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SLAG-METAL EQUILIBRIA FOR FERROCHROMIUM REFINING

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Abstract

A systematical investigation for the refining of ferrochromium has been conducted by means of metal/gas equilibria in alumina crucibles and metal/slag/gas equilibria in Cr-oxide crucibles at 1500 °C. The relationship of Si, C and Pco in metal/gas at 1500 °C in the range of Si 0.0 to 3.0 wt%; C 0.0 to 7.8 wt%, and Pco in Ar/CO gas 0.0 to 0.83 atm, shows that carbon content increases with increase of Pco and Si content. Two dimensional and three dimensional plots are used to express the relationships. In slag/metal/gas equilibria in Cr-oxide crucibles at CO atmosphere at 1500 °C, the equilibration time is determined as 13 hours by measuring the changes of all components in slag. The relationships of Cr_2O_3 with C at different ratios of$(Al_2O_3+MgO+CaO)/SiO_2$ and the iso-concentration lines for C and Cr have been established.

Introduction

The changes in the technique of stainless steel production considerably affected the consumption pattern of chromium alloys in the past decade because about 79 per cent of the world's chromite products are used for the production of the steel and other special alloys. Low-carbon ferrochromium was used to a large extent in the past, but high-carbon ferrochromium become dominant as the conventional processes utilizing electric arc furnace is replaced by oxygen-blowing processes, such as AOD and VOD. However, the problems due to the use of high-carbon ferrochromium,such as long refining time, high slag volumes, high refractory consumption, and high consumption of oxygen in steelmaking processes, may result in a tendency to increase the use of medium-carbon ferrochromium refined from high-carbon ferrochromium.

The demand for refining of high-carbon ferrochromium may also increase in the future because the high grade chromites (chromium-rich, high-ratio, hard and lumpy) reserves are declining fast[1]. There are about 2270 mt of chromite ores (about 68 per cent of the world' reserves) in South Africa but only 30 per cent of the reserves can be classed as high-grade chromite ores. Upgrading techniques and agglomeration techniques, consequently, have to be employed for the conventional production of ferrochromium in submerged arc furnaces, which

will make the alloy several percentage points higher in carbon and silicon than that produced from hard, lumpy, high-grade chromites[2,3].The alloy produced from low-grade chromites, called "charge-chrome", usually contains above 6 per cent of carbon and above 2 per cent of silicon with a chromium content below 58 per cent. Low-grade chromites can not be converted to low-carbon(C<0.5%) or medium-carbon(C 0.5%-4%) ferrochromium via the conventional silicothermic ore/lime reduction under economically feasible conditions[4]. Decarbonization of charge chrome by oxygen-blowing processes may suggest a production path to a lower-carbon, lower-silicon, high-quality ferrochromium, which could be utilized more efficiently by steelmakers.

Oxygen-blowing processes by both top-blowing and bottom-blowing have be used on an industrial scale[5-13]. New attempt to increase decarbonation of the metal by adding nickel was investigated recently by W.Dresler[5,14]. The knowledge of the equilibria related to the concerned processes is of fundamental importance to handle the problems, such as loss of chromium in slag, removal of sulphur from metal, and control of silicon, etc.

Equilibria in Oxygen-Blowing Processes

There are two types of equilibria in the oxygen-blowing processes, metal/gas equilibrium and slag/metal/gas equilibrium. When oxygen or oxygen and argon gas is introduced into metal bath, the oxidation reactions take place at the interfaces of metal and gas bubbles. CO bubbles or (CO+Ar) Bubbles produced from oxygen or oxygen and argon by the reactions reach equilibrium with the metal at the interfaces very quickly due to the easiness of the mass transfer and the quickness of the reactions at the elevated temperature. The metal/gas equilibrium will be carried out until the bubbles come up to the interfaces of metal/slag at the top of the bath. At the same time, metal/slag/gas equilibrium takes place at interfaces of metal and slag, involving CO or (CO+Ar) gas, as shown in figure 1. The metal/gas equilibrium may play a important role to control the content of carbon. Meanwhile, the removal of sulphur, the loss of chromium and the control of silicon would be more closely related to the metal/slag/gas equilibrium.

