

The Effect of Al_2O_3 on Liquidus Temperatures of Fayalite Slags

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The effect of alumina on the liquidus temperatures of fayalite slags at iron saturation has been investigated experimentally. Equilibrated synthetic slags were quenched, and the samples were subsequently examined using optical microscopy and electron probe microanalysis (EPMA). The isotherms in the fayalite primary field and boundary lines were determined, and the results were presented in the form of pseudo-ternary phase diagrams of "FeO"-CaO-SiO₂ with 0, 2, 4, and 6 wt pct Al_2O_3 in the slag. The experimental results show that the alumina addition expands the fayalite primary phase field and decreases the liquidus temperatures in the fayalite primary phase field.

I. INTRODUCTION

THE slag compositions used in copper smelting lie in the vicinity of the fayalite ($2\text{FeO}\cdot\text{SiO}_2$) primary phase field. To date, the FeO-Fe₂O₃-SiO₂ and "FeO"-CaO-SiO₂ phase diagrams have been used to estimate the liquidus temperatures of these copper smelting slags.*^[1-7] In practice,

*In this article, all iron is given as FeO, which actually represents FeO + Fe₂O₃.

however, the slags contain not only "FeO", CaO and SiO₂, but also other components, such as, Al_2O_3 and MgO.^[8,9,10] These additional components are introduced through the mineral concentrates, fluxes, recycled converter slag, coal ash, or dissolved refractories.

The "FeO"-CaO-SiO₂ system, in equilibrium with metallic iron, was first investigated by Bowen *et al.*,^[11] who carried out research in the high-silica region. Allen and Snow^[12] investigated this system in the low-silica region. Muan and Osborn^[13] then constructed the entire ternary diagram based on these experimental data.

The "FeO"- Al_2O_3 -SiO₂ system, in equilibrium with metallic iron, has been studied by a number of investigators.^[14,15,16] These results can be used to evaluate the effect of an alumina addition on the liquidus temperatures of fayalite slag.

Henrich^[17] discussed the function of alumina in copper smelting slags. He proposed that, in slags containing larger quantities (20 to 30 wt pct) of alumina, the alumina should be considered as an acid, and the liquidus temperature of a slag will rise with increasing alumina content. However, no experimental data were given to support this conclusion. According to Newton and Wilson,^[18] "alumina is never added intentionally, as it makes the slag viscous, and is generally an undesirable constituent of slags." Lankford *et al.*^[19] stated that alumina is seldom employed as a flux, but it is present in a large number of raw materials as an impurity and, therefore, is present in slag.

Schairer^[20] investigated phase equilibria in the Al_2O_3 -CaO-"FeO"-SiO₂ system in equilibrium with metallic iron.

Five sections were presented in the form of pseudo-ternary phase diagrams. Muan and Osborn^[21] also studied several sections in this system. However, investigations of alumina-containing slags have not been carried out in the composition ranges relevant to copper smelting slags. In fact, to date, no experimental information has been found on the effect of alumina on the liquidus temperatures of copper smelting slag. Verney^[6] has shown that the liquidus temperatures for alumina-containing slags cannot be accurately estimated from the "FeO"-CaO-SiO₂ system.

The objective of the present work is, then, to determine the liquidus temperatures in the fayalite primary phase field of the multicomponent Al_2O_3 -"FeO"-CaO-SiO₂ system in equilibrium with metallic iron. The investigation concentrates on the composition range relevant to copper smelting slags, *i.e.*, in the fayalite primary phase field near silica saturation. The results can be directly used to more accurately predict the liquidus temperatures of copper smelting slag.

II. EXPERIMENTAL

A. Experimental Procedure

The experimental procedure is similar to the one previously used by the PYROSEARCH group at the University of Queensland.^[22-28] The slag samples were prepared from the following chemicals, obtained from Sigma-Aldrich Pty. Ltd. (Australia): 99.8 pct Al_2O_3 , 99.95 pct CaCO₃, 99.9 pct Fe powder, 99.98 pct Fe₂O₃ and 99.9 pct SiO₂. The chemicals were mixed in an agate mortar to the required compositions. Then, 15 to 20 pct excess Fe powder (<10 μm in size) was added to the slag samples to ensure that the slag was equilibrated with metallic iron. About 0.3 g of the mixture was pelletized and placed in platinum foil (0.025-mm thick) or Fe foil (99.9 pct, 0.1-mm thick) envelopes. The experiments were carried out in a vertical silicon carbide furnace. The furnace temperature was controlled within ± 1 K. A Pt-Pt/13 pct Rh thermocouple placed in an alumina sheath was located adjacent to the sample to accurately measure the sample temperature. The thermocouple was calibrated by a reference thermocouple supplied by National Measurement Laboratory (CSIRO, Melbourne, Australia) and was periodically checked against the melting point of pure gold. The overall temperature accuracy was estimated to be within ± 2 K.

