Phase Equilibria and Oxygen Potential in SiO_2-CrO-MgO-Al_2O_3 Slags (MgO/Al_2O_3=2.0)

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Introduction

Slags for high carbon ferrochromium and ferrosilicochromium production are best described by the SiO_2-MgO-Al_2O_3-CrO_x system. It is well known that the solubility of Cr_2O_3 is very low in the slag systems SiO_2-MgO, MgO-Al_2O_3 and SiO_2-Al_2O_3 at temperatures of practical interest and accordingly also in the system SiO_2-MgO-Al_2O_3. Only limited data is available about the solubility of divalent chromium oxide, CrO, in the same slag systems.

The CrO-SiO_2 system has been investigated at low oxygen pressures by Healy [1]. According to this investigation, the melting temperature of pure CrO is about 1630°C, whereas Collins and Muan [4] reported the corresponding melting temperature at 1665°C. The liquid area in the pseudo-binary CrO-SiO_2 system is located between 55 mol% and 90 mol% of CrO at 1600°C. The solubility of CrO_x in CaO-SiO_2 and CaO-Al_2O_3-SiO_2 has been determined at 1500°C by Pretorius and Muan [2]. It was shown that the oxygen pressure and the basicity of the melt has very strong influence on the solubility of chromium oxide and on the valency of chromium in the oxide phase.

Knowledge of the component, especially chromium oxides, activities in slag is of great importance from a theoretical and practical point of view. However, little information is available in the literature. Kay and Taylor [7] measured activities in the CaO-MgO-Al_2O_3-SiO_2 system. Activities in MgO-Al_2O_3-SiO_2 slags were investigated by Chipman [8] and by Henderson [9]. Pavlov *et al* [10] studied the enthalpies of Cr_2O_3 and CrO dissolution in CaO-SiO_2 and CaO-SiO_2-Al_2O_3 by calorimetric investigation with monitoring of oxygen potential in the melt. The activities of chromium oxides in liquid CaO-SiO_2-CrO_x slags were determined by the using of electromotive force measurements [11].

The purpose of this investigation has been to make an approximate determination of phase relations and liquidus isotherms at 1600°C and 1700°C for the system SiO_2-CrO-MgO-Al_2O_3 where the weight ratio MgO/Al_2O_3=2.0, and to measure the oxygen potential of the slag system at 1600°C by the electromotive force (EMF) method.

Experimental

Phase relation experiments

The experiments on phase relations in the present slag system were carried out in an induction furnace in argon atmosphere. 5g of slag with appropriate composition were placed in a chromium crucible and kept at 1600°C or 1700°C for 60 or 30 minutes. When the slag was entirely molten the crucible was then pulled out of the furnace and rapidly quenched in water. Hence, equilibrium relations prevailing at the high temperature were "frozen".

The initial slag compositions were prepared as mixtures of a master slag (SiO_2=34.2%, MgO=44.8%, Al_2O_3=21.0%) and pure oxide components. The range of initial slag composition was 5-50% SiO_2, 1.3-40% MgO, 0.7-20% Al_2O_3 and 10-93% CrO. CrO was added to the slag samples as Cr_2O_3 and Cr_{met} in weight proportion according to the reaction:

$$Cr_2O_3 + Cr = 3CrO \tag{1}$$

The idea behind these experiments was as follows: solid phases present at the high temperatures are retained, stable or metastable, after quenching and the liquid phase solidifies as glass. So, if the slag is completely liquid it solidifies completely as a glass with fast cooling; if the slag is partially melted, it will contain crystals of a primary solid phase together with a glass phase.

The slag samples were analyzed using electron microprobe to determine the content of SiO_2, Cr_2O_3, MgO and Al_2O_3 in originally solid and liquid phases. The analyzed sum of oxides in the solid phases was very close to 100%, whereas the total in the liquid (glass phase) usually exceeded 100%. This indicates that the chromium oxide in the liquid was mainly present as CrO and not as a Cr_2O_3. Formation of CrO from added Cr_2O_3 proceeds according to the reaction 1. In these cases the chromium oxide contents were recalculated to CrO. All slag compositions were normalized to 100%.

