

Effect of Al_2O_3 and Cr_2O_3 on Liquidus Temperatures in the Cristobalite and Tridymite Primary Phase Fields of the MgO –“ FeO ”– SiO_2 System in Equilibrium with Metallic Iron

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The effects of alumina and chromite impurities on the liquidus temperatures in the cristobalite/tridymite (SiO_2) primary phase fields in the MgO –“ FeO ”– SiO_2 system in equilibrium with metallic iron have been investigated experimentally. Using high temperature equilibration and quenching followed by electron probe X-ray microanalysis (EPMA), liquidus isotherms have been determined in the temperatures range 1 673 to 1 898 K. The results are presented in the form of pseudo-ternary sections of the MgO –“ FeO ”– SiO_2 system at 2, 3 and 5 wt% Al_2O_3 , 2 wt% Cr_2O_3 , and 2 wt% Cr_2O_3 +2 wt% Al_2O_3 . The study enables the liquidus to be described for a range of SiO_2/MgO and MgO/FeO ratios. It was found that liquidus temperatures in the cristobalite and tridymite primary phase fields, decrease significantly with the addition of Al_2O_3 and Cr_2O_3 .

KEY WORDS: slag; liquidus; phase equilibria; MgO –“ FeO ”– SiO_2 – Al_2O_3 – Cr_2O_3 system

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1. Introduction

The phase equilibria in the MgO –“ FeO ”– SiO_2 system in the cristobalite and tridymite primary phase fields have been reported by the present authors,¹⁾ extending and updating earlier studies on this system²⁾ for conditions in equilibrium with metallic iron.

The term “ FeO ” is used advisedly here since iron occurs in different oxidation states. The trivalent, Fe_2O_3 , predominates at high oxygen partial pressures, whereas the divalent oxide, FeO predominates at low oxygen partial pressures. In the present work, all iron was calculated as FeO . The MgO –“ FeO ”– SiO_2 system is not true ternary system, however in contact with metallic iron only small concentrations of Fe^{3+} are present in the system.

The slags encountered in nickel smelting operations are based on the system MgO – FeO – Fe_2O_3 – SiO_2 – Al_2O_3 – Cr_2O_3 . There are many aspects of the phase equilibria in these complex slags that have not yet been fully characterised. Of particular importance to industrial practice are issues, such as, furnace operation temperature and related energy costs, refractory integrity and life, slag flow and slag tapping. The starting point for the solution of these problems is a clear understanding of the slag phase equilibria in these systems, in particular, liquidus and the thermodynamic characteristics of the slags.

Laterite nickel smelting slag consists principally of MgO , “ FeO ” and SiO_2 , also present are other components including Al_2O_3 , Cr_2O_3 , MnO and CaO . The high SiO_2/MgO ratio in the slag encountered at the Cerro Matoso SA operation places the slag composition in the region of the primary

phase field of cristobalite (SiO_2) (see Fig. 7, Ref. 1)). The liquidus temperature of the ferronickel alloy is approximately 1 603 K, however superheats of up to 200 K maybe necessary to reach the liquidus of the slag.³⁾ Data in the MgO –“ FeO ”– SiO_2 system have traditionally been used to determine operation temperatures, however, the experimental information available on this system is limited to temperatures below 1 773 K.²⁾

Limited experimental data in the MgO –“ FeO ”– SiO_2 – Al_2O_3 system are available in the literature. The pseudo-binary system $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ – $2\text{FeO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, part of the MgO –“ FeO ”– SiO_2 – Al_2O_3 system, was investigated by Miyashiro⁴⁾ using optical microscopy and X-ray diffraction. The study presents information on the conditions of formation of cordierites ($(\text{Mg}, \text{Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$) and indialite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$). Holdaway⁵⁾ investigated the “ FeO ”– MgO – Al_2O_3 system with excess SiO_2 at 1 073 K, 3 kb. Subsolvus equilibria and tie lines were determined in their studies using X-ray diffraction and the petrographic microscope. The assessment of thermodynamic properties of phase relations in the “ FeO ”– MgO – Al_2O_3 – SiO_2 system at pressures up to 30 GPa was reported by Fabrichnaya.⁶⁾ There are no experimental data on phase equilibria in the MgO –“ FeO ”– SiO_2 – Cr_2O_3 system reported in the literature.

The objective of the present investigation is to obtain experimental data on the liquidus in the MgO –“ FeO ”– SiO_2 – Al_2O_3 system with 2–5 wt% Al_2O_3 , 2 wt% Cr_2O_3 , and 2 wt% Cr_2O_3 +2 wt% Al_2O_3 over the composition and temperature ranges relevant to laterite nickel smelting slags.

Table 1. EPMA measurements of phases in the MgO–“FeO”–SiO₂–Al₂O₃ system with 2 wt% Al₂O₃ in equilibrium with metallic iron.

