The Effect of Chromium Oxide on the Phase Relations in the CaO-MgO-Al_2O_3-SiO_2-FeO_x System

Rachel Rait, Sharif Jahanshahi

and Shouyi Sun.

G K Williams Co-operative Research Centre for
Extractive Metallurgy, CSIRO - Division of Minerals,

Box 312, Clayton South, Victoria 3169.

Fax (61-3) 95628919

Keywords: Chromium, liquidus temperature, spinel, phase equilibria, ironmaking slags.

ABSTRACT

A drop-quench experimental technique coupled with optical and microprobe analyses of quenched samples were used to determine the liquidus temperature and phases in the CaO-MgO-Al_2O_3-SiO_2-FeO_x system. Addition of 1 wt % CrO_x to the slag under an atmosphere of air increased the liquidus temperature by up to 200°C in the spinel field. When the atmosphere was changed to CO_2, the liquidus temperature increased by about 50°C, with respect to the same chromium containing slags in air. There was little effect of chromium on the liquidus temperatures for slags in the melilite phase field. The solubility of chromium in the melt was found to decrease with increasing MgO content of the melt. Chromium was seen to partition strongly into the spinel structure with respect to the melt. No partitioning into melilite was evident from this study. Microprobe analyses of the spinel gave spinel composition as $Mg(AlCr_{0.9}Fe_{0.1})O_4$ to $Mg(Al_{1.3}Cr_{0.35}Fe_{0.35})O_4$. The saturated slag contained 0.4 to 0.9 wt% of Cr_2O_3, at temperature between 1520 and 1650 °C.

1. INTRODUCTION

New iron and steel making processes are usually highly intensified and therefore place stringent requirements on the refractory lining of the smelting vessels. Information on the interaction between metal, slag and refractory in the iron and steel making processes is very important to developing these new processes and technologies.

In previous studies[2], the authors have determined the liquidus temperatures of the CaO-MgO-Al_2O_3-SiO_2-FeO_x slag in the phase field of melilite and spinel. The effect of the addition of FeO_x and MgO and the oxygen potential has been studied. The liquidus temperature was seen to decrease by up to 50 °C in the melilite and spinel phase fields, with respect to the iron free slag. Reducing the oxygen potential, from $10^{-0.34}$ to 10^{-6} atm, increased the liquidus temperatures by up to 70 °C in the spinel and melilite phase fields. The major aim of this continuing study is to examine the stability of the relevant phases in contact with typical new iron-making slags containing small amounts of chromium oxide.

2. EXPERIMENTAL

Master slags were prepared by mixing appropriate amounts of analytical grade $CaCO_3$, SiO_2, Al_2O_3, MgO, Cr_2O_3 and Fe_2O_3 (purity>99%). The mixture was melted in a platinum crucible using a muffle furnace. Table I shows the analytical results of these master slags obtained by induction coupled plasma -atomic absorption spectrometry. A molybdenum disilicide vertical tube furnace fitted with water-cooled end caps was used for the drop-quench experiments. The bottom of the tube was sealed with plastic cling wrap. The atmosphere inside the furnace was controlled by a flowing stream of air or purified CO_2. A Pt-6%Rh/Pt-30%Rh thermocouple was used for measuring the temperature. The thermocouple was inserted from the top end cap and placed close to the sample in the tube furnace.

For each experiment about 300 mg of the pre-melted slag sample was placed in a platinum capsule and the capsule was lowered into the hot zone of the furnace. The sample was heated to the experimental temperature, where it was held for the required amount of time to reach chemical and thermal equilibrium before being dropped to quench in water. Preliminary experiments were carried out to ascertain the required equilibrium time.

Table I: Composition of master slags.