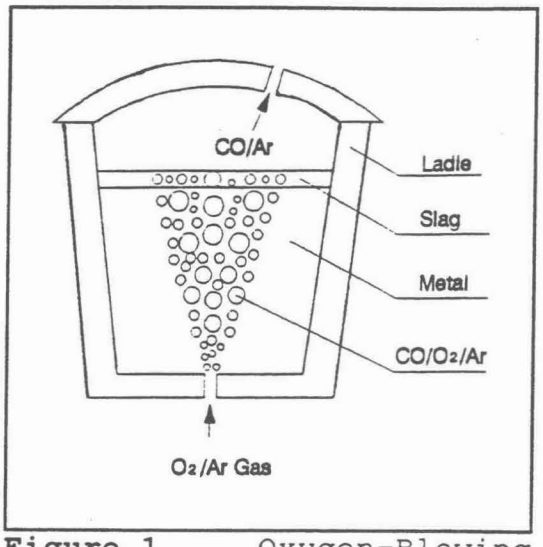

Figure 1. Oxygen-Blowing Processes

Experimental Results for Metal/Gas Equilibria

Experimental Procedure

All materials used in the experiments were of chemically pure grade.The metals used were in powder form and the starting composition of the alloy was 65%Cr, 0-5%Si, 0-0.1%S and Fe,as listed in table 1. Alumina crucible in size of H 40 mm, I.D. 25 mm and O.D. 28 mm was charged with metal powder and was located in the 20 mm hot zone of a molybdenum wound resistance furnace, which maintained constant temperature within 1 °C at 1500 °C. The experimental apparatus can be seen in figure 2. The partial pressure of CO in CO/Ar gas was

TABLE 1. Starting Composition of Metal, wt%

No.	Cr	Si	S	Fe
1	65.00	0.00	0.10	34.90
2	65.00	0.50	0.10	34.40
3	65.00	1.00	0.10	33.90
4	65.00	2.00	0.10	32.90
5	65.00	5.00	0.10	29.90

controlled by two tri-flat flowmeters, calibrated by a 50 ml Bunsen Tower. 8 g of alloy (without carbon) was kept in an alumina crucible at 1500 °C in the furnace with Pco changing from 0.0 to 0.83 atm in different experiments for 20 hours,based on the measured equilibration time in figure 3. The quenched metal was then analyzed by chemical methods.