Experiment I.D.	Temp. (K)	Phases in equilibrium	Composition (wt%)			
			MgO	FeO	SiO ₂	Al ₂ O ₃
<u>Cristobalite primary phase field</u>						
1600S10m3	1873	L + C	3.0	40.5	54.7	1.8
1600S63m1	1873	L + C	15.8	20.1	62.4	1.7
1600S49m7	1873	L + C	10.6	28.5	59.0	1.9
1600S12m5	1873	L + C	13.8	23.7	60.6	1.9
1600S52m10	1873	L + C	15.3	21.4	61.3	2.0
1600S102m15	1873	L + C	17.7	18.1	62.2	2.0
1600S101m13	1873	L + C	17.2	18.2	62.5	2.1
1600S99m12	1873	L + C	21.6	12.1	64.4	1.9
1575S46m8	1848	L + C	11.0	29.8	57.4	1.8
1575S53m7	1848	L + C	12.4	27.0	58.4	2.2
1575S56m8	1848	L + C	13.5	24.9	59.5	2.1
1575S54m9	1848	L + C	15.3	22.6	60.2	1.9
1575S110m13	1848	L + C	16.6	21.3	60.3	1.8
1575S55m10	1848	L + C	16.9	20.7	60.4	2.0
1575S75m11	1848	L + C	16.3	21.7	60.4	1.6
1575S53m6	1848	L + C	20.2	15.6	62.1	2.1
1575S109m12	1848	L + C	18.7	18.9	60.8	1.6
1575S111m14	1848	L + C	19.4	17.2	61.4	2.0
1575S56m1	1848	L + C	18.3	19.2	60.7	1.8
1575S108m11	1848	L + C	21.0	14.2	62.7	2.1
1550S14m4	1823	L + C	1.3	46.8	50.0	1.9
1550S60m10	1823	L + C	12.8	28.3	57.2	1.7
1550S58m8	1823	L + C	13.4	26.7	57.7	2.2
1550S59m9	1823	L + C	15.9	23.9	58.4	1.8
1550S127m14	1823	L + C	15.0	25.0	58.4	1.6
1550S37m5	1823	L + C	17.0	21.6	59.2	2.2
1550S87m15	1823	L + C	16.7	22.1	59.2	2.0
1550S16m6	1823	L + C	21.2	16.4	60.7	1.7
1550S83m11	1823	L + C	20.7	16.0	61.2	2.1
1550S3m1	1823	L + C	22.6	14.4	61.3	1.7
1550S15m5	1823	L + C	22.7	13.8	61.5	2.0
1550S34m6	1823	L + C	25.0	11.0	61.9	2.1
1550S54m6	1823	L + C	20.9	16.1	60.8	2.2
1525S63m9	1798	L + C	13.1	29.5	55.6	1.8
1525S61m7	1798	L + C	12.8	29.6	55.5	2.1
1525S62m8	1798	L + C	14.0	27.7	56.1	2.2
1525S41m7	1798	L + C	13.4	28.2	56.1	2.3
1525S90m15	1798	L + C	14.5	27.1	56.6	1.8
1525S115m13	1798	L + C	14.8	26.3	57.3	1.6
1525S116m14	1798	L + C	16.2	23.9	58.1	1.8
1525S113m11	1798	L + C	17.6	22.6	58.3	1.5
1525S84m12	1798	L + C	18.8	20.2	59.0	2.0
1525S69m1	1798	L + C	20.7	18.4	59.3	1.6
1525S79m11	1798	L + C	20.6	18.4	59.3	1.7
1525S91m15	1798	L + C	21.2	16.9	59.6	2.3
1500S30m3	1773	L + C	3.6	44.7	49.5	2.2
1500S66m8	1773	L + C	14.3	27.6	55.8	2.3
1500S93m15	1773	L + C	15.7	26.1	56.3	1.9
1500S18m5	1773	L + C	15.7	25.6	56.5	2.2
1500S68m10	1773	L + C	16.8	24.4	56.7	2.1
1500S92m14	1773	L + C	17.9	22.5	57.6	2.0
1500S1m1	1773	L + C	20.4	19.6	58.2	1.8
1500S80m12	1773	L + C	19.2	20.5	58.3	2.0
1500S77m12	1773	L + C	21.1	17.9	59.1	1.9
1500S78m11	1773	L + C	21.4	17.0	59.4	2.2
1500S38m1	1773	L + C	23.5	14.7	59.6	2.2
1500S70m1	1773	L + C	24.3	13.7	60.2	1.8
1500S19m6	1773	L + C	26.2	10.5	61.1	2.2
1500S32m5	1773	L + C	21.0	18.3	58.6	2.1
1500S111m7	1773	L + C	10.9	32.9	54.0	2.2
1470S106m8	1743	L + C	11.8	33.5	52.6	2.1
1470S107m9	1743	L + C	16.5	25.7	55.6	2.2
1470S94m14	1743	L + C	17.9	23.9	56.5	1.7
1470S95m13	1743	L + C	19.5	20.7	57.5	2.3

Table 1. (Continued)

Experiment I.D.	Temp. (K)	Phases in equilibrium	Composition (wt%)			
			MgO	FeO	SiO ₂	Al ₂ O ₃
1470S119m13	1743	L + C	21.6	17.9	58.4	2.1
1470S81m12	1743	L + C	22.3	17.2	58.4	2.1
1470S118m12	1743	L + C	23.8	14.9	59.2	2.1
<u>Tridymite primary phase field</u>						
1450T104m9	1723	L + T	15.5	27.7	54.3	2.5
1450T105m9	1723	L + T	16.0	27.7	54.3	2.0
1450T103m9	1723	L + T	15.9	27.6	54.5	2.0
1450T124m15	1723	L + T	19.1	22.3	56.5	2.1
1450T97m14	1723	L + T	19.2	22.1	56.5	2.2
1450T82m11	1723	L + T	21.2	20.0	56.8	2.0
1350T32m3	1623	L + T	3.6	49.7	44.2	2.5
<u>Univariant</u>						
1500SP35m6	1773	L	27.4	8.8	60.9	2.9
		P	37.8	2.9	59.3	0
		C	0	0.2	99.8	0
1470SP36m6	1743	L	23.7	14.8	58.7	2.8
		P	34.9	7.4	57.7	0
		C	0	0.9	99.1	0
1450TP26m1	1723	L	22.1	18.6	56.7	2.6
		P	25.7	20.0	54.3	0
		T	0	0.5	99.5	0
1450TP72m1	1723	L	22.0	18.9	57.1	2.0
		P	33.2	8.4	58.4	0
		T	0	0.5	99.5	0
1350TPm33m2	1623	L	12.7	31.8	51.1	4.4
		P	27.8	17.2	54.8	0.2
		T	0.0	0.7	99.3	0
1305TOP22m2	1687	L	8.8	35.7	48.8	6.7
		P	27.0	17.7	55.3	0
		O	24.2	40.6	35.2	0
		T	0	0.8	99.2	0

L = Liquid, C = Cristobalite, SiO₂, T = Tridymite, SiO₂, P = Pyroxene, (Mg,Fe)SiO₃, O = Olivine, (Mg,Fe)₂SiO₄.

2. Experimental

The experimental procedure used in the present investigation is one that has been developed specifically to provide accurate liquidus data in complex slag systems.⁷⁻⁹ The details of the procedure as adopted specifically for slags in the system under investigation are given in previous publication by the present authors.¹⁾ The procedure essentially involves the preparation of the synthetic slag compositions from high purity oxide and metallic iron powders; high temperature equilibration in Mo or Fe foil with metallic iron excess in a neutral gas atmosphere (temperature is within ± 2 K); rapid quenching of the samples enabling the phases present at temperature to be retained at room temperature; and determination of the compositions of the phases present of the samples using electron probe X-ray microanalysis (EPMA). Standards supplied by Charles M Taylor Co. Stanford, CA were used in EPMA measurement. The phase analyses have been shown to be accurate within ± 1 wt%.

Only metal cation contents were measured by EPMA; the oxygen content was added according to the assumed oxidation state. All iron was calculated as FeO in the present work. However, it should be kept in mind that small amounts of Fe³⁺ are always present in the sample, even in contact with metallic iron.

3. Results and Discussion

To consider the effects of Al₂O₃ and Cr₂O₃ on liquidus

Table 2. EPMA measurements of phases in the MgO–“FeO”–SiO₂–Al₂O₃ system with 3 wt% Al₂O₃ in equilibrium with metallic iron.