Sample	H1.5	H1.10	G4.0	H3.5	H4.5	H6.5	I3.5
SiO_2 (wt%)	35.49	32.36	32.84	31.66	28.58	30.38	23.86
CaO	38.72	35.85	34.97	30.50	32.54	29.52	39.67
Al_2O_3	21.09	20.87	19.95	19.46	20.89	19.65	20.29
MgO	0.27	0.00	11.68	9.27	11.18	10.83	8.79
Fe_2O_3	5.73	10.36	0.33	4.99	5.74	5.46	5.27
Cr_2O_3	0.99	0.98	0.73	1.21	0.98	0.89	0.99
Total	102.29	100.42	100.5	97.10	99.91	96.73	98.87

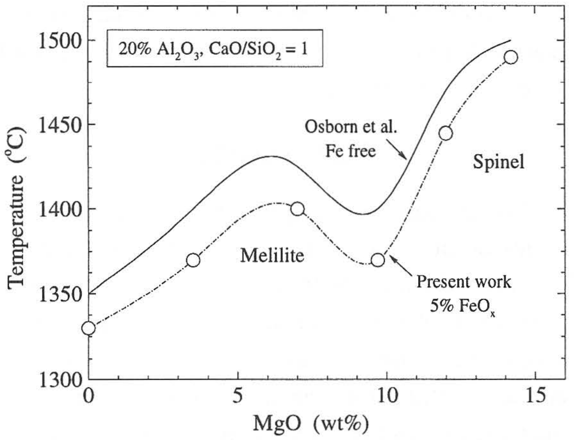

Figure 1. Liquidus temperatures for iron-free and iron-containing slags.

The quenched samples were then mounted, sectioned, polished and examined using an optical microscope. Sections that showed 100% glassy phase were at or above the liquidus temperature and those containing euhedral crystals were below it. Crystals were considered primary when they all exhibited the same habit, composition and size. Crystals that were formed during cooling were seen to have irregular form, a range of composition and size. By carrying out a number of these experiments on each master slag at different temperatures and examining the polished sections of products with a microscope the liquidus temperatures of the samples were determined. Samples were analysed on a JOEL Superprobe to determine the solid and melt phase composition. ICP-AA (induction coupled plasma -atomic absorption spectrometry) was used to determine the bulk slag composition.

3. RESULTS

Iron free samples were used for validating the method against the established data in the CaO-MgO-Al_2O_3-SiO_2 system of Osborn et al.[1] The results were within 10 °C of Osborn et al.'s data. Two crystal phases were identified by optical microscopy and microprobe analysis. These were:

- Melilite (a solid solution of gehlenite $Ca_2Al_2SiO_7$ and akermanite $Ca_2MgSi_2O_7$), a tetragonal crystal showing euhedral to subhedral tabular habit;
- Spinels ($MgAl_2O_4$) which were distinguished by their cubic euhedral habit and high reflectivity. These findings are in general accord with those by Osborn et al.[1]

Experiments were carried out to determine the effect of iron addition to the CaO-MgO-Al_2O_3-SiO_2 phase equilibria[2].

Table IIa. Microprobe analyses of liquid and crystalline phases in iron containing slags.

Sample	H1.10	H1.10	G4.0 256	G4.0 256	G4.0 256	G4.0 256	H3.5 267	H3.5 267	H4.5 279	H4.5 279	H4.5 267
Experimental Temperature °C	1357	1357	1548	1548	1601	1601	1600	1600	1602	1602	1600
Atmosphere	Air	Air	Air	Air	Air	Air	CO_2	CO_2	Air	Air	CO_2
Stable Crystal Phases	Mel	Mel	sp	sp	sp	sp	sp	sp	sp	sp	sp
Phase analysed	Mel	Mel	sp	liq	sp	liq	sp	liq	sp	liq	sp
Determined liquidus °C	1360	1360	1610	1610	1610	1610	1645	1645	1670	1670	1670
MgO(wt%)	5.34	0.05	25.62	11.16	24.64	11.46	23.75	9.11	25.81	13.60	25.79
Al_2O_3	24.50	25.18	47.40	19.25	41.33	19.96	38.46	20.29	45.99	19.23	46.58
SiO_2	27.35	29.08	1.37	31.30	0.05	33.09	0.05	33.32	0.08	27.95	0.08
CaO	35.04	36.58	1.84	34.63	0.40	33.39	0.55	32.36	0.43	30.95	0.40
Fe_2O_3	5.8	8.00	0.51	0.32	0.51	0.35	4.38	4.21	6.91	5.12	6.26
Cr_2O_3	0.41	0.57	22.62	0.61	31.87	0.91	32.03	0.61	20.75	0.72	21.52
Total	98.45	99.46	99.36	97.28	98.79	99.17	99.22	99.89	99.97	97.56	100.63
CrX/CrLiq	0.70		37.28		34.86		52.68		28.78		55.90

* mel=melilite, sp=spinel, liq=liquid

Table IIb. Microprobe analyses of liquid and crystalline phases in iron containing slags.