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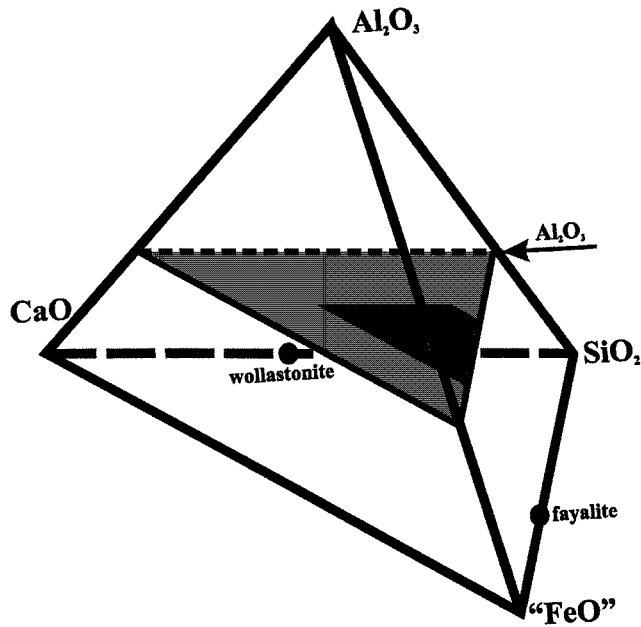


Fig. 1—Pseudo-ternary sections in the Al_2O_3 -“FeO”-CaO- SiO_2 system with wt. pct Al_2O_3 in slag in equilibrium with metallic iron (temperature in K).

The sample was first placed in the cool zone, and the bottom end of the furnace was sealed by a plastic film. After ultra high purity nitrogen (total impurities ≤ 5 ppm, oxygen ≤ 1 ppm) was passed through the furnace tube for 15 to 30 minutes to remove the air, the sample was raised into the hot zone adjacent to the thermocouple. The experiment was usually carried out in two steps. The first step was to premelt the sample at a temperature higher than the liquidus to ensure that the sample is homogeneous. The sample was then equilibrated at the desired temperature for a time sufficient to achieve equilibrium. The equilibration usually takes from 2 to 20 hours, depending on the mixture composition and temperature, *i.e.*, at higher temperatures or lower silica contents, a shorter time was employed; otherwise, the sample was kept for a longer time. If the sample has not attained local equilibrium, then the composition of the glass phase, as measured by the electron microprobe, will not be uniform, and this sample will be rejected. There was no attempt to control the oxygen partial pressure of the system in the gas phase, since local equilibrium with iron metal is achieved in the sample. After equilibration, the sample was quenched directly in the cooling water.

B. Sample Examination

The quenched sample was mounted and polished for analysis. First, optical microscopy was employed to identify the phases present in the sample. The compositions of the phases were then measured using a JEOL* 8800L electron probe

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

X-ray microanalyser. An accelerating voltage of 15 kV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with the JEOL 8800L was applied. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California): Al_2O_3 for Al,

Table I. Experimental Results on the CaO-“FeO”- SiO_2 System in Equilibrium with Metallic Iron