Experiment I.D.	Temp. (K)	Phases in equilibrium	Composition (wt%)			
			MgO	FeO	SiO ₂	Al ₂ O ₃
Cristobalite primary phase field						
1600S39m3	1873	L + C	12.9	22.2	62.1	2.8
1600S42m7	1873	L + C	23.5	8.7	64.8	3.0
1600S7m3	1873	L + C	17.9	15.3	63.4	3.4
1600S29m3	1873	L + C	6.4	32.3	58.1	3.2
1575S41m1	1848	L + C	18.0	17.2	61.9	2.9
1575S4m1	1848	L + C	20.6	13.6	62.6	3.2
1550S40m7	1823	L + C	27.3	6.2	63.7	2.8
1550S74m1	1823	L + C	14.8	22.8	59.8	2.6
1550S46m4	1823	L + C	14.5	22.5	59.8	3.2
1550S75m1	1823	L + C	14.4	22.8	60.0	2.8
1550S65m4	1823	L + C	15.5	21.2	60.0	3.3
1550S5m1	1823	L + C	21.5	13.7	61.7	3.1
1550S10m3	1823	L + C	21.8	12.8	62.3	3.1
1525S77m1	1798	L + C	14.3	25.3	57.6	2.8
1525S76m1	1798	L + C	18.9	18.5	59.5	3.1
1525S66m4	1798	L + C	16.2	21.5	58.8	3.5
1500S33m4	1773	L + C	13.8	26.4	56.9	2.9
1500S110m7	1773	L + C	17.1	21.3	58.3	3.3
1500S34m3	1773	L + C	18.8	18.3	59.2	3.7
1500S57m6	1773	L + C	20.0	15.6	59.9	4.5
1500S35m2	1773	L + C	24.4	11.7	60.8	3.1
1475S112m7	1648	L + C	18.8	20.0	57.8	3.4
1475S55m6	1648	L + C	18.5	20.3	57.9	3.3
1475S113m7	1648	L + C	19.9	18.7	58.1	3.3
Tridymite primary phase field						
1450S104m8	1723	L + T	15.5	27.7	54.3	2.5
1450T3m1	1723	L + T	20.6	19.4	57.1	2.9
1450T115m7	1723	L + T	16.4	24.0	56.3	3.3
1450T114m7	1723	L + T	19.1	20.4	57.0	3.5
Univariant						
1475SP31m5	1648	L	22.3	16.1	58.7	2.9
		S	0	0.9	99.1	0
		P	33.8	7.6	58.6	0
1450TP30m5	1723	L	19.0	19.2	57.0	4.8
		T	0	0.7	99.3	0
		P	33.6	7.7	58.7	0

L = Liquid, C = Cristobalite, SiO₂, T = Tridymite, SiO₂, P = Pyroxene, (Mg,Fe)SiO₃, O = Olivine, (Mg,Fe)₂SiO₄.

Table 3. EPMA measurements of phases in the MgO–“FeO”–SiO₂–Al₂O₃ system with 5 wt% Al₂O₃ in equilibrium with metallic iron.

Experiment I.D.	Temp. (K)	Phases in equilibrium	Composition (wt%)			
			MgO	FeO	SiO ₂	Al ₂ O ₃
Cristobalite primary phase field						
1600S2m2	1873	L + C	13.6	17.6	63.8	5.0
1600S1m1	1873	L + C	14.4	16.6	64.1	4.9
1575S4m2	1848	L + C	13.6	18.7	62.6	5.1
1575S3m1	1848	L + C	15.6	17.0	62.7	4.7
1550S5m1	1823	L + C	12.8	21.9	60.3	5.0
1525S7m1	1798	L + C	15.1	19.2	60.2	5.5
1525S30m5	1798	L + C	16.5	18.3	60.4	4.8
1525S25m4	1798	L + C	17.4	16.3	61.2	5.1
1525S24m3	1798	L + C	18.0	16.1	61.3	4.6
1525S13m1	1798	L + C	16.9	17.4	60.5	5.2
1500S20m5	1773	L + C	16.3	19.7	59.1	4.9
1500S19m4	1773	L + C	20.3	13.6	61.0	5.1
1500S18m3	1773	L + C	18.1	15.8	60.4	5.7
1500S12m2	1773	L + C	13.9	21.8	58.7	5.6
1475S23m5	1648	L + C	18.6	15.8	59.9	5.7
1475S22m4	1648	L + C	17.4	18.4	59.2	5.0
1475S21m3	1648	L + C	22.0	11.8	61.0	5.2
Tridymite primary phase field						
1450S27m4	1723	L + T	16.7	20.0	58.0	5.3
1450S26m5	1723	L + T	22.0	12.4	60.4	5.2
1450S10m2	1723	L + T	15.9	20.4	57.7	6.0
1425S33m4	1698	L + T	20.3	13.4	59.8	6.5
1425S32m3	1698	L + T	18.6	16.1	59.0	6.3
1400S31m5	1673	L + T	19.2	16.4	58.3	6.1
Univariant						
1400TP28m3	1673	L	19.2	14.9	58.4	7.5
		T	0	0.5	99.5	0
		P	33.7	7.8	58.1	0.4
1375S35m5	1648	L	16.3	21.2	54.9	7.6
		T	0	0.5	99.5	0
		P	31.2	11.8	56.6	0.4
1350S36m5	1623	L	14.7	23	53.5	8.8
		T	0	0.6	99.4	0
		P	30.2	13.5	55.9	0.4

L = Liquid, C = Cristobalite, SiO₂, T = Tridymite, SiO₂, P = Pyroxene, (Mg,Fe)SiO₃, O = Olivine, (Mg,Fe)₂SiO₄.

temperatures in the region relevant to the laterite nickel smelting slags, the experimental results are presented in a form of pseudo-ternary sections MgO–“FeO”–SiO₂ at fixed weight percentages of Al₂O₃ or Cr₂O₃ in the liquid phase.

3.1. The MgO–“FeO”–SiO₂–Al₂O₃ System

The experiments were carried out in the cristobalite and tridymite primary phase fields in the MgO–“FeO”–SiO₂–Al₂O₃ system in equilibrium with metallic iron. EPMA measurements of the phase compositions obtained in the present study are reported in Tables 1, 2 and 3. The data obtained have been used to construct liquidus isotherms in the MgO–“FeO”–SiO₂–Al₂O₃ system with 2, 3, and 5 wt% Al₂O₃ (Figs. 1(a), 1(b), and 1(c)) at temperatures in the range 1723 to 1873 K. The liquidus surfaces on the limiting ternary systems of MgO–Al₂O₃–SiO₂ and “FeO”–Al₂O₃–SiO₂ were taken from Osborn and Muan.^{10,11)} The general shape of the cristobalite/tridymite liquidus surfaces for the slags containing 2, 3 and 5 wt% Al₂O₃ is similar to the ternary system MgO–“FeO”–SiO₂.¹⁾ It can be seen from Fig. 1 that, compared with the MgO–“FeO”–SiO₂ system, there is a decrease in the liquidus temperature in the cristobalite and tridymite primary phase fields in the MgO–“FeO”–SiO₂–Al₂O₃ system with Al₂O₃ additions. No new phases were detected on the additions of Al₂O₃ to the system in this range of compositions and temperatures in-

vestigated. No solubility of MgO or Al₂O₃ was found in tridymite and cristobalite phases. The solubility of FeO was found to be insignificant in tridymite and cristobalite phases and less than 0.9 wt%.