Sample	H4.5 267	H4.5 268	H4.5 268	H4.5 270	H4.5 270	H6.5 262	H6.5 262	H6.5 267	H6.5 267	I3.5 269	I3.5 269
Experimental Temperature °C	1600	1619	1619	1651	1651	1583	1583	1600	1600	1524	1524
Atmosphere	CO_2	CO_2	CO_2	CO_2	CO_2	Air	Air	CO_2	CO_2	CO_2	CO_2
Stable Crystal Phases	sp	sp	sp	sp	sp	sp	sp	sp	sp	sp	sp
Phase analysed	liq	sp	liq	sp	liq	sp	liq	sp	liq	sp	liq
Determined liquidus °C	1670	1670	1670	1670	1670	1665	1665	1665	1665	1590	1590
MgO(wt%)	13.25	25.30	13.36	23.14	9.45	24.74	13.65	23.68	10.56	24.49	8.42
Al_2O_3	18.68	46.80	18.86	32.83	20.18	39.60	19.56	40.90	19.64	43.33	19.53
SiO_2	29.13	0.07	28.80	1.72	29.96	0.07	28.61	0.07	31.54	0.20	26.23
CaO	31.91	0.38	31.78	3.17	33.00	0.47	31.50	0.46	31.89	0.88	40.07
Fe_2O_3	4.41	6.27	4.53	5.59	4.23	5.01	4.23	7.69	5.71	7.09	4.99
Cr_2O_3	0.39	20.94	0.48	34.54	0.93	30.30	0.75	26.53	0.42	23.27	0.50
Total	97.78	99.76	97.80	100.97	97.75	100.18	98.29	99.33	99.76	99.26	99.73
CrX/CrLiq		44.05		36.97		40.20		63.25		46.61	

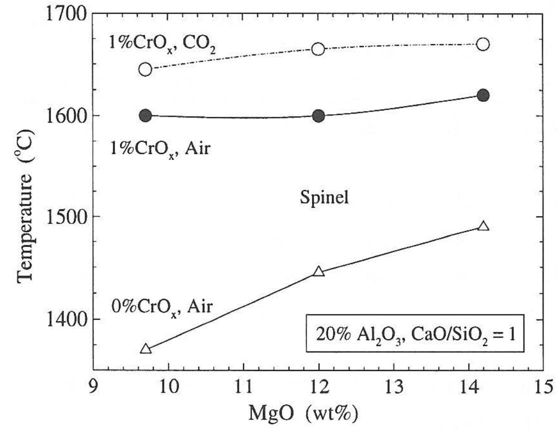

Figure 2. Effect of 1% CrO_x addition on the liquidus temperature of slags with CaO/SiO_2 ratio of 1, 5wt% FeO_x and 20 wt% Al_2O_3

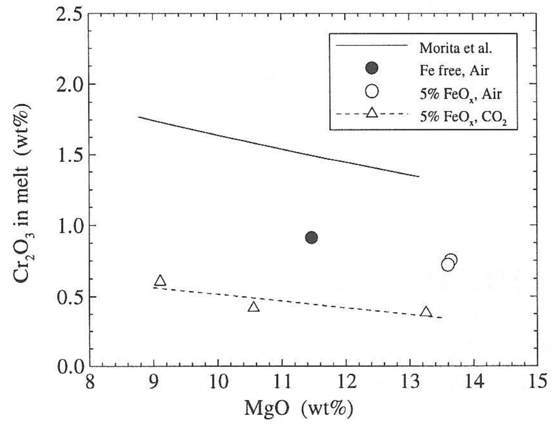

Figure 3. Solubility of Cr_2O_3 in the melt versus MgO content in the melt at 1600 °C. Results from this work are compared to the iron free slags from Morita et al.[3]at 1600 °C, in air.