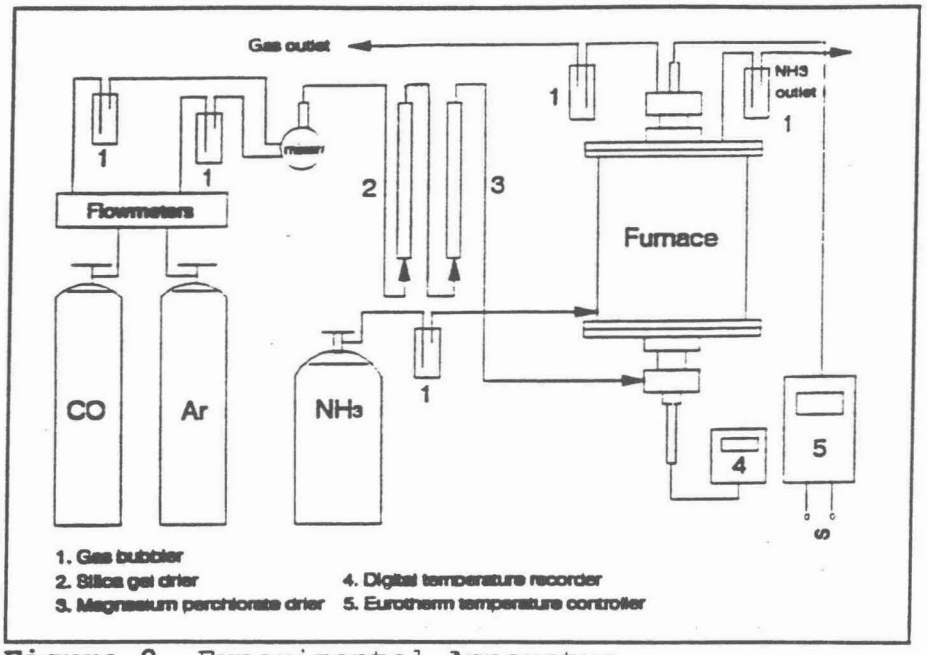

Figure 2. Experimental Apparatus

Relationship of C, Si Contents and Pco in CO/Ar Gas

Carbon content increases in the alloy with the increase of Si content and Pco. There is no carbon in the alloy when there is no CO in the gas. The carbon picked up in the alloy increases slowly with the increase of Pco when the Si content is low in the alloy. The carbon pick-up increases when there is more Si in the alloy. When no Si exists in the alloy, the carbon content also increases with Pco. The specific results are discussed in the following sections.The results are expressed in a 3-dimensional drawing in figure 4. Sulphur in the alloy does not change with Pco and Si. The way that carbon is picked up is from CO gas by reactions, such as:

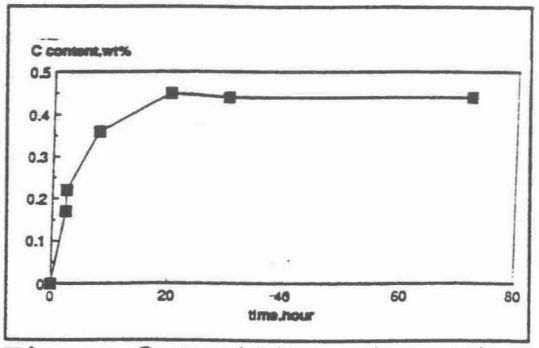

Figure 3. Equilibration Time at 1500 °C at 0.05 atm of Pco, 60-64%Cr,32-34%Fe,0.8-1.3%Si, and 0.1%S.

$$[Si] + 2CO = 2[C] + SiO_2 \quad (1)$$

$$2[Cr] + 3CO = 3[C] + Cr_2O_3 \quad (2)$$

$$[Cr] + CO = [C] + CrO \quad (3)$$

$$[Fe] + CO = [C] + FeO \quad (4)$$

$$2[Cr] + [Fe] + 4CO = 4[C] + FeOCr_2O_3 \quad (5)$$

Here [ ] refers to in metal. There may be more reactions like reaction (5), forming complex components. It can be shown that reaction (1),(2),(5), and (3) are the major reactions to cause the alloy to pick up carbon from gas.The result of the calculation is shown in figure 5, based on the free-energy changes of the reactions at 1500 °C, metal of 63%Cr, 3%Si, 34%Fe and pure oxides produced,assuming that the species in the alloy behaviour ideally.

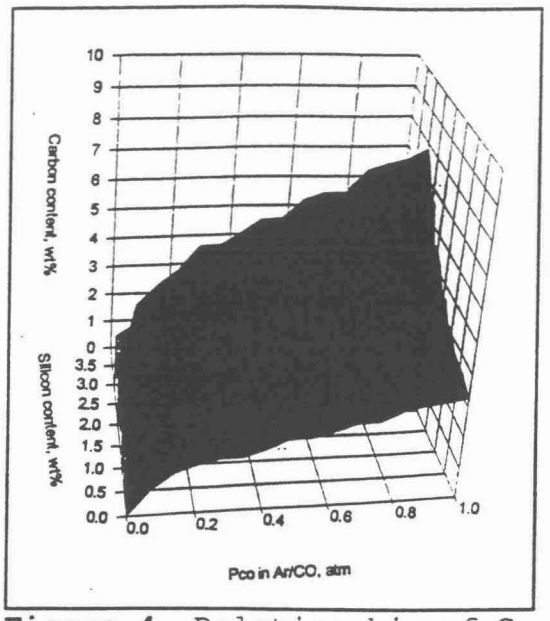

Figure 4. Relationship of C, Si and Pco in CO/Ar gas at 1500 °C, 61%Cr-Fe-C-Si.

Relationship of C and Pco

The result shows that carbon content in the alloy without Si increases from 0.0% to about 2.6% when Pco increases from 0 to 0.83 atm. Carbon content in the metal of 3wt%Si increases from 0.0 wt% to about 7.2 wt% with increase of Pco. Within 0.0 to 0.15 atm of Pco, the carbon content increases very quickly. The more Si in the metal, the more C content the metal gets. Figure 6 shows the results.

Relationship of C and Si

Carbon content of the alloy increases with increasing Si when CO exists in the gas phase. But when there is no CO in the gas, metal can not pick up carbon at all. The result is shown in figure 7.

