Phase relations and liquidus surfaces in SiO_2-CrO_x-MgO-Al_2O_3 slags (MgO/Al_2O_3=2.0).

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1. INTRODUCTION

Slags for high carbon ferrochromium and ferrosilicochromium production are best described by the SiO_2-MgO-Al_2O_3-CrO_x system. The complete graphical representation of a condensed quaternary system requires four dimentional space. So, this system can be presented as a tetrahedron with SiO_2-MgO-Al_2O_3 in the base and with CrO_x in the top corner. Here CrO_x represents two types of chromium oxides: Cr_2O_3 and CrO. Any intersection drawing through the SiO_2-CrO_x side of tetrahedron is a reflection of equilibrium in the system at some constant MgO to Al_2O_3 ratio (M/A).

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_x-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.

The purpose of this investigation is to make an approximate determination of phase relations and liquidus isotherms at 1600°C and 1700°C for the system SiO_2-CrO_x-MgO-Al_2O_3 where weight ratio MgO/Al_2O_3=2.0.

2. EXPERIMENTAL

The experiments 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 chosen temperature (1600°C or 1700°C) for 60 or 30 minutes, accordingly. Each crucible had 6 holes, so 6 slag samples were investigated in each test. When the slags were entirely molten the crucible was then pulled out of the furnace and rapidly quenched by dropping it instantaneously into a liquid at low temperature (water) and equilibrium relations prevailing at the high temperature were "frozen".

The slags 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 slags as Cr_2O_3 and Cr_{met} in weight proportion according to the reaction:

$$Cr_2O_3 + Cr = 3CrO \qquad (1)$$

After experiments slag samples were analyzed by electron microprobe analysis 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 phases) usually exceeded 100%. This indicates that the chromium oxide in the liquid was 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%.

The results of electron microprobe analysis are listed in the table 1.

Some experiments were carried out in a resistance furnace with slow cooling (1 °C/min) to determine phase relations in solidified slag samples. However, these results were very difficult to interpret as the MgO/Al_2O_3 ratios were different in the various solid phases. This will not be further discussed here.

3. RESULTS AND DISCUSSION

The idea behind these experiments was as follows: solid phases present at the high temperatures are retained, stable or metastable, at ordinary temperature; phases which are liquid at temperatures of experiments exist as glasses at low temperatures. So, if the slag is completely liquid it solidify completely as a glass with fast cooling; if the slag is partially melted, it contains crystals of a primary solid phase together with a glass phase after quenching. Here the glass phase represents the original liquid phase.

In the CrO_x rich corner (sample 61) the following phases have been observed in solidified slag: glass (liquid) and Cr_2O_3 (Figure 1a). 1.5% MgO and 0.7% Al_2O_3 were taken into solid solution by Cr_2O_3. This solid phase coexists

Table I Results of electron microprobe investigation

№ of samples		present phases	phase composition, %(mass.)					
1600°C	1700°C		SiO_2	CrO	Cr_2O_3	MgO	Al_2O_3	M/A
61	-	glass	49.8	49.0	-	0.4	0.8	0.5
		Cr_2O_3	0.1	-	97.7	1.5	0.7	2.14
62,63 64	81,82	glass	38.3-49.7	20.1-51.4	-	2.3-21.8	3.8-9.6	0.52-2.60
		spinel· Cr_2O_3	0.1-0.4	-	61.9-84.7	10.6-20.8	4.6-17.1	1.22-2.71
71	84	glass	51.6, 51.7	39.7, 19,6	-	5.1, 20.5	3.6, 8.2	1.42, 2.5
		???	23.1, 24.6	-	64.2, 48.8	9.5, 18.5	3.2, 8.1	2.97, 2.28
66, 76	86	glass	40.7-42.8	15.2-26.1	-	16.3-17.4	15.8-25.7	0.63-1.10
		forsterite	39.2-41.5	-	4.9-14.7	45.3-52.6	0.3-1.0	-
	85	glass	50.5	17.5	-	18.2	13.8	1.32
		???	49.3	-	19.9	17.0	13.8	1.23
		???	42.9	-	16.2	31.2	9.7	3.22
72,73 74,75	-	glass	35.8-44.6	27.6-49.4	-	9.7-18.4	5.1-9.4	1.86-1.96

with a liquid having 49% CrO and a ratio M/A=0.5. In addition to oxide phases, small metallic inclusions were observed in solidified slag sample. These were not analyzed. But it is belived 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 solid phases in samples № 66, 76 and 86 corresponds to forsterite, $2MgO\cdot SiO_2$, with dissolved 4.9-14.7 % of Cr_2O_3. Solid phase in samples 62-64 and 81, 82 have a more complex composition: $MgAl_2O_4\cdot xMgCr_2O_4\cdot yCr_2O_3$, where x vary 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 various spinels. Besides, a various quantity of small metallic inclusions were observed in these samples. From visual observations it was concluded, that high concentration of metallic inclusions corresponds to the samples with a high value of y, in other words, with high concentration of "free" Cr_2O_3. Thus, this phase is presented as a (spinel+Cr_2O_3+Cr). In our opinion, the right part of this phase is a spinel as well: $CrO\cdot Cr_2O_3$. Finally, this phase can be expressed as $(Mg,Cr)O\cdot(Al,Cr)_2O_3$.

