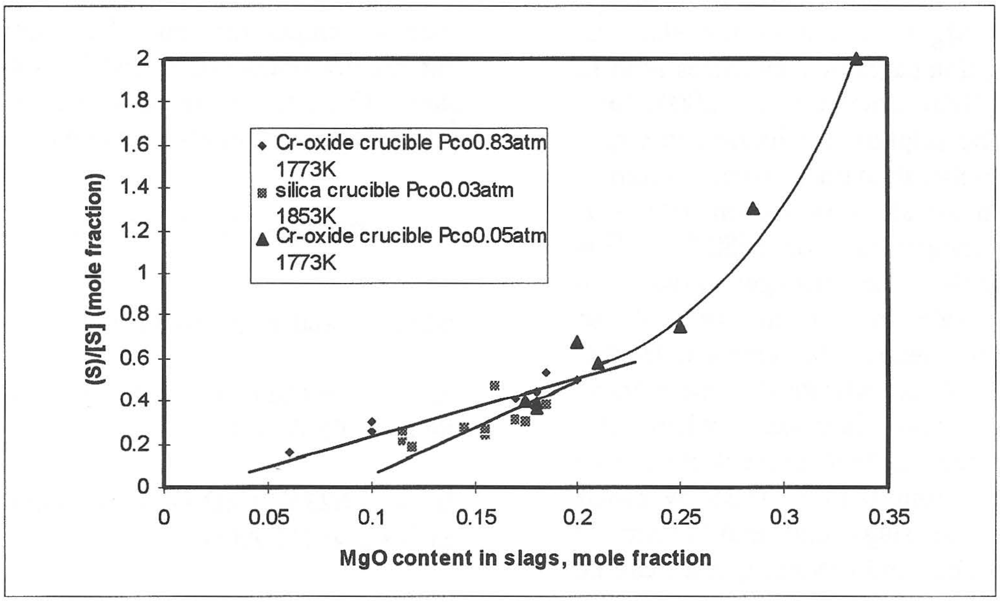

Figure 1. Effect of MgO on sulphur distribution with metal of Cr-Fe-C-0.25%Si-S and slag of 1.4%CaO-0.7%Fe_2O_3-MgO-Cr_2O_3-SiO_2-Al_2O_3-S by mass% with Al_2O_3/MgO = 1.6.

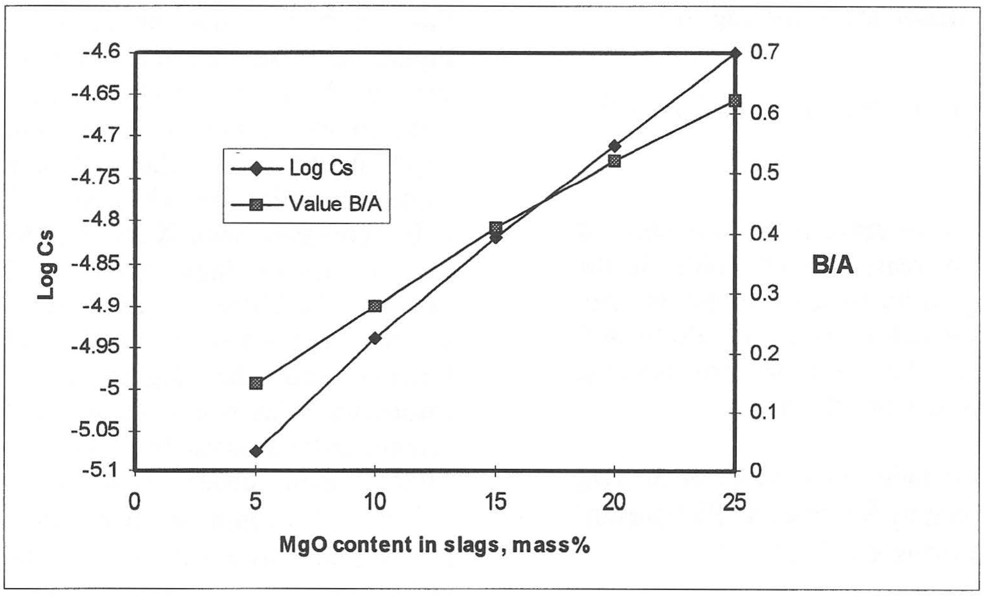

Figure 2. Relationship between B/A and MgO, sulphide capacity Cs and MgO with slag containing 5%CaO, 20%Al_2O_3, 45%SiO_2, 0.5% Fe_2O_3, MgO and Cr_2O_3 (as balance).