The relationships of C,Si contents and Pco are very important to determine the O_2/Ar ratio for the decarbonization process via O_2/Ar blowing, such as in VOD and AOD, because the Pco in the bubbles of CO/Ar, which comes from the reaction of decarbonization, determines the final content of Si and carbon in the alloy. For example, when Si content and Pco are fixed, the minimum carbon content,reduced by blowing in the metal, can be predicted. On the other hand, when the contents

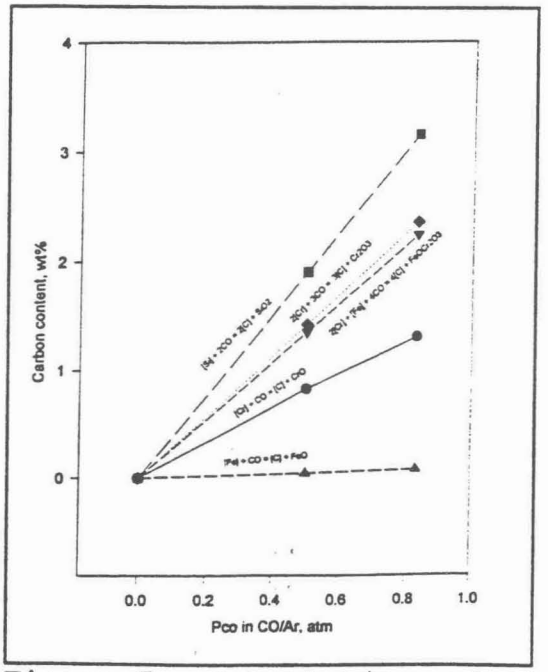

Figure 5. Calculation of C picked up from CO at 1500°C, 63%Cr-34%Fe-3%Si-C.

of Si and C in the alloy are decided,the maximum O_2/Ar, which can be converted from the maximum Pco, should be used. The carbon content of the metal can not be reduced to the level if the Pco used is higher than the maximum Pco predicted from the figures.

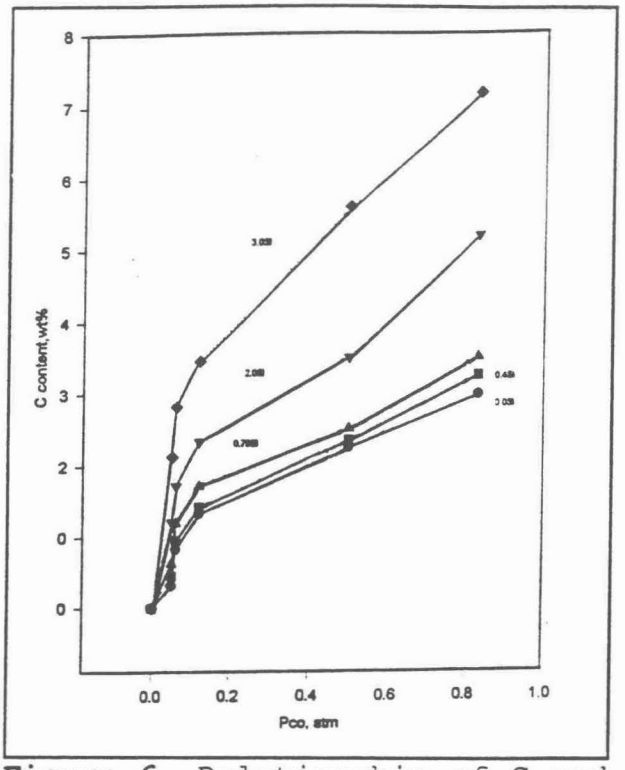

Figure 6. Relationship of C and Pco in CO/Ar gas at 1500 °C, 61%Cr-Fe-Si-C.

Experimental Results for Metal/Slag/Gas Equilibrium

Experiments started with 2-3g of metal, 3-5g slag in pure Cr_2O_3 crucibles of H18mm, I.D.25mm, and O.D.30mm. Different ratios of Al_2O_3 to MgO and SiO_2 content were made by adding alumina and silica into the master slag. Only one metal composition was used. Table 2 and 3 list the compositions of master slag and metal. Experiments were conducted at 1500 °C at 0.83 atm of Pco for 13 hours, based on the experimental measurement of equilibration time in terms of changes of all components in slag. The equilibration time for the system can be seen in figure 8.