Oxygen potential experiments

The oxygen potential of the slag corresponding to the complete liquid area at 1600°C has been investigated. These experiments were carried out in a resistance furnace with a graphite heating element in argon atmosphere. The slag samples (40 g) were equilibrated in a chromium crucible at chosen temperature.

The initial slag compositions shown as a square points in Figure 1. These starting materials were prepared in the same way as described above. The molten slag was continuously bubbled with argon gas through a zirconia pipe with molybdenum tip for faster

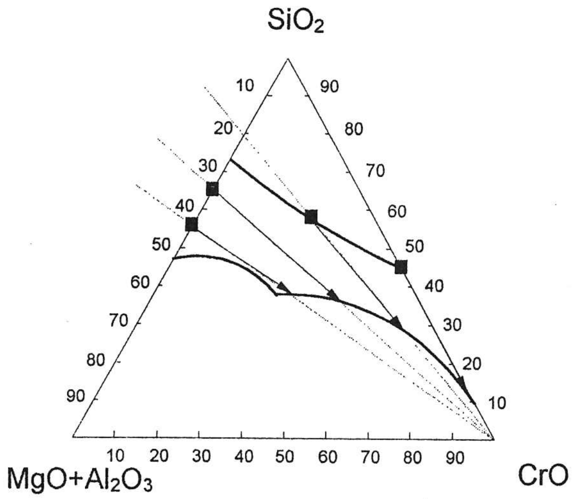


Fig.1. Slag compositions investigated by EMF method.

establishment of equilibrium. The temperature was measured by a W/W-Re thermocouple in an alumina protection tube, also with molybdenum tip. After 10 min the oxygen potential of the slag was measured and a certain amount of (Cr_2O_3+Cr) was added to the melt to change the slag composition in the direction of the CrO corner (see Fig.1) and so on with further additions. Figure 2 shows a sketch of experimental apparatus.

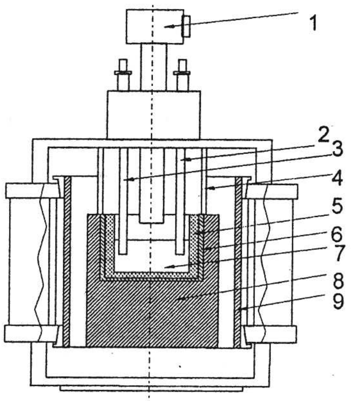


Fig.2. Experimental apparatus.

1 - equipment for adding materials to melt;
2 - Ar lance;
3 - thermocouple and oxygen probe;
4 - Al_2O_3 pipe;
5 - Cr crucible;
6 - Al_2O_3 crucible;
7 - slag;
8 - graphite block;
9 - heating element

The oxygen potential in the liquid slag was measured by the using of $ZrO_2(Y_2O_3)$ electrolyte probes. A mixture of Mo and MoO_2 connected with a Mo wire was used as a reference electrode in the electrolyte probe. The measured electromotive force of the cell is given by the following equation [12]:

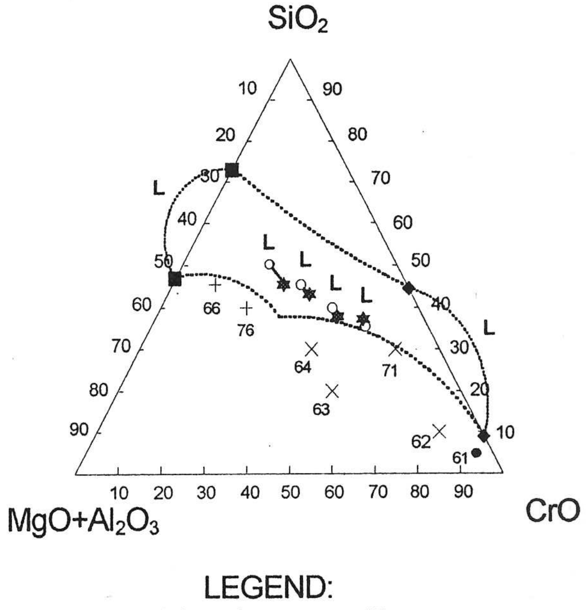
$$E=\frac{RT}{F}\ln\frac{P_{O_2(ref.)}^{1/4}+P_e^{1/4}}{P_{O_2(x)}^{1/4}+P_e^{1/4}} \qquad (2)$$