The effect of Al₂O₃ on the liquidus can be evaluated in a number of ways since although the pseudo-ternary section is constructed at fixed Al₂O₃ concentrations in the liquid this plane can be approached from a number of directions in compositional space; each of which will provide a different relationship. For example, the comparison at the liquidus at 2 wt% Al₂O₃ with the ternary MgO–“FeO”–SiO₂ can be made as follows, i) with 2 wt% Al₂O₃, having the same SiO₂/MgO/FeO ratio as in the ternary (Fig. 2(a)); ii) 2 wt% Al₂O₃, fixed SiO₂/MgO ratio, FeO concentration fixed (Fig. 2(b)), or iii) 2 wt% Al₂O₃, fixed MgO/FeO ratio, SiO₂ concentration fixed (Fig. 2(c)).

In Fig. 2(a), A and B are points that are on a line joining the Al₂O₃ apex and the plane parallel to the MgO–“FeO”–SiO₂ base at 0 and 2 wt% Al₂O₃ respectively, and these points have same ratio of SiO₂/MgO/FeO. Two compositions in the MgO–“FeO”–SiO₂ system were selected to compare the effects. Point A1 has bulk composition 61.5SiO₂, 21.4MgO and 17.1FeO in wt%, and point A2 is 59.3SiO₂, 22.1MgO and 18.6FeO in wt%, liquidus temperatures for these compositions are 1873 K and 1823 K respectively. The ratios of SiO₂/MgO/FeO are for A1: 3.60:

Table 4. Comparison of predicted liquidus temperatures (methods I, II and III) in the silica primary phase field in the MgO–“FeO”–SiO₂–Al₂O₃ system with 0, 2, 3, and 5 wt% Al₂O₃.

Calculation method	Points	Liquidus T(K)	SiO ₂	MgO	FeO	Al ₂ O ₃	SiO ₂ /MgO	MgO/FeO	SiO ₂ /MgO/FeO
I	A1	1873	61.5	21.4	17.1	0	2.87:1	1.25:1	3.59:1.25:1
	B1	1813	60.3	20.9	16.8	2	2.87:1	1.25:1	3.59:1.25:1
	B1'	1773	59.7	20.8	16.6	3	2.87:1	1.25:1	3.59:1.25:1
	B1''	1673	58.4	20.3	16.2	5	2.87:1	1.25:1	3.59:1.25:1
	A2	1823	59.3	22.1	18.6	0	2.68:1	1.19:1	3.19:1.19:1
	B2	1743	58.1	21.7	18.2	2	2.68:1	1.19:1	3.19:1.19:1
	B2'	1723	57.5	21.4	18.0	3	2.68:1	1.19:1	3.19:1.19:1
	II	A1	1873	61.5	21.4	17.1	0	2.87:1	
C1		1798	60.0	20.9	17.1	2	2.87:1		
C1'		1773	59.3	20.6	17.1	3	2.87:1		
C1''		1673	57.8	20.1	17.1	5	2.87:1		
A2		1823	59.3	22.1	18.6	0	2.68:1		
C2		1738	57.8	21.6	18.6	2	2.68:1		
C2'		1723	58.2	20.2	18.6	3	2.68:1		
III		A1	1873	61.5	21.4	17.1	0		1.25:1
	D1	1843	61.5	20.3	16.2	2		1.25:1	
	D1'	1823	61.5	19.7	15.8	3		1.25:1	
	D1''	1783	61.5	18.6	14.9	5		1.25:1	
	A2	1823	59.3	22.1	18.6	0		1.19:1	
	D2	1788	59.3	21.0	17.7	2		1.19:1	
	D2'	1773	59.3	21.0	16.7	3		1.19:1	
	D2''	1723	59.3	19.4	16.3	5		1.19:1	

1788 K respectively, indicating that the replacement of MgO and FeO (fixed ratio of MgO/FeO) by 2 wt% Al₂O₃ decreases the liquidus temperature in the MgO–“FeO”–SiO₂–Al₂O₃ system by approximately 30–35 K.

Similarly the comparisons between point A in the MgO–“FeO”–SiO₂ system and point B', C' and D'; B'', C'' and D'' at 3 and 5 wt% Al₂O₃ additions respectively in the MgO–“FeO”–SiO₂–Al₂O₃ system were also made and presented in Table 4.

According to all of the above comparisons, 2, 3 and 5 wt% Al₂O₃ additions in the MgO–“FeO”–SiO₂–Al₂O₃ system decreases the liquidus temperature in the cristobalite and tridymite primary phase fields in the composition range relevant to nickel smelting slags. Careful consideration should be given to the method used in making these comparisons.

The liquidus temperatures in the MgO–“FeO”–SiO₂–Al₂O₃ system in the cristobalite and tridymite primary phase fields in equilibrium with metallic iron based on experimental data obtained in the present investigation are shown in Figs. 3 and 4. Figure 3(a) shows the liquidus temperatures as a function of FeO concentration for the SiO₂/MgO ratios of 2.4, 2.6, 2.8, 3.0 and 3.2 in the MgO–“FeO”–SiO₂ system without Al₂O₃.¹⁾ It can be seen (Fig. 3(a)) that with increase of FeO concentration for fixed SiO₂/MgO ratio, each 1 wt% increase in FeO concentration decrease liquidus temperature by 10–12 K in this composition range. Figures 3(b) to 3(d) show the liquidus temperatures as a function of the concentration of FeO at fixed SiO₂/MgO ratios in the MgO–“FeO”–SiO₂–Al₂O₃ system at 2, 3 and 5 wt% Al₂O₃ respectively. It can be seen that with increase of concentration of FeO at fixed SiO₂/MgO ratio,

there is a non-linear decrease of liquidus temperature by approximately 10–17 K, 11–25 K and 13–20 K for each 1 wt% increase in FeO concentration for 2, 3 and 5 wt% Al₂O₃ respectively.

Figure 4 (a) shows the liquidus temperatures as a function of SiO₂ concentration for MgO/FeO ratios of 0.8, 1.0, 1.2, 1.4 and 1.6 in the MgO–“FeO”–SiO₂–Al₂O₃ system with 0 wt% Al₂O₃. For a fixed MgO/FeO ratio there is an increase in liquidus temperature with increasing SiO₂ concentration (Fig. 4(a)). The liquidus temperature was found to increase by 23–35 K with increasing the SiO₂ concentration by 1 wt%. Figures 4(b) to 4(d) show the liquidus temperatures as a function of the concentration of SiO₂ at fixed MgO/FeO ratios. With an increase in the concentration of SiO₂, there is a non-linear increase of liquidus temperature by 23–40 K, 19–36 K and 17–46 K for each 1 wt% SiO₂ concentration increase for 2, 3 and 5 wt% Al₂O₃ respectively.