It was found that the liquidus decreased by up to 50 °C due to iron oxide addition of 5 wt% (Figure 1). Experiments to determine the effect of CrO_x addition on the liquidus temperature of the $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}FeO_x$ slags were carried out. Chromium oxide addition to the slag had little effect in the melilite field; therefore, the study concentrated on the spinel phase field. The liquidus temperatures determined from these experiments are shown in Figure 2 and the results of the probe analyses of equilibrium phases are listed in Table II. As shown in Figure 2, addition of 1 wt% Cr_2O_3 to the slag under an atmosphere of air increased the liquidus temperature by up to 200°C in the spinel field (Figure 2). When the atmosphere was changed to CO_2, the liquidus temperature increased by about 50°C with respect to the same chromium -ontaining slags in air. A similar increase was seen for the chromium-free slags.

The solubility of Cr_2O_3 in the melt was between 0.4 and 0.9 wt% and decreased with increasing MgO in the melt when saturated with the spinel (Figure 3).

Chromium partitioned preferentially into the solid phases with respect to the melt. Analyses of these phases in the slags containing chromium oxide showed chromium substituted into the spinel structure (Table II). Microprobe analyses of the spinel gave a spinel composition range of $Mg(AlCr_{0.9}Fe_{0.1})O_4$ to $Mg(Al_{1.3}Cr_{0.35}Fe_{0.35})O_4$ (Table II).

The chromite spinels, in air, contained lower smaller amounts of chromium than those in CO_2. The iron-free slag containing chromium had spinels with higher amounts of chromium than the iron-containing slags. Spinels in the higher basicity slag (CaO/SiO_2=1.55) seemed to have more chromium than the slags with CaO/SiO_2=1. It was seen that in the spinel the chromium content negatively correlates to iron oxide and Al_2O_3 content of the spinel (Figure 4). Increasing the temperature increased the Cr_2O_3 in the spinel but there was no obvious trend in the melt.

4. DISCUSSION

Figure 3 shows the solubility of Cr_2O_3 in the melt with respect to the MgO content of the melt. Morita et al.[3] reported a decrease in the solubility of $MgO.Cr_2O_3$ with increasing MgO for 20% $MgO\text{-}CaO/SiO_2$=1 slag at 1600 °C in air. The data from the present study showed a similar trend but at lower solubility levels for the iron-containing slags. The only iron-free sample in our study showed a slightly lower chromium solubility than that of Morita et al.[3]. Morita et al.[4] reported that the solubility of $MgO.Cr_2O_3$ increased from 0.2 to 0.7 wt % Cr_2O_3 with the increase in oxygen potential from 10^{-6} to $10^{-0.32}$ atm for a 20 wt% MgO-20 wt% Al_2O_3-30 wt% CaO-30 wt% SiO_2 slag at 1600 °C. The Cr_2O_3 content in the spinel increased with decreasing oxygen potential but the melt did not seem to show any correlation. There was no dependence of solubility of $MgO.Cr_2O_3$ on the basicity (CaO/SiO_2 ratio) for slags with $CaO/SiO_2>0.3$ which contain 20 wt% MgO and 20 wt% Al_2O_3 at 1600 °C in air.[3] The present study showed a slightly lower solubility of Cr_2O_3 than the $CaO/SiO_2=1$ slags. Morita et al.[4] reported that the solubility of $MgO.Cr_2O_3$ decreased with increasing Al_2O_3 in the melt for 20 wt% $MgO-CaO/SiO_2=1$ slags at 1600 °C, in air. This study also showed a similar trend.

In Figure 5, the distribution ratio for Cr, L_{cr}, $L_{Cr} = \dfrac{wt\%Cr_2O_3 \text{ in crystal}}{wt\%Cr_2O_3 \text{ in melt}}$ is plotted versus the ratio of MgO/Al_2O_3. An increasing trend is suggested both in air and CO_2.