where,
E - the electromotive force measured,
R - gas constant; 8.314 J/K/mol,
F - Faraday constant; 96487 J/V/mol,
T - temperature, K,
$P_{O2(ref.)}$ - the oxygen partial pressure referring to the Mo-MoO_2 (reference electrode):
$\lg P_{O2(ref.)} = 25635/T+6.181$ [12],
P_e - the characteristic of oxygen partial pressure at which the ionic and electronic conductivity are equal:
$\lg P_{e\,(ZrO2(Y2O3))} = -130200/T+59.2$ [6],
$P_{O2(x)}$ - the oxygen partial pressure in investigated slag system.

Results and discussion

Phase relation experiments

The experimental results at 1600°C are shown in Figure 3. In Fig.3, the liquid area for the CrO_x-free system, SiO_2-MgO-Al_2O_3, have been taken from Levin et. al [3] and for SiO_2-CrO from Healy [1]. The final slag compositions are shown only for completely liquid slag. This is because the liquid phase in partially melted slag have had a M/A ratio different from the original mixture, M/A=2, due to the presence of solid phases: spinel or forsterite. Values near the points give the number of the sample.



LEGEND:
○ - initial slag compositions
✱ - final slag compositions
■ - liquid area in SiO_2-MgO-Al_2O_3
◆ - liquid area in SiO_2-CrO
○, ✱ - liquid (L)
\+ - L+forsterite
× - L+(Mg,Cr)O·(Al,Cr)$_2$O$_3$
● - L+(Cr_2O_3+Cr)

Fig.3. Experimental results at 1600°C.

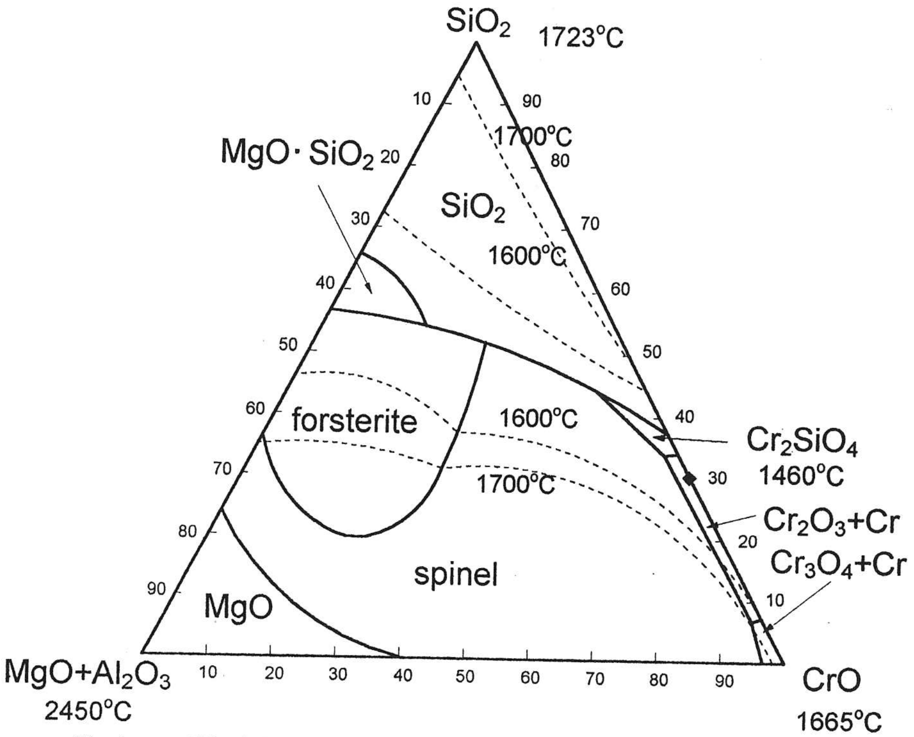


Fig.4. SiO_2-CrO-MgO-Al_2O_3 (M/A=2) phase diagram.