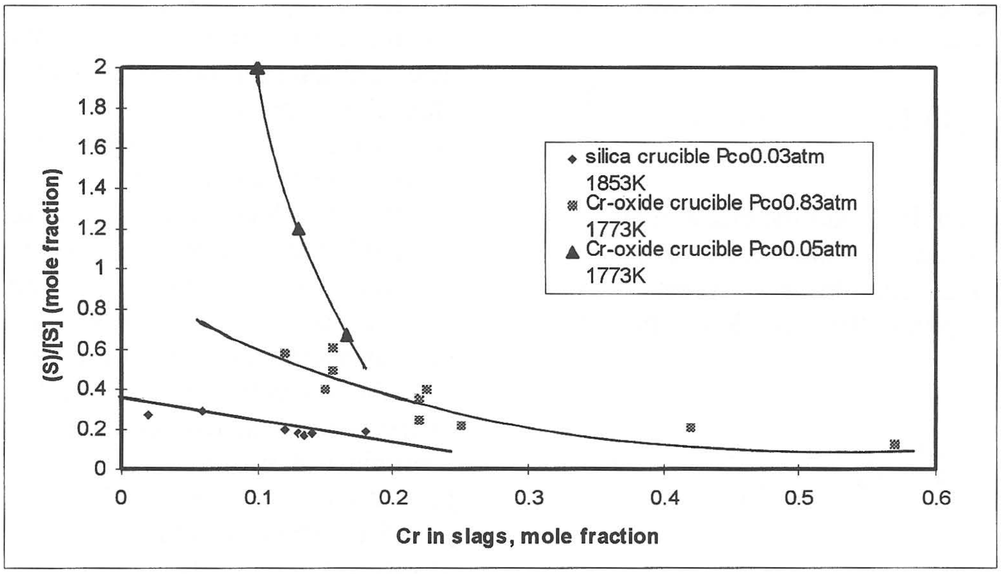

Figure 3. Effect of Cr of slag on sulphur distribution with metal of Cr-Fe-C-0.25%Si-S and slag of 1.4%CaO-0.7%Fe_2O_3-MgO-Cr_2O_3-SiO_2-Al_2O_3-S by mass% with Al_2O_3/MgO = 1.7.

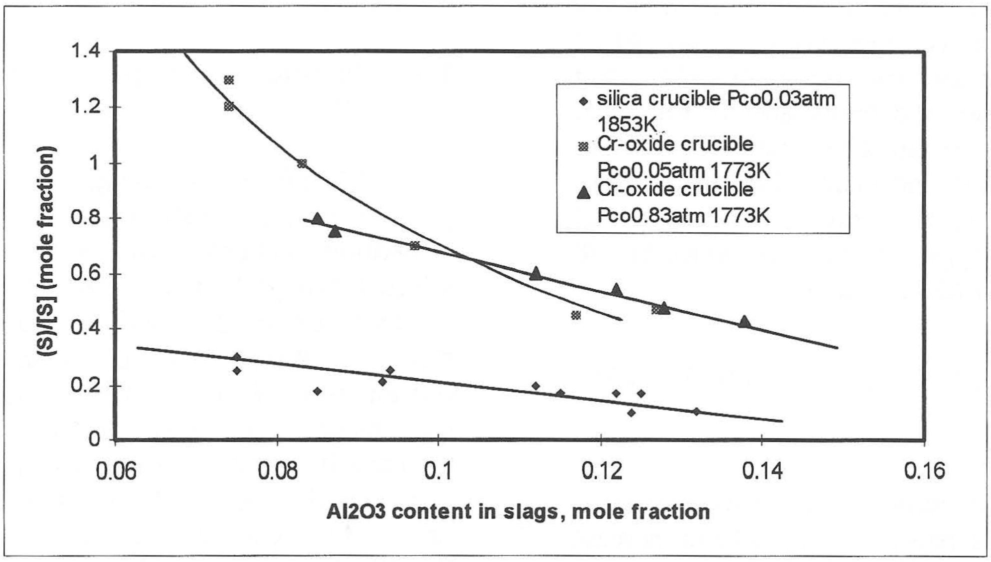

Figure 4. Effect of Al_2O_3 on sulphur distribution with metal of 55%Cr-Fe-C-0.25%Si-S and slag of 1.4%CaO-Fe_2O_3-MgO-Cr_2O_3-SiO_2-Al_2O_3-S by mass% with Al_2O_3/MgO = 1.7, 3-5%/0.1-2% Si in Cr/Si oxide crucible.