There have been very few thermodynamic data on ferrite-chromite spinel solid solutions. Recently, Hino et al.[5] studied the phase equilibria of $FeO.Cr_2O_3-MgO.Cr_2O_3-MgO.Al_2O_3$ spinels saturated with $(Cr, Al)_2O_3$ at 1300 °C, under a $CO-CO_2$ atmosphere with an oxygen potential of $9.7x10^{-10}$ atm. At higher temperatures, Morita et al.[4], determined the activities of Cr_2O_3 in $MgO.(Al_{1-x}Cr_x)_2O_3$ solid solution, in their study of the solubility of chromite phases in $MgO-Al_2O_3-CaO-SiO_2$ slags, at 1600 °C.

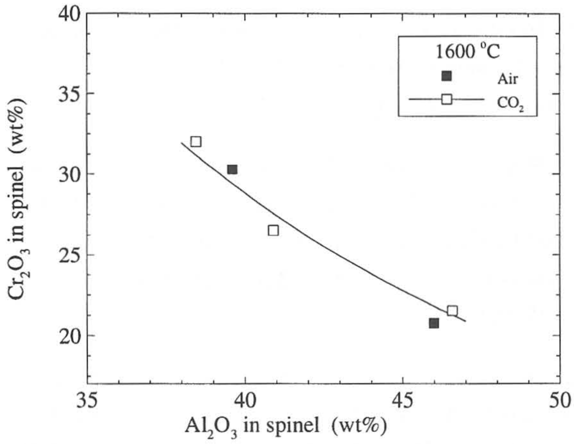

Figure 4a. Variation in Cr_2O_3 content in the spinel with MgO and Al_2O_3 contents in the spinel at 1600 ° C

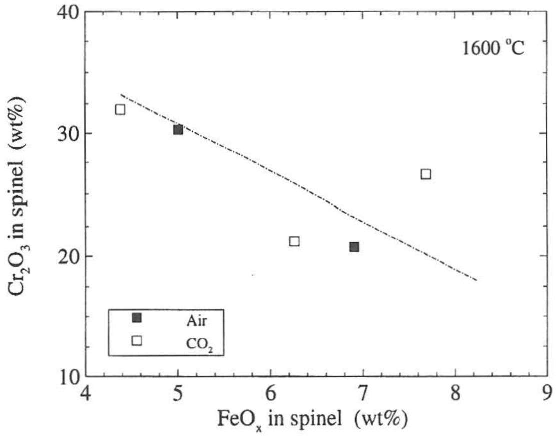

Figure 4b. Variation of Cr_2O_3 with the FeO_x content of the spinel at 1600 °C.

Using Morita et al.'s[4] data, the activity of Cr_2O_3 in the spinel phase can be evaluated once the spinel composition is determined. In the current study, the spinel phases of the H series contained a small amount of iron oxide. Assuming this small addition did not change the thermodynamic behaviour of the Cr in the $MgO.(Al, Cr)_2O_3$ spinel, the activity of Cr_2O_3 for samples G4.0, H3.5, H4.5 and H6.5 in air and in CO_2 at 1600 °C was evaluated, by referring to Morita et al.'s[4] data of a_{Cr2O3} versus spinel composition. These were then used to calculate the activity coefficient, γ_{Cr2O3}, for the slag melt in equilibrium with the spinel. The obtained value of γ_{Cr2O3} was about 4 in air and 7 in CO_2 at 1600 °C.

Morita et al[3] showed that for a $MgO-SiO_2-CaO-Cr_2O_3$ slag, at 1600 °C in air, the Cr^{6+}/Cr^{3+} ratio is less than 0.1 at a CaO/SiO_2 ratio of 1, i.e. most of the chromium is present as Cr^{3+}. It is thus reasonable to expect that most of the chromium in the slags studied by the present study is present as Cr^{3+}.

Based on Morita et al's[4] slag-chromite equilibrium data, the activity coefficient, γ_{Cr2O3}, for $MgO-SiO_2$ slags at 1600 °C under reducing conditions (oxygen potential of 10^{-13} to 10^{-8} atm) increases from about 2 to 16. Under a fixed pO_2 of $2.11x10^{-9}$ atm, γ_{Cr2O3} increases with CaO addition (0-14 wt%) from 11 to 27. For slag-chromite equilibrium in air at 1600 °C, activity coefficient for a series of $MgO-Al_2O_3-SiO_2-Cr_2O_3$ slags could be derived. The values vary between 14 and 26, the low value of 14 being for a slag containing 20% Al_2O_3 and 36% MgO. This is 2 to 3 times the value of γ_{Cr2O3} estimated from the current study. According to Morita el al[4], the Cr_2O_3 solubility in $MgO-Al_2O_3-CaO-SiO_2$ slags decreases with increasing MgO. With consideration of the difference in the levels of MgO in their and this study, the difference in γ_{Cr2O3} is in accord with the trend suggested by Morita et al's[4] results.