In the CrO rich corner (sample 61) the following phases have been observed in solidified slag: glass (liquid) and Cr_2O_3 with 1.5% MgO and 0.7% Al_2O_3 in solid solution. This solid phase coexists with a liquid having 49% CrO and a ratio M/A=0.5. In addition to oxide phases, small metallic inclusions were observed in the solidified slag sample. These were not analyzed, but it is believed to be chromium.

The composition of solid phases which are in equilibrium with the liquid were calculated based on the results of analysis. The composition of the solid phases in the samples 66 and 76 corresponds to forsterite, $2MgO \cdot SiO_2$, with 4.9-14.7 % of Cr_2O_3 in solution. A solid forsterite phase with up to 15% of Cr_2O_3 coexists with liquids in samples containing less than 30% CrO.

The solid phase in the samples 62-64 have a more complex composition: $MgAl_2O_4 \cdot xMgCr_2O_4 \cdot yCr_2O_3$, in which x varies from 2.5 to 5.5 and y from 0.3 to 7.6. $MgO \cdot Al_2O_3$ and $MgO \cdot Cr_2O_3$ are spinels. Besides, a some quantity of small metallic inclusions were observed in these samples. From visual observations it was concluded, that high concentrations of metallic inclusions correspond to the samples with a high value of y, in other words, with high concentration of "free" Cr_2O_3. In our opinion this phase can be expressed as $(Mg,Cr)O \cdot (Al,Cr)_2O_3$ - high chromium spinel. The solid spinel phase, $(Mg,Cr)O \cdot (Al,Cr)_2O_3$, coexisted with the liquid in samples with concentration of CrO from approximately 30% to 80% depending on silica concentration in the slag. It should be mentioned that the composition of the solid phase in sample 71 did not correspond to the chemical formulae $(Mg,Cr)O \cdot (Al,Cr)_2O_3$ as it had a very high content of SiO_2. However, the brightness and configuration of these particles were very similar to $(Mg,Cr)O \cdot (Al,Cr)_2O_3$. Probably this is because the initial slag composition was very close to the liquidus line and the solid phase is a solidified mixture of $(Mg,Cr)O \cdot (Al,Cr)_2O_3$ and liquid.

Four samples at 1600°C had only the glass phase. Thus, these slag samples were in the completely liquid area.

Very similar results were observed at 1700°C. Based on the present results a proposed and tentative phase diagram with liquidus isotherms at 1600°C and 1700°C have been constructed and is shown in Figure 4 for the SiO_2-CrO-MgO-Al_2O_3 (MgO/Al_2O_3=2.0) slag system. The liquidus isotherms along silica saturation were estimated. The liquidus isotherms in the lower silica area have been observed in present experiments. They have breaks at the borderline between forsterite and spinel phase.

According to Healy [1], Cr_2SiO_4 is the solid stable phase in equilibrium with the liquid in the SiO_2-CrO system at 33-38 %(mass) SiO_2. From results of Muan investigation [4], (Cr_2O_3+Cr) and (Cr_3O_4+Cr) are formed as a primary solid phases in this system at low concentration of silica depending on the temperature. It seems safe to assume that all these phases may also be formed with some concentration of MgO and Al_2O_3 in the slag.

The fields of SiO_2, protoenstatite and MgO were estimated. The presence of spinel is also well known in SiO_2-MgO-Al_2O_3 system. In this system, for M/A=2, the SiO_2 forms a solid stable phase in equilibrium with the liquid at 65-100% SiO_2; protoenstatite

($MgO \cdot SiO_2$) - at 57-65% SiO_2; forsterite ($2MgO \cdot SiO_2$) - at 36-57% SiO_2; spinel ($MgO \cdot Al_2O_3$) - at 23-36% SiO_2 and periclase (MgO) - at concentration of SiO_2 less than 23%.

According to Figure 4 there is a total of five eutectics and peritectics inside this pseudo-ternary system where three different solid phases are in equilibrium with liquid at some temperatures. From this follows that there is a total of eight fields of primary crystallization: SiO_2, protoenstatite, forsterite, spinel, periclase, Cr_2SiO_4, (Cr_2O_3+Cr) and (Cr_3O_4+Cr).