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al_2O_3	SiO_2
464	liquid	1473	45.2	24.7	0.0	30.1
	fayalite		35.3	32.4	0.0	32.3
	wustite		99.5	0.3	0.0	0.2
468	liquid	1423	51.4	17.7	0.0	30.9
	fayalite		41.5	26.8	0.0	31.7
	wustite		99.5	0.2	0.0	0.3
480	fayalite	1393	60.3	8.9	0.0	30.8
	wustite		99.6	0.0	0.0	0.4
485	liquid	1473	63.9	0.0	0.0	36.1
	fayalite		70.0	0.0	0.0	30.0
495	liquid	1403	58.1	11.4	0.0	30.5
	fayalite		64.2	5.2	0.0	30.6
	wustite		99.6	0.0	0.0	0.4
499	liquid	1463	62.5	0.0	0.0	37.5
	fayalite		70.1	0.0	0.0	29.9
514	liquid	1423	58.3	9.1	0.0	32.6
	fayalite		69.1	0.9	0.0	30.0
534	liquid	1473	67.7	2.1	0.0	30.2
	fayalite		69.1	0.8	0.0	30.1
	wustite		99.6	0.0	0.0	0.4
535	liquid	1403	52.0	12.7	0.0	35.3
	fayalite		66.6	3.1	0.0	30.3
537	liquid	1423	45.6	20.2	0.0	34.2
	fayalite		40.8	27.3	0.0	31.9
551	liquid	1393	50.2	14.2	0.0	35.6
	fayalite		65.6	4.1	0.0	30.3
	wustite		99.6	0.0	0.0	0.4
552	liquid	1403	44.8	19.1	0.0	36.1
	fayalite		42.8	25.3	0.0	31.9
556	liquid	1423	53.4	5.5	0.0	41.1
	fayalite		69.8	0.5	0.0	29.7
	silica		1.7	0.1	0.0	98.2
557	liquid	1403	49.9	7.7	0.0	42.4
	fayalite		69.7	0.6	0.0	29.7
	silica		1.1	0.0	0.0	98.9
560	liquid	1423	39.5	23.6	0.0	36.9
	fayalite		39.2	28.9	0.0	31.9
	wollastonite		5.3	44.1	0.0	50.6
566	liquid	1393	48.0	8.8	0.0	43.2
	fayalite		69.2	0.6	0.0	30.2
	silica		1.3	0.0	0.0	98.7
567	liquid	1383	47.7	15.1	0.0	37.2
	fayalite		66.6	3.2	0.0	30.2
574	liquid	1383	44.1	18.4	0.0	37.5
	fayalite		50.1	18.3	0.0	31.6
	wollastonite		18.0	32.2	0.0	49.8
591	liquid	1383	46.1	10.0	0.0	43.9
	fayalite		68.9	0.7	0.0	30.4
	silica		1.2	0.0	0.0	98.8
593	liquid	1373	45.0	17.2	0.0	37.8
	fayalite		50.1	18.3	0.0	31.6
	wollastonite		32.2	18.0	0.0	49.8
594	liquid	1393	42.2	19.9	0.0	37.9
	wollastonite		18.0	32.2	0.0	49.8
	fayalite		50.1	18.3	0.0	31.6
595	liquid	1393	48.2	11.1	0.0	40.7
	fayalite		68.3	1.4	0.0	30.3
596	liquid	1423	53.6	8.4	0.0	38.0
	fayalite		68.7	1.1	0.0	30.2
597	liquid	1403	49.4	10.4	0.0	40.2
	fayalite		68.5	1.3	0.0	30.2
601	liquid	1423	39.3	18.3	0.0	42.4
	wollastonite		24.2	26.6	0.0	49.2
617	liquid	1373	45.0	12.8	0.0	42.2

Table I. Continued

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
618	fayalite	1373	68.5	1.6	0.0	29.9
	liquid		44.9	11.0	0.0	44.1
	fayalite		68.7	1.2	0.0	30.1
629	silica	1423	1.0	0.1	0.0	98.9
	liquid		38.0	15.5	0.0	46.5
	silica		0.8	0.1	0.0	99.1
661	wollastonite	1373	28.5	22.8	0.0	48.7
	liquid		45.5	17.1	0.0	37.4
	fayalite		55.2	13.9	0.0	30.9
662	wollastonite	1373	20.3	30.4	0.0	49.3
	liquid		45.6	14.6	0.0	39.8
	fayalite		66.9	3.2	0.0	29.9
663	liquid	1423	39.8	22.1	0.0	38.1
	wollastonite		6.5	42.8	0.0	50.7
	liquid		39.3	23.5	0.0	37.2
664	fayalite	1423	39.6	28.5	0.0	31.9
	liquid		66.3	3.9	0.0	29.8
	wollastonite		29.2	22.5	0.0	48.3
683	liquid	1403	52.4	16.8	0.0	30.8
	fayalite		43.5	25.0	0.0	31.5
	wustite		99.6	0.1	0.0	0.3
706	liquid	1396	54.8	13.6	0.0	31.6
717	liquid	1463	45.0	23.2	0.0	31.8
	fayalite		37.3	30.3	0.0	32.4
752	liquid	1373	45.7	10.6	0.0	43.7
	fayalite		69.0	1.2	0.0	29.8
	liquid		45.1	10.5	0.0	44.4
846	fayalite	1373	68.3	1.2	0.0	30.5
	silica		1.0	0.0	0.0	99.0
	silica		1.0	0.0	0.0	99.0
847	fayalite	1363	66.9	1.4	0.0	31.7
	wollastonite		34.5	17.2	0.0	48.3
	liquid		44.6	10.9	0.0	44.5
848	fayalite	1368	67.9	1.4	0.0	30.7
	silica		1.0	0.0	0.0	99.0
	silica		1.0	0.0	0.0	99.0