The above results indicate that the system relevant to nickel smelting slag is highly sensitive to the concentration of Al₂O₃, and increasing concentration of Al₂O₃ decreases the liquidus temperatures dramatically. Figure 5 shows the liquidus temperature as a function of minor component Al₂O₃ additions for specific slag composition Al:61.5SiO₂, 21.4MgO and 17.1FeO in wt%, indicating the magnitude of the effect of Al₂O₃ on the liquidus temperature of the MgO–“FeO”–SiO₂–Al₂O₃ system. Each weight percent of Al₂O₃ increase in composition of the silica-saturated slag decreases the liquidus temperature by approximately 40 K.

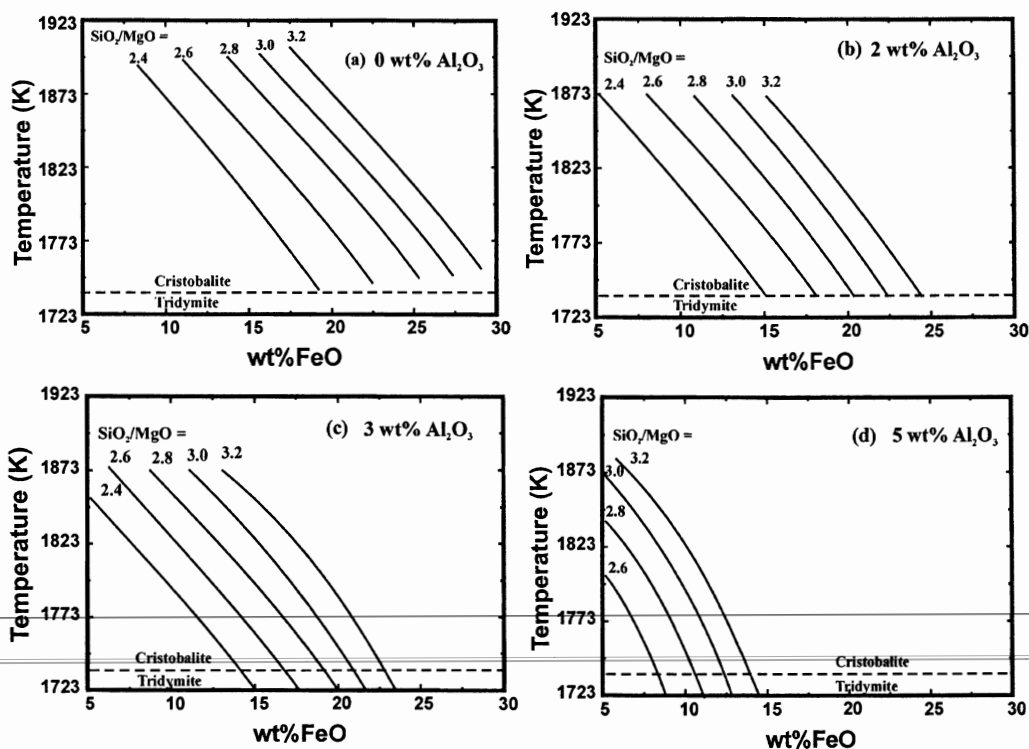


Fig. 3. Predicted liquidus temperatures in the cristobalite and tridymite primary phase fields in the MgO-“FeO”-SiO₂-Al₂O₃ system with 2, 3 and 5 wt% Al₂O₃ in equilibrium with metallic iron, based on the present experimental data.

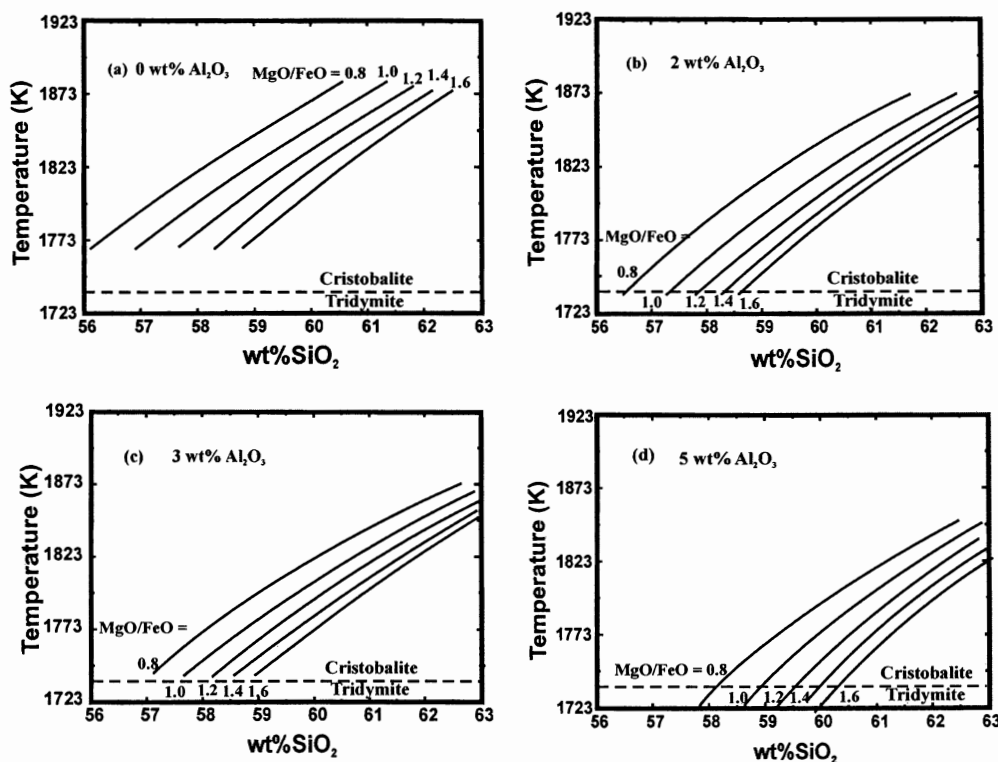


Fig. 4. Predicted liquidus temperatures in the cristobalite and tridymite primary phase fields in the MgO-“FeO”-SiO₂-Al₂O₃ system with 2, 3 and 5 wt% Al₂O₃ in equilibrium with metallic iron, based on the present experimental data.