increasing Al_2O_3 content in the slag showing that Al_2O_3 when dissolved in the slag tends to consume O^{2-} ions which reduces the basicity of slags via :

$$(Al_2O_3)+(O^{2-}) = 2(AlO_2^-) \tag{8}$$

Figure 5 illustrates the effect of silica in the slag on the partition ratio of sulphur. The slag-metal equilibrium expressed in reaction (1) gives the partition ratio of sulphur as :

$$\frac{(X_S)}{[X_S]}=K_1\frac{a_{O^{2-}}}{a_O}\frac{\gamma_S}{\gamma_{S^{2-}}} \tag{9}$$

It is apparent from equation 9 that the partition ratio of sulphur increases with increasing activity of oxygen ion in the slag and with decreasing activity of oxygen dissolved in the metal.

As the SiO_2 in the slag increases more free oxygen ions will be consumed by SiO_2 and in turn the sulphur partition ratio will decrease as demonstrated in Figure 5. The silicon content of the metal, meanwhile, increases with increasing SiO_2 in the slag. This will tend to lower the activity of dissolved oxygen in the metal, since Si will react with it (deoxidation).

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

When activity of oxygen dissolved in the metal decreases, it may help to increase the partition ratio somewhat countering the effect of increased SiO_2 in the slag, but this effect is probably minimal.

3.2 Influence of metal composition on sulphur distribution

The effects o the constituents of the metal phase, namely Cr, Si and C on the equilibrium partition ratio of sulphur are illustrated in figures 6 to 8 respectively. The partition ratio decreases with increasing chromium and silicon levels (at low Si concentrations). According to sulphur distribution relationship from equation (9), the factors which decrease the activity of oxygen in the metal and increase the activity coefficient of sulphur in the metal will increase the partition ratio of sulphur. In ferrochromium alloys the increase in carbon and silicon can lower the activity of oxygen in the metal and can increase the activity coefficient of sulphur in the metal. In the present case when $X_{si} < 0.02$ the sulphur partition decreases as Si content increases as shown in figure 7. It may mean that in the metal of lower silicon, increase of silicon does not make remarkable contribution to reduce the activity coefficient of sulphur, but does decrease the basicity of the slag by adding silica into slags by combining with dissolved oxygen and thus lower the partition ratio of sulphur. Where else the behaviour of carbon is as expected as shown in Figure 8.

3.3 Influence of the partial pressure of CO.

The effect of lowering P_{CO} on sulphur partition ratio is in fact similar to the effect of vacuum treatment. The partition ratio is affected through basicity of slag and activity of dissolved oxygen and sulphur in the metal. When P_{CO} is reduced, the concentration of some of the components of the metal and slag phases change, particularly silicon, carbon and chromium which in turn affect the sulphur partition ratio. As a general rule, with decreasing P_{CO} the following equilibria will be more favourable :

$$[C] + [O] = CO(g) \tag{11}$$
$$2[C] + (SiO_2) = [Si]+2CO(g) \tag{12}$$
$$[C] + (Cr_2O_3) = 2(CrO) + CO(g) \tag{13}$$
$$[C] + (CrO) = [Cr] + CO(g) \tag{14}$$
$$[Si] + (CrO) = [Cr] + (SiO_2) \tag{15}$$