A solid spinel phase, $(Mg,Cr)O\cdot(Al,Cr)_2O_3$, coexisted with the liquid in samples with less than 30% SiO_2 and concentration of CrO_x from 30% to 80% (Figure 1b). Must be mentioned that the composition of the solid phase in samples 71 and 84 does not correspond to the chemical formulae of a $(Mg,Cr)O\cdot(Al,Cr)_2O_3$ as it has 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 compositions were 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.

A solid forsterite phase with up to 15% of Cr_2O_3 coexists with the liquid in samples with CrO_x less than 30% (Figure 1c). Two different solid phases coexist with the liquid in sample 85. Their compositions are not quite clear, but one of them has brightness and configuration similar to $(Mg,Cr)O\cdot(Al,Cr)_2O_3$. The dark phase looks like forsterite. This means that the slag composition has been close to the $(Mg,Cr)O\cdot(Al,Cr)_2O_3$-forsterite borderline.

Besides that, four samples at 1600°C had only glass phases. Thus, these slags were in a completely liquid area.

The experimental results are shown in Figure 2. In Figure 2, 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_x from Healy [1]. The final slag compositions are shown only for completely liquid slags. This is because the liquid phase in partially melted slags have had a M/A ratio different from the original mixture, M/A=2, due to the presens of solid phases $(Mg,Cr)O\cdot(Al,Cr)_2O_3$ or forsterite.

Based on the present results a proposed and very tentative phase diagram with liquidus isotherms at 1600°C and 1700°C have been constructed and is shown in Figure 3 for the SiO_2-CrO_x-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 $(Mg,Cr)O\cdot(Al,Cr)_2O_3$.

According to Figure 3 there is a total of six eutectics and peritectics inside this pseudo-ternary system where three different solid phases are in equilibrium with liquid at some temperatures. From this follows, there is a