3.2. The MgO-“FeO”-SiO₂-“Cr₂O₃” System

Chromium may be present in the slag as Cr³⁺ or Cr²⁺, depending on slag temperature and oxygen partial pressure. In present investigation, EPMA measurement could not determine Cr²⁺ and Cr³⁺ individually. There are no specific

data available on the proportions of Cr²⁺ and Cr³⁺ in the FeO-MgO-SiO₂-CrO_x system. Some indications on Cr²⁺/Cr³⁺ ratio can be obtained using information available on the SiO₂-CrO_x system¹²⁾ and MgO-CrO_x-SiO₂ system.¹³⁾ According to Xiao and Hoplappa’s studies,¹²⁾ de-

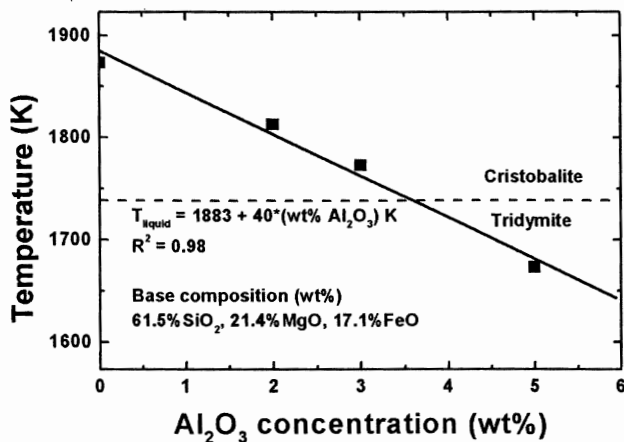


Fig. 5. Liquidus temperature in the cristobalite and tridymite primary phase fields as a function of Al_2O_3 addition in the MgO -“ FeO ”- SiO_2 system based on the specific point A1 in Table 4 at fixed $\text{SiO}_2/\text{MgO}/\text{FeO}$ ratios.

pending on slag composition 10–30% total Cr is present as Cr^{2+} in the SiO_2 - CrO_x system in equilibrium with Cr metal at 1873 K and $P_{\text{O}_2} = 10^{-12}$ atm. Morita *et al.*¹³⁾ investigated the oxygen partial pressure dependence of $\text{Cr}^{2+}/\text{Cr}^{3+}$ ratio in the MgO - CrO_x - SiO_2 system at $2\text{MgO} \cdot \text{SiO}_2$ saturation and at 1873 K. From their studies, at $P_{\text{O}_2} = 10^{-9}$ – 10^{-10} atm, the ratio of Cr^{2+}/Cr is approximately 0.09; at $P_{\text{O}_2} = 10^{-12}$ atm, the ratio of Cr^{2+}/Cr is approximately 0.24 which agrees with the results of Xiao and Holappa.¹²⁾ In the present study the P_{O_2} at metallic Fe saturation is approximately 10^{-10} atm. According to FactSage calculations¹⁴⁾ there is little difference in oxygen partial pressure between silica and olivine primary phase field in the MgO -“ FeO ”- SiO_2 system at metallic iron saturation. It can therefore be reasonably anticipated that the Cr^{2+}/Cr total ratio in the “ FeO ”- MgO - SiO_2 - CrO_x system at metallic iron saturation will be lower than 0.1. In the present study the chromium concentration in the slag is therefore expressed as “ Cr_2O_3 ” indicating that there are certain Cr^{2+} concentrations in the slag. The presence of Cr^{2+} in the slag can also lower the liquidus temperature. At $P_{\text{O}_2} = 2.73 \times 10^{-10}$ atm,¹³⁾ the liquidus temperature in spinel primary phase field of the MgO - CrO_x - SiO_2 system was decreased by approximately 250 K compared with the system in air.¹⁵⁾

EPMA measurements of the liquid and solid phases present under these conditions are reported in Table 5. Liquidus isotherms in the cristobalite and tridymite primary phase fields in the MgO -“ FeO ”- SiO_2 system with 2 wt% Cr_2O_3 were determined in the temperatures range from 1723–1873 K (Fig. 6). It can be seen from Fig. 6 that the general shape of the cristobalite/tridymite liquidus surface for the slags containing 2 wt% Cr_2O_3 is similar to the ternary system MgO -“ FeO ”- SiO_2 .¹⁾ The addition of 2 wt% Cr_2O_3 does not introduce any new primary phase in the range of compositions and temperatures investigated. The EPMA measurements show that practically no significant amount of Cr_2O_3 is dissolved in the cristobalite and tridymite phases in the range of conditions investigated. It can be seen from Fig. 6 that compared with the MgO -“ FeO ”- SiO_2 system, there is a decrease in the liquidus temperature in the cristobalite/tridymite primary phase fields in the MgO -“ FeO ”- SiO_2 - Cr_2O_3 system with 2 wt% Cr_2O_3 .

Table 5. EPMA measurements of the phases formed in the MgO -“ FeO ”- SiO_2 -“ Cr_2O_3 ” system with 2 wt% Cr_2O_3 addition in equilibrium with metallic iron.

Experiment	Temp. (K)	Phases in equilibrium	Composition (wt%)			
			MgO	FeO	SiO_2	Cr_2O_3
Cristobalite primary Phase field						
1600S7m14	1873	L + C	15.8	22.5	59.7	2.0
1600S8m15	1873	L + C	14.7	24.7	58.9	1.7
1600S13m11	1873	L + C	17.0	21.1	60.2	1.7
1600S14m11	1873	L + C	17.0	21.1	60.2	1.7
1600S15m13	1873	L + C	18.2	21.5	58.3	2.0
1600S16m13	1873	L + C	14.6	23.1	60.6	1.7
1575S17m11	1848	L + C	14.2	25.1	59.2	1.5
1575S18m11	1848	L + C	18.9	18.2	60.8	2.1
1575S19m13	1848	L + C	16.4	23.9	57.9	1.8
1575S20m13	1848	L + C	21.1	16.6	60.2	2.1
1575S9m14	1848	L + C	17.9	20.5	59.3	2.3
1575S10m15	1848	L + C	18.2	21.0	58.8	2.0
1550S21m11	1823	L + C	20.2	18.4	59.2	2.2
1550S11m14	1823	L + C	16.2	24.2	57.8	1.8
1550S22m13	1823	L + C	18.5	21.5	58	2.0
1550S12m15	1823	L + C	17.0	23.3	57.6	2.1
1525S23m11	1798	L + C	18.6	21.8	57.6	2.0
1525S24m13	1798	L + C	18.8	22.0	57.2	2.0
1500S25m11	1773	L + C	17.5	24.7	55.8	2.0
1500S26m13	1773	L + C	21.2	19.4	57.2	2.2
1470S4m15	1743	L + C	18.6	23.9	55.4	2.1
Tridymite primary phase field						
1450S5m14	1723	L + T	17.2	26.7	54.2	1.9
1450Cr6m15	1723	L + T	18.8	23.9	55.1	2.2
Univariant						
1470S3m14	1743	L	19.4	22.9	55.6	2.1
		P	31.7	10.1	56.7	1.5
		C	0	0.6	99.4	0

L = Liquid, C = Cristobalite, SiO_2 , T = Tridymite, SiO_2 , P = Pyroxene, (Mg, Fe) SiO_3 .