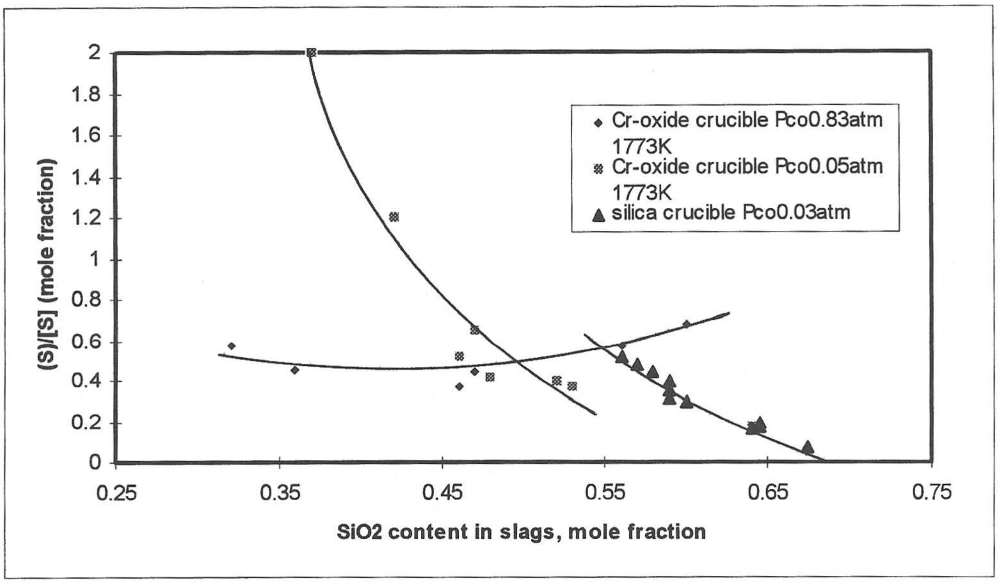

Figure 5. Effect of SiO_2 on sulphur distribution with metal of 55%Cr-Fe-C-Si-S and slag of 1.4%CaO-0.7%Fe_2O_3-MgO-Cr_2O_3-SiO_2-Al_2O_3-S by mass% with $Al_2O_3/MgO = 1.7$.

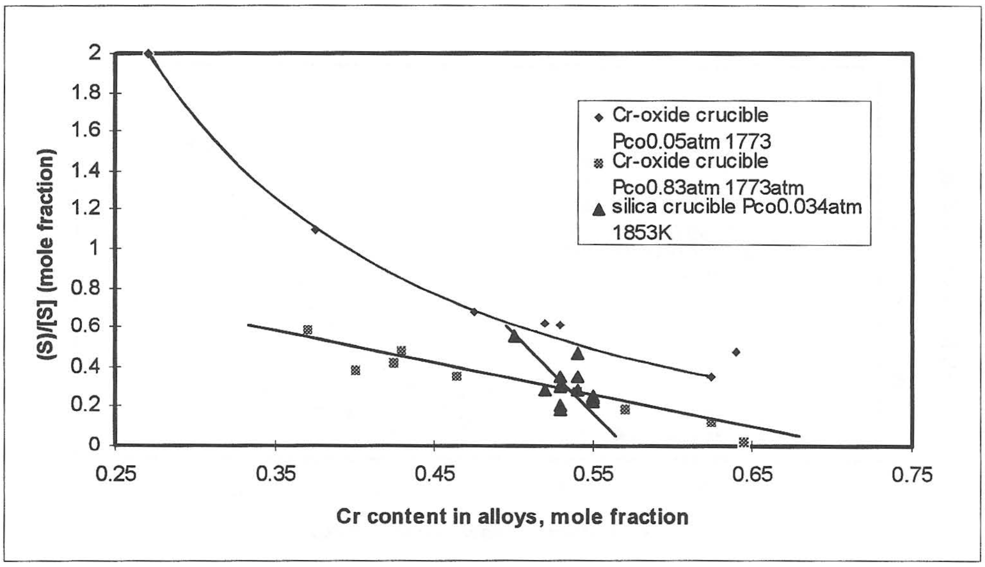

Figure 6. Effect of [Cr] on sulphur distribution with metal of Cr-Fe-C-Si-S and slag of 1.4%CaO-0.7Fe_2O_3-MgO-Cr_2O_3-SiO_2-Al_2O_3-S by mass% with $Al_2O_3/MgO = 1.7$, 3-5%/0.1-2% Si in Cr/Si oxide crucible.