Fe₂O₃ for Fe, and CaSiO₃ for Ca and Si. The average accuracy of the electron probe microanalysis (EPMA) measurements was estimated to be within ± 1 pct of element concentration in wt pct.

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.

III. RESULTS AND DISCUSSION

Experiments were carried out in the fayalite primary phase field in the Al₂O₃-“FeO”-CaO-SiO₂ system in equilibrium with metallic iron. The results are presented in the form of pseudo-ternary sections “FeO”-CaO-SiO₂ at a fixed weight percentage of Al₂O₃, as shown in Figure 1. The quaternary system is viewed as a compositional tetrahedron with one component at each apex. The base is the “FeO”-CaO-SiO₂ system, and Al₂O₃ is the top apex. Horizontal planes in the tetrahedron represent levels of constant alumina content. In Figure 1, the position of selected planes is indicated as a grey

Table II. Experimental Results on the Al₂O₃-CaO-“FeO”-SiO₂ System with Al₂O₃ in Liquid Close to 2 Wt Pct in Equilibrium with Metallic Iron

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
1	liquid	1453	60.3	0.0	2.3	37.4
	fayalite		69.9	0.0	0.0	30.1
5	liquid	1413	50.8	7.9	2.4	38.9
	fayalite		68.5	0.8	0.0	30.7
6	liquid	1413	54.5	9.1	2.3	34.1
	fayalite		67.8	1.7	0.0	30.5
7	liquid	1463	60.3	0.0	2.1	37.6
	fayalite		69.5	0.0	0.0	30.5
11	liquid	1393	46.7	9.2	2.9	41.2
	fayalite		68.6	0.9	0.0	30.5
14	liquid	1423	55.2	8.5	2.1	34.2
	liquid		52.3	7.0	2.1	38.6
15	liquid	1433	52.3	7.0	2.1	38.6
	liquid		58.6	0.0	2.1	39.3
18	liquid	1453	58.6	0.0	2.1	39.3
	silica		1.1	0.0	0.0	98.9
19	liquid	1433	54.6	5.0	2.1	38.3
	liquid		59.1	6.1	2.1	32.7
20	liquid	1433	59.1	6.1	2.1	32.7
	liquid		50.9	7.9	2.1	39.1
21	liquid	1415	50.9	7.9	2.1	39.1
	liquid		53.1	9.0	2.1	35.8
22	liquid	1415	53.1	9.0	2.1	35.8
	liquid		59.5	0.0	2.1	38.4
23	liquid	1443	59.5	0.0	2.1	38.4
	fayalite		70.2	0.0	0.0	29.8
24	silica	1433	1.2	0.0	0.0	98.8
	liquid		55.7	5.3	2.1	36.9
25	fayalite	1413	69.7	0.5	0.0	29.8
	liquid		52.1	7.4	2.3	38.2
26	fayalite	1433	69.3	0.8	0.0	29.9
	liquid		60.9	6.0	2.0	31.1
27	fayalite	1413	69.1	1.1	0.0	29.8
	liquid		51.3	8.0	2.0	38.7
28	liquid	1393	48.5	10.4	1.9	39.2
	fayalite		68.6	1.5	0.0	29.9
31	liquid	1447	76.0	0.0	2.0	22.0
	fayalite		70.8	0.0	0.0	29.2
32	liquid	1433	55.6	2.3	2.1	40.0
	fayalite		70.5	0.1	0.0	29.4
35	silica	1453	1.3	0.0	0.0	98.7
	liquid		64.6	2.7	2.3	30.4
36	fayalite	1413	70.5	0.4	0.0	29.1
	liquid		51.4	4.8	2.2	41.6
38	fayalite	1393	70.2	0.3	0.0	29.5
	silica		1.1	0.0	0.0	98.9
40	liquid	1355	47.9	7.0	2.1	43.0
	fayalite		69.5	0.6	0.0	29.9
49	silica	1393	1.0	0.0	0.0	99.0
	liquid		42.0	11.4	2.1	44.5
52	fayalite	1373	68.5	1.3	0.0	30.2
	wollastonite		35.2	16.8	0.0	48.0
53	liquid	1373	52.7	11.9	2.4	33.0
	fayalite		65.5	4.0	0.0	30.5
54	liquid	1373	44.3	9.4	2.2	44.1
	fayalite		68.3	0.9	0.0	30.8
55	silica	1373	0.9	0.1	0.0	99.0
	liquid		44.5	12.8	2.2	40.5
59	fayalite	1345	67.0	2.3	0.0	30.7
	liquid		49.1	14.5	3.1	33.3
59	fayalite	1373	59.3	9.5	0.0	31.2
	liquid		50.0	14.6	2.8	32.6
59	fayalite	1345	57.0	12.0	0.0	31.0
	liquid		40.1	11.7	2.7	45.5
59	fayalite	1345	68.6	1.3	0.0	30.1
	wollastonite		35.0	16.7	0.1	48.2
59	silica	1345	1.0	0.1	0.0	98.9
	silica		1.0	0.1	0.0	98.9