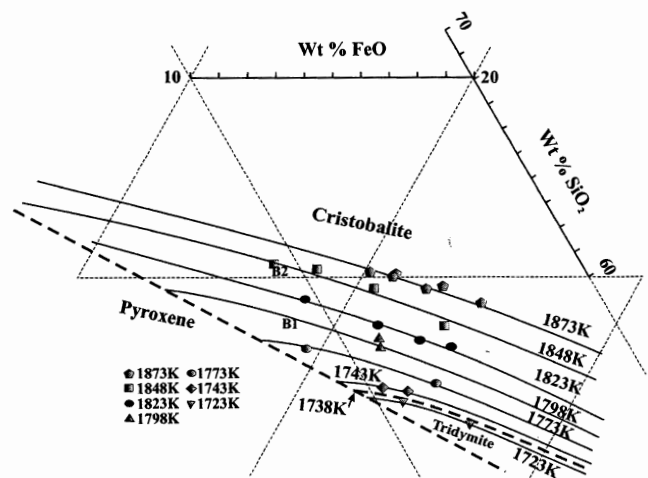


Fig. 6. Experimentally determined liquidus surface in the cristobalite and tridymite primary phase fields in the MgO -“ FeO ”- SiO_2 -“ Cr_2O_3 ” system with 2 wt% Cr_2O_3 in equilibrium with metallic iron using data in Table 5.

The results in the multi-component system MgO -“ FeO ”- SiO_2 - Cr_2O_3 with 2 wt% Cr_2O_3 are consistent with the trends observed in the relevant ternary end-members. No solubility of Cr_2O_3 in cristobalite and tridymite was found in this investigation.

Two selected compositions in the MgO -“ FeO ”- SiO_2 system (A1: 61.5 wt% SiO_2 , 21.4 wt% MgO and 17.1 wt% FeO; A2: 59.2 wt% SiO_2 , 22.1 wt% MgO and 18.6 wt% FeO at 1873 and 1823 K respectively) were used to com-

pare the changes in the MgO–“FeO”–SiO₂–Cr₂O₃ system with 2 wt% Cr₂O₃ addition with the fixed SiO₂/MgO/FeO ratios. It has been found that in the cristobalite primary phase field 2 wt% Cr₂O₃ addition decreases the liquidus temperature by approximately 35 K, which is less than that observed with 2 wt% Al₂O₃.

On a weight basis for these dilute solutions in the cristobalite primary phase field the effect of Cr₂O₃ in lowering liquidus temperature is approximately 0.6 times that of Al₂O₃ (2 wt% Al₂O₃ lower the liquidus by approximately 60 K). Since the molecular weight of Al₂O₃=101.96, Cr₂O₃=151.99, on a mole basis 2 wt% Cr₂O₃ is approximately 0.67 that of 2 wt% Al₂O₃. This would seem to indicate that the effects of these components on the liquidus temperature in cristobalite primary phase field on a mole basis are near equivalent.

3.3. The MgO–“FeO”–SiO₂–Al₂O₃–“Cr₂O₃” System

To consider the simultaneous effects from minor components Al₂O₃ and Cr₂O₃ on the liquidus temperatures in the MgO–“FeO”–SiO₂–Al₂O₃–“Cr₂O₃” system, the experimental results are presented in a form of pseudo ternary section MgO–“FeO”–SiO₂ at fixed weight percentage of Al₂O₃ and Cr₂O₃. The liquidus temperatures from 1773 to 1873 K

were determined in the cristobalite primary phase field in the system in equilibrium with metallic iron (Fig. 7). EPMA measurements of the phases formed under these conditions are presented in Table 6. No Al₂O₃ and Cr₂O₃ were detected in cristobalite (SiO₂) solid phase in the

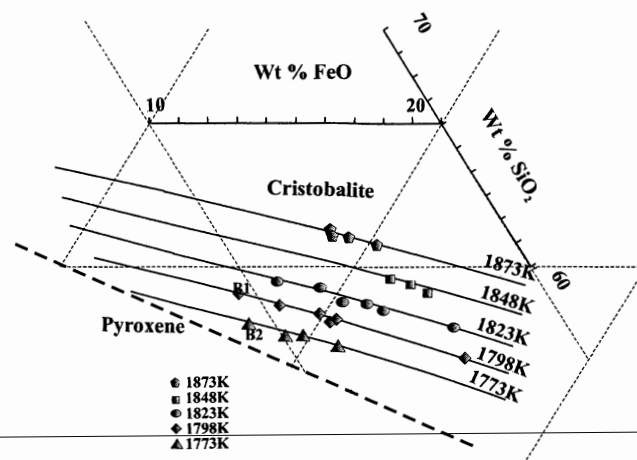


Fig. 7. Experimentally determined liquidus surface in the cristobalite primary phase field in the MgO–“FeO”–SiO₂–Al₂O₃–“Cr₂O₃” system with 2 wt%Al₂O₃+2 wt%Cr₂O₃ in equilibrium with metallic iron using data in Table 6.

Table 6. EPMA measurements of the phases formed in the silica primary phase field of the MgO–“FeO”–SiO₂–Al₂O₃–“Cr₂O₃” system with 2 wt%Al₂O₃+2 wt%Cr₂O₃ additions in equilibrium with metallic iron.

Experiment	Temp. (K)	Phases in equilibrium	Composition (wt%)				
			MgO	FeO	SiO ₂	Al ₂ O ₃	Cr ₂ O ₃
Silica primary Phase field							
1600S1m1	1873	L + C	16.7	18.6	60.9	1.8	1.7
1600S2m2	1873	L + C	15.8	20.0	60.1	2.0	1.8
1600S3m3	1873	L + C	14.4	22.5	59.3	1.9	1.7
1600S4m4	1873	L + C	14.4	22.4	59.0	2.1	1.9
1600S21m1	1873	L + C	15.7	19.2	61.2	1.7	1.6
1600S22m2	1873	L + C	16.2	18.6	61.2	1.8	1.8
1600S23m3	1873	L + C	13.4	23.8	59.0	1.7	1.7
1600S24m4	1873	L + C	14.6	20.3	60.9	1.9	1.8
1575S5m1	1848	L + C	19.3	16.4	60.0	2.1	2.0
1575S6m2	1848	L + C	15.6	22.1	58.3	1.8	1.8
1575S7m3	1848	L + C	15.4	22.1	58.1	2.1	2.0
1575S8m4	1848	L + C	14.4	23.6	58.0	1.9	1.8
1575S25m1	1848	L + C	15.6	21.5	59.4	1.7	1.6
1575S26m2	1848	L + C	14.5	22.9	29.0	1.8	1.6
1575S27m3	1848	L + C	14.3	23.1	58.8	1.9	1.8
1575S28m4	1848	L + C	13.5	24.5	58.1	1.9	1.7
1550S29m1	1823	L + C	13.9	24.7	57.4	2.0	1.8
1550S10m2	1823	L + C	18.7	18.0	59.1	2.0	1.9
1550S11m3	1823	L + C	16.1	21.8	57.9	2.0	2.0
1550S30m2	1823	L + C	16.8	20.4	58.3	2.1	2.0
1550S31m3	1823	L + C	18.5	19.3	59.1	1.9	1.9
1550S32m4	1823	L + C	16.4	21.2	58.4	1.9	1.8
1525S17m2	1798	L + C	19.0	21.2	56.5	2.0	2.0
1525S18m2	1798	L + C	19.7	18.5	57.3	2.0	2.0
1525S14m2	1798	L + C	20.0	17.6	58.1	2.0	2.0
1525S15m1	1798	L + C	14.5	26.6	55.3	1.9	1.6
1525S16m1	1798	L + C	18.8	21.0	56.0	2.0	2.0
1525S33m1	1798	L + C	17.8	20.5	57.7	1.9	1.8
1525S34m2	1798	L + C	14.5	25.7	56.1	1.8	1.7
1525S35m3	1798	L + C	17.6	20.4	57.5	2.1	2.1
1525S36m4	1798	L + C	18.0	19.8	58.0	2.0	2.0
1500S19m2	1773	L + C	19.7	19.8	56.2	2.0	2.0
1500S20m2	1773	L + C	19.7	18.8	56.6	2.5	2.1
1500S37m1	1773	L + C	18.2	21.2	56.5	1.9	1.8
1500S38m2	1773	L + C	18.6	19.7	57.0	2.2	2.2
1500S39m3	1773	L + C	13.3	29.2	54.1	1.6	1.4
1500S40m4	1773	L + C	16.7	22.8	56.5	2.0	2.0