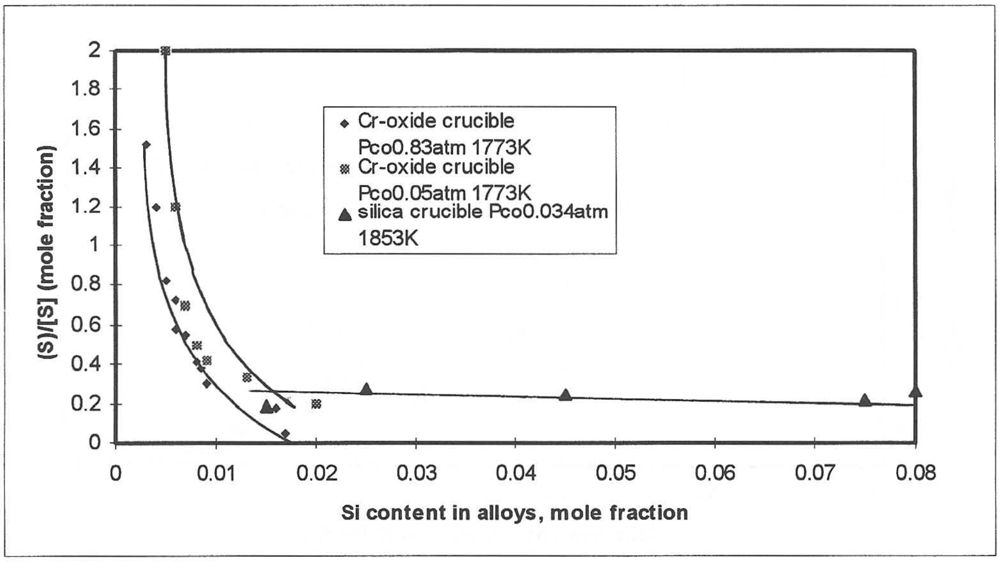

Figure 7. Effect of [Si] on sulphur distribution with metal of 55%Cr-Fe-C-Si-S and slag of 1.4%CaO-0.7Fe_2O_3-MgO-Cr_2O_3-SiO_2-Al_2O_3-S by mass% with Al_2O_3/MgO = 1.7.

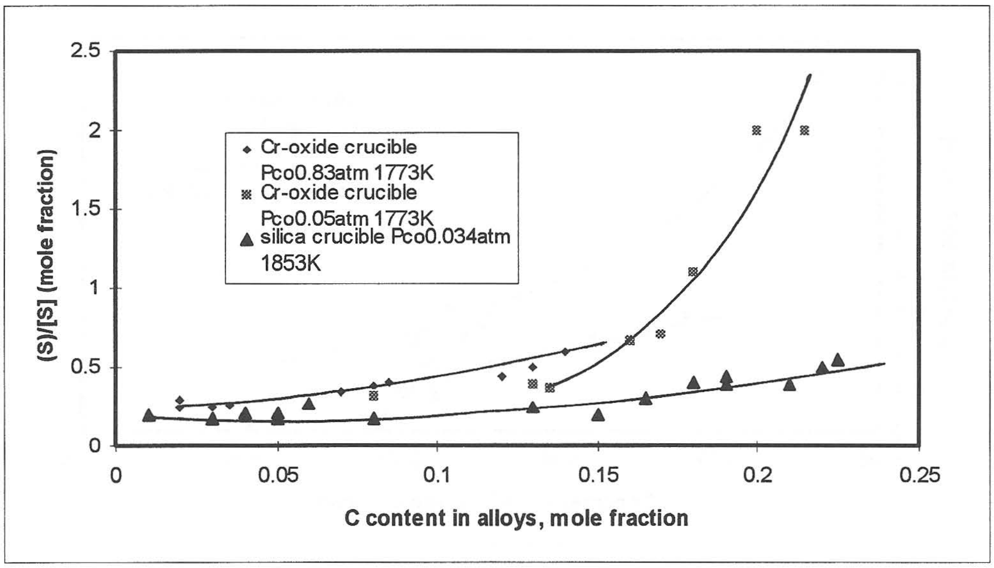

Figure 8. Effect of [C] on sulphur distribution with metal of 55%Cr-Fe-C-Si-S and slag of 1.4%CaO-Fe_2O_3-MgO-Cr_2O_3-SiO_2-Al_2O_3-S by mass% with Al_2O_3/MgO = 1.7, 3-5%/0.1-2% Si in Cr/Si oxide crucible.

Thus the effect of P_{CO} will actually follow similar lines to the effects of changes in the composition of the slag and metal as outlined earlier.

The carbon-oxygen equilibrium in reaction (11) may help explain one of the reasons that with the same carbon content in the metal, sulphur partition ratio increase with a decrease in P_{CO} through a possible decrease in the activity and/or concentration of oxygen as illustrated in Figure 8.

4. CONCLUSION

The distribution of sulphur between slag and metal phases encountered in refining of FeCr alloys has been investigated at 0.034, 0.05 and 0.83 atm partial pressure of CO at 1500° using chromium oxide crucibles and at 1580°C using silica crucibles. It is shown that sulphur distribution is related to P_{CO} and the compositions of both the slag and the metal phases.

Sulphur transfer from metal to slag increases with decreasing P_{CO}, increasing MgO content of the slag, and decreasing silica, alumina and chromium oxide content of the slag. It is also demonstrated that sulphur transfer to slag from metal increase with increasing carbon and decreasing chromium and silicon in the metal, particularly when the P_{CO} decreases.

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