Relationships of Cr_2O_3 and Carbon

Chromium oxide in slag decreases with the increase of C content in metal at CO atmosphere at 1500 °C. Increase of $(Al_2O_3+MgO+CaO)/SiO_2$ ratio also helps reduce Cr oxide in slag.In equilibrated slags,the Al_2O_3/MgO ratio was around 1.6 and CaO content was around 1.4%.In the metal phase,Si content was around 0.25% and S between 0.03 and 0.4%.The results are shown in figure 9.

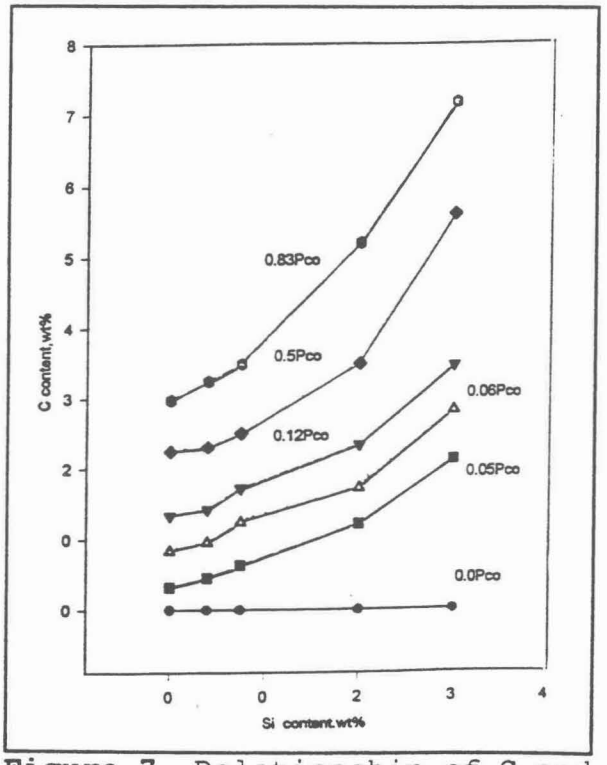

Figure 7. Relationship of C and Si in CO/Ar gas at 1500 °C, 61%Cr-Fe-Si-C.

C and Cr contents of the Metal Phase

The results are expressed in SiO_2-$(Al_2O_3+CaO+MgO)$-$(Cr_2O_3+Fe_2O_3)$ ternary diagrams by iso-concentration lines for C and Cr in figures 10 and 11. Si in metal is 0.21 wt% to 0.29 wt%(0.25wt% average), S 0.03wt% to 0.4wt% and Fe the balance. More experiments are needed to determine the S-content line.

TABLE 2. Composition of Master Slag, wt%

MgO	CaO	Al_2O_3	SiO_2	Total
18.56	2.05	25.01	54.38	100.00

TABLE 3. Composition of Metal, wt%

Cr	C	Fe	Si	S
65.00	10.00	21.50	3.00	0.50

All data from the experiments are the compositions of the slag phase and metal phase in terms of Al_2O_3, Cr_2O_3, Fe_2O_3, SiO_2, CaO, MgO, S in slag and Cr, Fe, C, Si, S in metal, with 12 variables in compositions. It is impossible to understand the relationships among those all variables. Systematic treatments are necessary both in the experimental design and in data treatment. The phase rule is a very useful tool to analyze the multi-phase equilibria[14,15]. The Gibbs Phase Rule is expressed as follows:

$$F + P = C + 2 - R$$

where F is the number of degrees of freedom, P the number of phases, C the number of components and R the number of independent restrictions.The system is comprised of the following:
phases: slag, metal, gas, Cr-oxide crucible
slag: Al_2O_3, Cr_2O_3, Fe_2O_3, SiO_2, CaO, MgO, S
metal: Cr, Fe, C, Si, S
gas: CO
crucible: Cr oxide

C is 9 , P is 4,

$$F = 9 + 2 - 4 - R$$
$$= 7 - R$$

In order to express all relations among the compositions of both slag and metal in a ternary diagram, F has to be 2. That means other three independent restrictions must be introduced to the system except Pco=0.83 atm and T=1500°C. When the saturation of slag by Cr-oxide from crucible is taken into account, the other 2 restrictions are Si