L = Liquid, C = Cristobalite, SiO₂, T = Tridymite, SiO₂, P = Pyroxene, (Mg, Fe)SiO₃, O = Olivine, (Mg, Fe)₂SiO₄

quenched samples. There are no new solid phases formed in the composition range investigated while 2 wt% Al_2O_3 and 2 wt% Cr_2O_3 were added in the MgO -“FeO”- SiO_2 system.

In Fig. 7, with the fixed $\text{SiO}_2/\text{MgO}/\text{FeO}$ ratios, two specific compositions (A1: 61.5 SiO_2 , 21.4 MgO and 17.1 FeO in wt%; A2: 59.2 SiO_2 , 22.1 MgO and 18.6 FeO in wt% at 1873 and 1823 K respectively) in the MgO -“FeO”- SiO_2 system were used to compare the changes in the MgO -“FeO”- SiO_2 - Al_2O_3 -“ Cr_2O_3 ” system with 2 wt% Al_2O_3 +2 wt% Cr_2O_3 . It has been found that in the cristobalite primary phase field with 2 wt% Al_2O_3 +2 wt% Cr_2O_3 additions in the MgO -“FeO”- SiO_2 system decreases the liquidus temperature by approximately 75 K.

For fixed $\text{SiO}_2/\text{MgO}/\text{FeO}$ ratios in this composition range, if there is a linear additive effect of additions, there will be approximately 95 K (60 K decrease from 2 wt% Al_2O_3 and 35 K decrease from 2 wt% Cr_2O_3) decrease of liquidus temperature for 2 wt% Al_2O_3 +2 wt% Cr_2O_3 . 2 wt% Al_2O_3 +2 wt% Cr_2O_3 , using the molar equivalence, should have the same effect as 3.3 wt% Al_2O_3 on the system. The experimental result for the (2 wt% Al_2O_3 +2 wt% Cr_2O_3) is close to that determined for the MgO -“FeO”- SiO_2 - Al_2O_3 system with 3 wt% Al_2O_3 (100 K decrease in liquidus temperature, Fig. 1(b)).

An important point to bear in mind is that the Al_2O_3 and Cr_2O_3 concentrations in the individual samples vary slightly. To obtain accurate predictions of the additive effects of these components a more rigorous analysis of the data is required to take these variations into account.

3.4. Industrial Applications

Laterite nickel smelting slag consists principally of MgO , “FeO” and SiO_2 . However, other minor components are also present including Al_2O_3 , Cr_2O_3 , MnO and CaO . The present study has shown that the presence of these impurities should be taken into account for the accurate prediction of liquidus temperatures. These new experimental data can be used directly to predict the effect of alumina and chromite on the liquidus temperatures in nickel smelting slags, and in the development of more accurate thermodynamic models of the slags.

4. Conclusions

Liquidus isotherms in the cristobalite and tridymite pri-

mary phase fields in the MgO -“FeO”- SiO_2 - Al_2O_3 system with 2, 3 and 5 wt% Al_2O_3 in equilibrium with metallic iron have been determined in the temperatures range 1673–1873 K.

(1) Each weight percent of Al_2O_3 added to the silica-saturated slag at fixed $\text{SiO}_2/\text{MgO}/\text{FeO}$ ratios decreases the liquidus temperature by approximately 40 K in the range of compositions investigated.

(2) Liquidus isotherms in the cristobalite and tridymite primary phase fields in the MgO -“FeO”- SiO_2 - Al_2O_3 -“ Cr_2O_3 ” system with 2 wt% Cr_2O_3 and 2 wt% Al_2O_3 +2 wt% Cr_2O_3 in equilibrium with metallic iron have been determined in the temperatures range 1673–1873 K.

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REFERENCES

- 1) S. Chen, E. Jak and P. C. Hayes: *ISIJ Int.*, **45** (2005), 791.
- 2) N. L. Bowen and J. F. Schairer: *Am. J. Sci.*, **29** (1935), 151.
- 3) C. M. Diaz, C. A. Landolt, A. Vahed, A. E. M. Warner and J. C. Taylor: *J. Met.*, **9** (1988), 28.
- 4) A. Miyashiro: *Am. J. Sci.*, **255** (1957), 43.
- 5) M. J. Holdaway: *Am. J. Sci.*, **276** (1976), 285.
- 6) O. B. Fabrichnaya: *Calphad*, **23** (1999), 19.
- 7) E. Jak, H. G. Lee and P. C. Hayes: *Kor. IMM J.*, **1** (1995), 1.
- 8) E. Jak, B. Zhao and P. C. Hayes: Proc. of the 5th Int. Conf. on Slags and Fluxes, ISS, Warrendale, PA, (1997), 719.
- 9) E. Jak, S. Degterov, B. Zhao, A. D. Pelton and P. C. Hayes: *Metall. Mater. Trans. B*, **31B** (2000), 621.
- 10) E. F. Osborn and A. Muan: Phase Equilibrium Diagrams of Oxide Systems, ed. by Edward Orton, Jr., Am. Ceram. Soc., Ceram. Found., Columbus, Ohio, (1960), 409.
- 11) A. Muan and E. F. Osborn: Phase Equilibria among Oxides in Steelmaking, Addison-Wesley Pub. Com., Inc., Reading, MA, (1965), 116.
- 12) Y. Xiao and L. Holappa: INFACON 7, FFF, Trondheim, (1995), 319.
- 13) K. Morita, A. Inoue, N. Takayama and N. Sano: *Tetsu-to-Hagané*, **74** (1988), 999.
- 14) C. W. Bale, P. Chartrand, S. A. Degterov, G. Eriksson, K. Hack, R. B. Mahfoud, J. Melancon, A. D. Pelton and S. Petersen: *Calphad*, **26** (2002), 189.
- 15) M. L. Keith: *J. Am. Ceram. Soc.*, **37** (1954), 490.