Table II. Continued

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
65	liquid	1363	43.1	13.5	2.1	41.3
	fayalite		67.3	2.4	0.0	30.3
66	liquid	1363	41.2	12.2	2.0	44.6
	fayalite		33.9	17.9	0.0	48.2
67	liquid	1352	41.4	14.3	2.4	41.9
	fayalite		67.6	2.5	0.0	29.9
68	wollastonite	1349	30.9	21.1	0.1	47.9
	liquid		40.5	11.9	2.5	45.1
74	fayalite	1360	69.4	1.3	0.0	29.3
	wollastonite		35.9	16.7	0.1	47.3
76	silica	1453	0.9	0.1	0.0	99.0
	liquid		41.4	17.7	2.0	38.9
89	liquid	1355	60.2	2.4	2.1	35.3
	fayalite		70.4	0.2	0.0	29.4
90	liquid	1373	42.3	16.8	2.2	38.7
	wollastonite		22.3	28.4	0.1	49.2
93	liquid	1436	38.8	20.5	2.8	37.9
	fayalite		41.6	26.5	0.0	31.9
94	liquid	1383	56.5	1.8	2.1	39.6
	silica		1.2	0.0	0.0	98.8
105	liquid	1373	45.4	8.9	2.1	43.6
	fayalite		69.1	0.9	0.0	30.0
107	silica	1363	0.9	0.1	0.0	99.0
	liquid		46.0	15.5	2.0	36.5
109	liquid	1353	41.6	18.4	2.4	37.6
	fayalite		45.7	22.5	0.0	31.8
126	liquid	1358	42.4	17.0	2.1	38.5
	fayalite		61.8	7.7	0.0	30.5
128	liquid	1353	42.3	16.8	2.1	38.8
	wollastonite		23.5	27.5	0.0	49.0
187	liquid	1433	42.9	14.7	2.3	40.1
	wollastonite		29.0	22.3	0.1	48.6
189	fayalite	1413	66.2	3.4	0.0	30.4
	liquid		55.1	4.0	2.2	38.7
	fayalite		69.5	0.3	0.0	30.2
	liquid		50.6	6.7	2.3	40.4
	fayalite		69.1	0.6	0.0	30.3

plane, and the composition range investigated is indicated as a dark zone.

The mixture compositions made up for study were selected in such a way that the liquid phase in the sample after equilibration had a composition lying in these horizontal planes, which are designated as 0, 2, 4, and 6 wt pct of the Al₂O₃ planes. The precipitation of solid phases changes the Al₂O₃ content in the liquid phase. The compositions of the phases present in the quenched samples are, however, measured by EPMA after the experiments; the bulk mixture compositions are not important in the current work. The bulk compositions were adjusted after preliminary experiments to obtain Al₂O₃ contents in the liquid phase close to the fixed values of 2, 4, and 6 wt pct Al₂O₃. Only those liquid compositions that have the Al₂O₃ content near the selected values have been used in the construction of the pseudo-ternary sections. Special attention was also paid to the positions of boundary lines of the fayalite primary phase field with the wollastonite ((Ca,Fe)₂SiO₄) and tridymite (SiO₂).