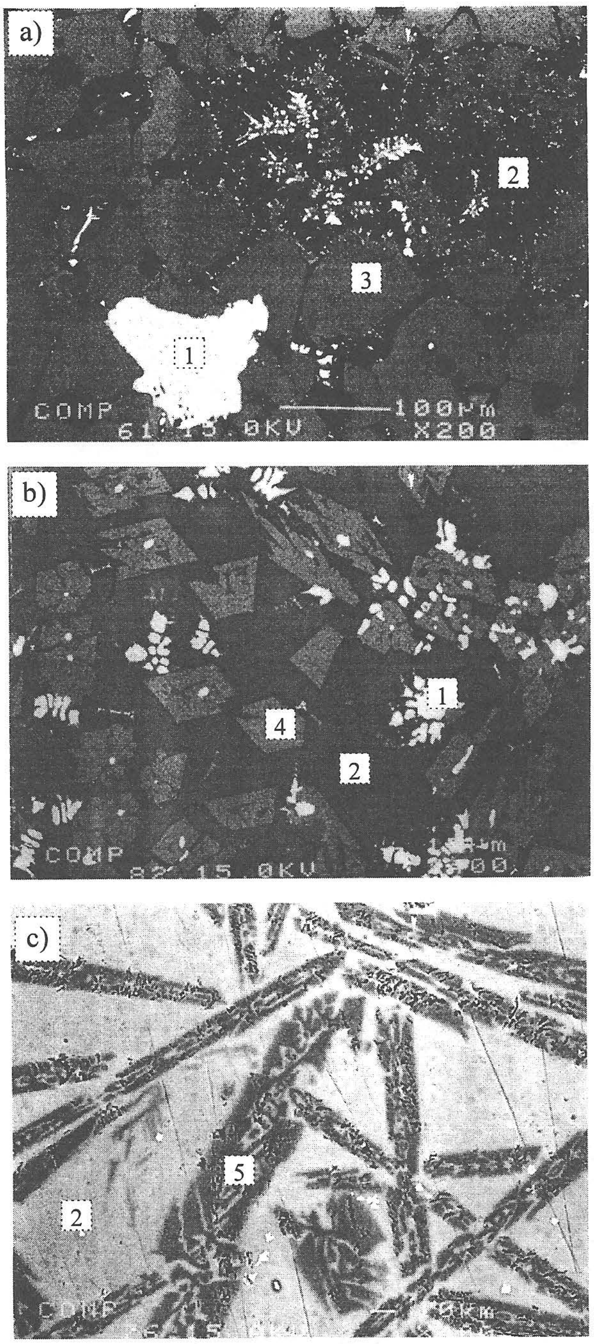

Fig. 1. Examples of metallographic observations for different stability areas: a) (Cr_2O_3+Cr) (x200); b) (Mg,Cr)O·$(Al,Cr)_2O_3$ (x400); c) forsterite (x400). 1 - metal; 2 - glass; 3 - Cr_2O_3; 4 - (spinel+Cr_2O_3): 5 - forsterite.

total of eight fields of primary crystallization: SiO_2, MgO·SiO_2 - protoenstatite, 2MgO·SiO_2 - forsterite, MgO·Al_2O_3 - spinel, MgO - periclase, (Mg,Cr)O·$(Al,Cr)_2O_3$, Cr_2SiO_4 and Cr_2O_3+Cr.

Forsterite, (Mg,Cr)O·$(Al,Cr)_2O_3$, and Cr_2O_3+Cr have been observed as primary solid phases by experiments.

According to Healy [1], Cr_2SiO_4 is the solid stable phase in equilibrium with the liquid in SiO_2-CrO system at 33-38 %(mass) SiO_2. It seems safe to assume that this phase may be formed also with some concentration of MgO and Al_2O_3 in the slag.

The fields of SiO_2, protoenstatite and MgO were estimated. It was also assumed that there is a ordinary spinel phase instead of (Mg,Cr)O·$(Al,Cr)_2O_3$ in the low CrO_x area. It is follows from the well known SiO_2-MgO-Al_2O_3 phase diagram. In this system at M/A=2 the SiO_2 is a solid stable phase in equilibrium with liquid at 65-100% SiO_2; protoenstatite - at 57-65% SiO_2; forsterite - at 36-57% SiO_2; spinel - at 23-36% SiO_2 and MgO - at concentration of SiO_2 less than 23%.

It should be mentioned that this 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.

4. CONCLUSION

A tentative phase diagram with liquidus isotherms at 1600°C and 1700°C have been constructed for the SiO_2-CrO_x-MgO-Al_2O_3 (MgO/Al_2O_3=2.0) slag system. If a more accurate diagram or diagrams with different M/A ratios are required, further experiments will be necessary.

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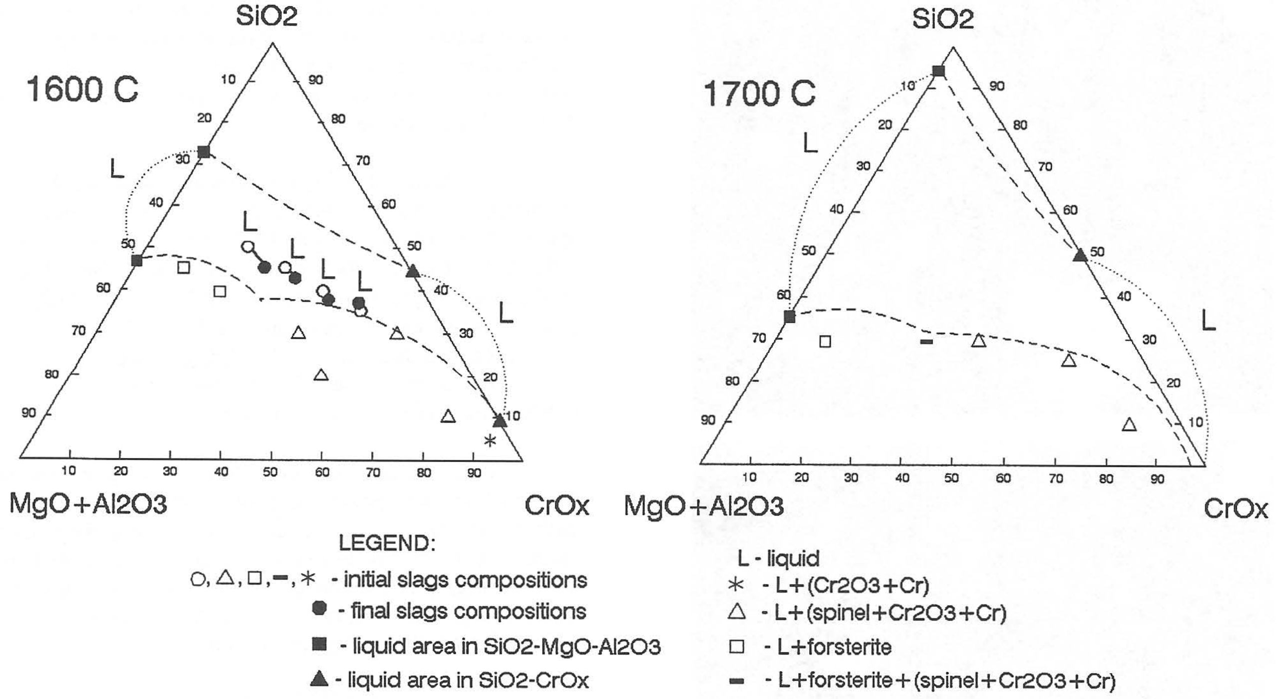