Obviously, further experimental work and further analysis is required before quantitative prediction of the

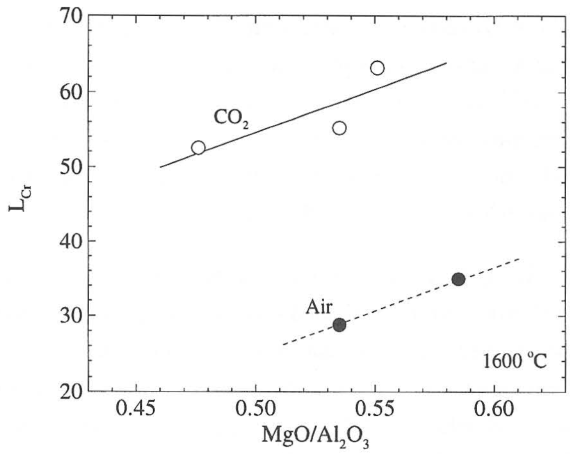

Figure 5. The distribution ratio for Cr is plotted versus the ratio of MgO/Al_2O_3.

slag-chromite spinel equilibrium can be made with some accuracy.

5. CONCLUSION

A drop-quench experimental technique coupled with optical and microprobe analyses of quenched samples were used to determine the liquidus temperature and phases in the $CaO-MgO-Al_2O_3-SiO_2-FeO_x$ system.

Addition of 1 wt % CrO_x to the $CaO-MgO-Al_2O_3-SiO_2$ slags increased the liquidus temperature by up to 200°C. The pronounced effect was thought to be due to the stabilisation of the spinel structure. Chromium partitioned strongly into the spinel structure but not into the melilte phase.

ACKNOLEDGEMENTS

Financial support for this work is provided by the AMIRA (Australian Minerals Industry Research Association) and Australian Government Cooperative Research Centres Program through the GK Williams CRC for Extractive Metallurgy, a joint venture between the CSIRO Division of Minerals and the University of Melbourne - Department of Chemical Engineering.

REFERENCES

1. E.F.Osborn, R.C DeVries., K.H Gee. and H.M Kraner. "Optimum Composition of Blast Furnace Slag as deduced from Liquidus Data for the Quaternary System $CaO-MgO-Al_2O_3-SiO_2$," J Metals, Vol. 6, 1954 pp 33-45.

2. R.J. Rait, S. Jahanshahi, and S Sun, "Phase Equilibria in the $CaO-Al_2O_3-MgO-SiO_2-FeO_x$ System," Second Australian Melt Chemistry Symposium, Melbourne, Australia, 1995.

3. K. Morita, N. Takayam, and N. Sano, "The Solubility of $MgO.Cr_2O_3$ in $MgO-Al_2O_3-SiO_2-CaO$ Slag at 1600 °C under Reducing Conditions," Tetsu-to-Hagane Vol. 74, 1988, pp 999-1005.

4. K. Morita, T. Shibuya, and N. Sano, "The Solubility of the Chromite in $MgO-Al_2O_3-SiO_2-CaO$ Melts at 1600 ° C in Air," Tetsu-to-Hagane, Vol 74, 1988, pp. 632-639.

5. M. Hino, K. Higuchi, T Nagasaka and S. Ban-ya, "Phase Equilibria and Thermodynamics of $FeO.Cr_2O_3-MgO.Cr_2O_3-MgO.Al_2O_3$ Spinel Structure Solid Solution Saturated with $(Cr,Al)_2O_3$," ISIJ International, Vol. 35, 1995, pp 851-858.

6. S. Ban-ya and M. Hino, Ed, "Thermochemical Properties of Selected Oxides and Slags," Chemical Properties of Molten Slags, The Iron and Steel Institute of Japan, 1991 pp 1-33.