Oxygen potential of the slag system

As was already discussed, the content of chromium in liquid slag was assumed to be mainly CrO. However small amount of Cr_2O_3 must also be dissolved in slag.

Equilibrium in Cr-CrO-Cr_2O_3 system can be presented by the following reactions:

$$Cr_{(s)} + 1/2O_2 = CrO_{(l)}$$

$$\Delta G^o = -334218 + 63.81 \cdot T \text{ (J) [5]}$$

$$K_3 = \frac{a_{CrO}}{a_{Cr} \cdot P_{O_2}^{1/2}} \qquad (3)$$

$$2Cr_{(s)} + 3/2O_2 = Cr_2O_{3(s)}$$

$$\Delta G^o = -1092442 + 237.94 \cdot T \text{ (J) [5]}$$

$$K_4 = \frac{a_{Cr_2O_3}}{a_{Cr} \cdot P_{O_2}^{3/2}} \qquad (4)$$

If the activity of chromium and chromium oxides is unity, the equilibrium partial oxygen pressure can be easily calculated:

$$\lg P_{O_2(CrO_{(l)})} = -34956/T + 6.67$$

$$\text{(-12.00 at 1600°C)} \qquad (5)$$

$$\lg P_{O_2(Cr_2O_{3(s)})} = -38104.68/T + 8.299$$

$$\text{(-12.05 at 1600°C)} \qquad (6)$$

Then the equilibrium in the present system can be expressed by the two reactions:

$$Cr + 1/2O_2 = (CrO) \qquad (7)$$

$$2Cr + 3/2O_2 = (Cr_2O_3) \qquad (8)$$

The oxygen partial pressure can be calculated from measured electromotive force according to equation (2). However, the correct calculations of chromium oxide activities in the slag could not be done. This is because even in chromium crucible the activity of chromium was not unity due to formation of some intermediate phase between material of crucible and liquid slag.

For that reason the experimental results are shown as lines of *iso-lgP_{o2}* (atm) in Figure 5. According to this figure, the oxygen potential of the slag depends on the concentration of chromium oxides in the system and reaches its maximum value near the CrO corner where liquid slag is saturated by (Cr_2O_3+Cr).

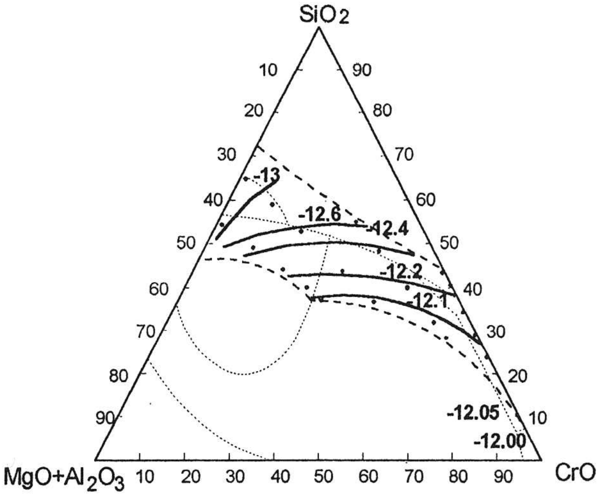


Fig.5. Iso-lgP_{o2} diagram for SiO_2-CrO-MgO-Al_2O_3 (M/A=2) equilibrated in chromium crucible at 1600°C.

Conclusions

A tentative phase diagram with liquidus isotherms at 1600°C and 1700°C have been constructed for the SiO_2-CrO-MgO-Al_2O_3 (MgO/Al_2O_3=2.0) slag system. The phase diagram shows liquidus lines and phases of primary crystallization. The path of crystallization and the kind of secondary solid phases are more difficult to guess. This is because after (or even during) precipitation of the primary phase, the rest liquid changes its composition from the presupposed ratio M/A=2 for which the diagram is valid. If a more accurate diagram or diagrams with different M/A ratios are required, further experiments will be necessary.

The *iso-lgP_{o2}* diagram in the liquid area for the present slag system were determined at 1600°C. The oxygen potential of the slag depends, naturally, on concentration of chromium oxides.

Acknowledgment

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