Fig. 2. Experimental results.

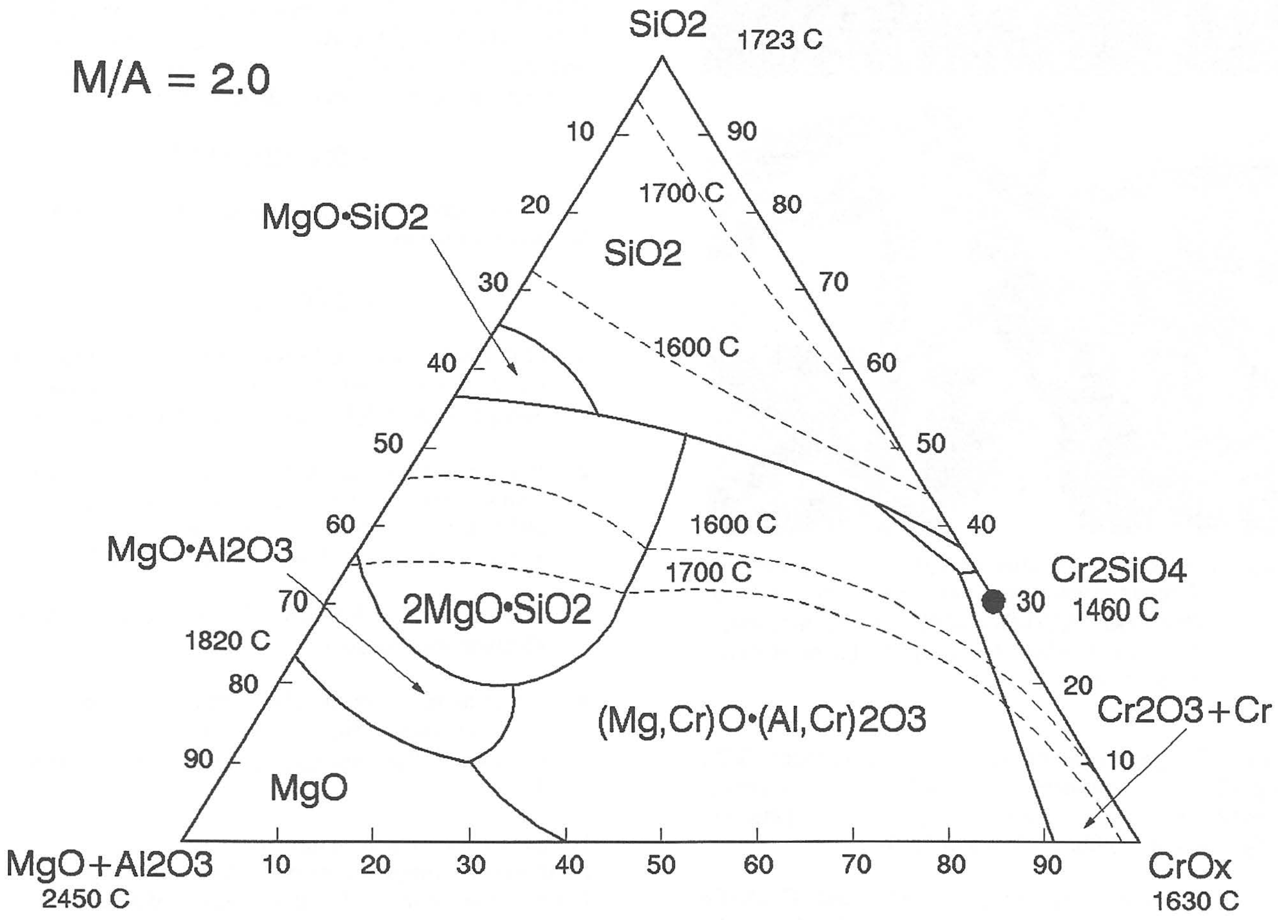

Fig. 3. Tentative SiO_2-CrO_x-MgO-Al_2O_3 (MgO/Al_2O_3=2.0) phase diagram.