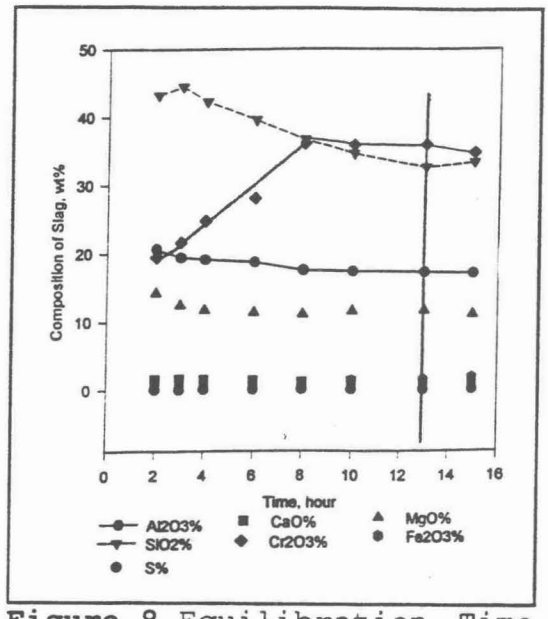

Figure 8. Equilibration Time for Metal/Slag/Gas at 1500°C in Cr-oxide crucibles.

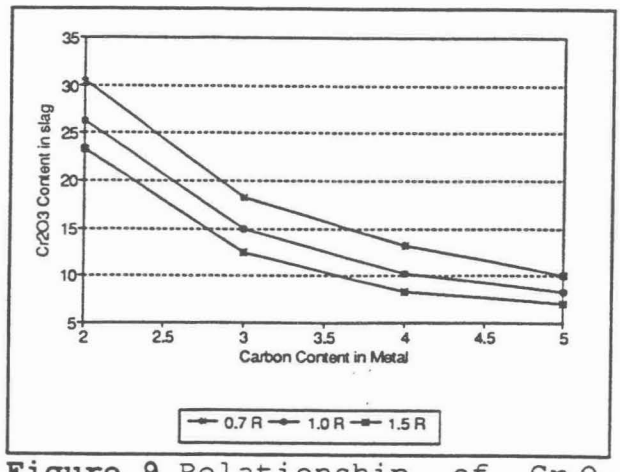

Figure 9. Relationship of Cr_2O_3 and Carbon at 1500°C at CO atm, Cr-Fe-C-0.25%Si-(0.03-0.4%)S R--$(Al_2O_3+MgO+CaO)/SiO_2$.

0.25wt% in metal and the ratio of Al_2O_3 to MgO 1.6 in slag. When any two of those compositions are fixed, all the other compositions can be read from a SiO_2-(Al_2O_3+CaO+MgO)-(Cr_2O_3+Fe_2O_3) ternary diagram. For instance, when SiO_2 and (Al_2O_3+CaO+MgO) are chosen, the slag's composition is fixed at a point in the ternary diagram and the metal composition can be found in the same ternary diagram by the iso-concentration lines for Cr, C, S and [S]/(S) with the restriction of 0.25wt% Si. Because CaO and Fe_2O_3 change very little, only from 1.3 to 1.5wt% and from 0.4 to 1.0 wt% respectively, they are taken into consideration together with other compositions in terms of (Al_2O_3+CaO+MgO) and (Cr_2O_3+Fe_2O_3). The ratio of Al_2O_3 to MgO can be controlled by the ratio in the slag, and the restriction of 0.25wt% Si can be realized by selection of the experimental data. The iso-concentration lines for S and [S]/(S), which are used to determine S in metal and slag, are not fitted in the diagrams because of only limited results from experiments.A layer of oxides has been found on the inner wall of the crucibles, which may be very important to maintain slag/metal equilibrium.

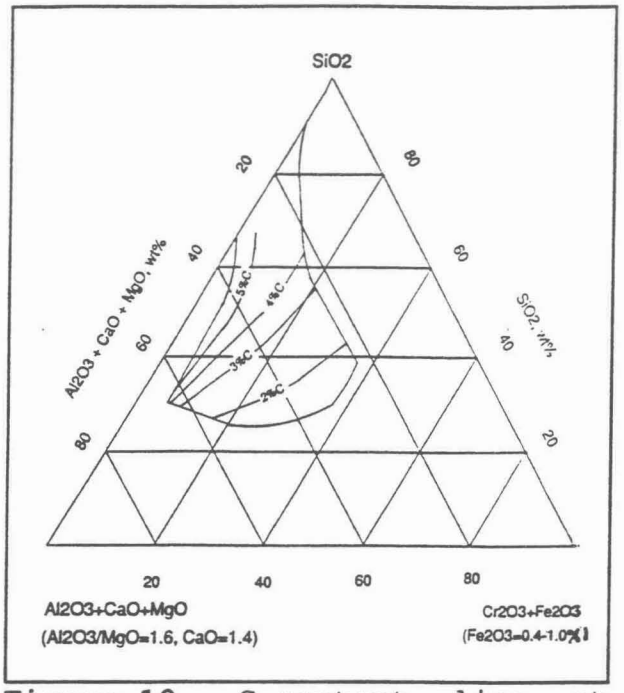

Figure 10. C-content line at 1500 °C at CO atm, Cr-Fe-C-0.25%Si-(0.03-0.4)%S.

Future Work

More experiments will continuously be conducted in the slag/metal/gas system in the chromium oxide crucibles at 1500 °C at 0.05 atm of Pco.The liquid area at 1500 °C for the slag in the SiO_2-(Al_2O_3+MgO+CaO)-(Cr_2O_3+Fe_2O_3) ternary diagram will be measured experimentally because this area is not clear enough in the ternary diagram from existing literature.The investigation of the layer on the inner crucibles used for the experiments by X-ray diffraction and other methods is necessary to confirm what species exist in the layer and to explain why the Cr-oxide crucibles could be used for the multi-phase experiments.

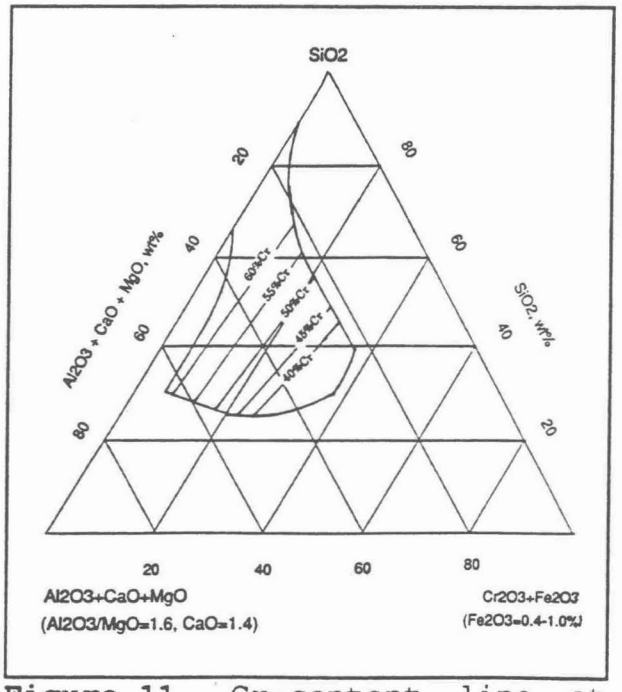

Figure 11. Cr-content line at 1500°C at CO atm, Cr-Fe-C-0.25%Si-(0.03-0.4%)S.

Conclusion

By the systematical investigation conducted for metal/gas and metal/slag/gas equilibria at

1500 °C, the following conclusions can be made:

1. The relationships of Si, C and Pco in metal/gas have been determined at 1500 °C in the range of Si 0.0 to 3.0 wt%; C 0.0 to 7.8 wt%, and Pco in Ar/CO gas 0.0 to 0.83 atm. The carbon content increases with increase of Pco and Si content. Two 2-dimensional and one 3-dimensional drawings are used to express the relations.

2. In slag/metal/gas equilibria in Cr-oxide crucibles at CO atmosphere and 1500 °C, the equilibration time is determined as 13 hours by measuring the changes of all components in slag. The relationships of Cr_2O_3 with C via different ratios of $(Al_2O_3+MgO+CaO)/SiO_2$ and the iso-concentration lines for C and Cr have been determined.

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