Experimental data for compositions of liquid and solid phases are given in Tables I through IV. The results of liquidus determination for the sections containing 0, 2, 4, and 6 wt pct of Al₂O₃ in the liquid phase are presented in

Table III. Experimental Results on the Al₂O₃-CaO-“FeO”-SiO₂ System with Al₂O₃ in Liquid Close to 4 Wt Pct in Equilibrium with Metallic Iron

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
8	liquid	1433	55.0	5.1	3.2	36.7
	fayalite		69.0	0.5	0.0	30.5
12	liquid	1393	49.2	11.6	3.2	36.0
	fayalite		67.5	2.2	0.0	30.3
13	liquid	1423	52.9	5.5	3.5	38.1
	fayalite		69.4	0.5	0.0	30.1
29	liquid	1413	49.2	8.0	4.1	38.7
	liquid		33	1393	30.1	15.5
39	fayalite	1393	70.0	0.7	0.0	29.3
	silica		1.0	0.0	0.0	99.0
41	liquid	1355	54.7	10.4	3.3	31.6
	fayalite		67.7	2.4	0.0	29.9
42	liquid	1433	40.4	11.9	3.9	43.8
	liquid		42	1433	56.7	0.0
43	fayalite	1433	70.3	0.0	0.0	29.7
	liquid		43	1433	57.1	3.6
44	fayalite	1413	69.2	0.4	0.0	30.4
	liquid		44	1413	51.1	6.8
45	fayalite	1413	69.1	0.7	0.0	30.2
	liquid		45	1413	53.6	8.3
46	liquid	1413	57.9	7.2	4.2	30.7
	fayalite		46	1413	68.1	1.6
47	liquid	1413	50.4	4.4	4.1	41.1
	liquid		48	1349	39.7	11.5
50	fayalite	1393	68.4	1.3	0.0	30.3
	wollastonite		50	1393	34.6	17.2
51	liquid	1335	54.8	9.6	4.3	31.3
	fayalite		51	1335	66.9	2.5
56	liquid	1373	37.1	12.9	4.8	45.2
	fayalite		56	1373	67.8	1.5
60	wollastonite	1433	33.5	17.9	0.1	48.5
	liquid		60	1433	42.1	9.0
61	silica	1413	1.0	0.1	0.0	98.9
	liquid		61	1433	37.2	11.4
63	fayalite	1393	69	1.1	0.0	29.9
	silica		63	1393	1.0	0.1
64	liquid	1393	51.6	2.9	4.0	41.5
	fayalite		64	1393	69.9	0.2
71	silica	1398	1.3	0.0	0.1	98.6
	liquid		71	1398	48.5	10.5
72	fayalite	1369	68	1.8	0.0	30.2
	liquid		72	1369	46.6	6.2
73	fayalite	1339	69.3	0.5	0.0	30.2
	silica		73	1339	0.8	0.1
75	liquid	1360	45.8	6.3	4.2	43.7
	silica		75	1360	1.2	0.0
77	liquid	1373	41.7	9.1	4.3	44.9
	silica		77	1373	0.9	0.1
78	liquid	1373	37.7	11.3	5.0	46.0
	fayalite		78	1373	69.2	1.1
79	silica	1358	1.0	0.1	0.0	98.9
	liquid		79	1358	38.0	20.3
80	liquid	1358	43.2	25.8	0.0	31.0
	fayalite		80	1358	45.2	13.4
85	liquid	1348	67.7	2.8	0.0	29.5
	fayalite		85	1348	50.2	13.1
	liquid		64.8	5.2	0.0	30.0
	liquid		40.3	18.4	4.0	37.3
	liquid		39.3	18.8	9.1	32.8
	fayalite		41.6	26.9	0.0	31.5
	liquid		40.4	14.3	4.0	41.3
	fayalite		67.9	2.3	0.0	29.8

Table III. Continued

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
	wollastonite		31.5	20.5	0.1	47.9
90	liquid	1355	40.4	18	4.1	37.5
101	liquid	1348	40.6	18.1	4.0	37.3
102	liquid	1343	40.1	12.1	4.0	43.8
103	liquid	1343	39.0	10.7	4.6	45.7
	fayalite		69.1	0.9	0.0	30.0
	silica		0.9	0.1	0.1	98.9
132	liquid	1328	37.9	11.7	4.7	45.7
	fayalite		69.2	1.3	0.0	29.5
	silica		0.9	0.1	0.1	98.9
137	liquid	1345	40.1	17.9	4.1	37.9
	fayalite		69.2	1.3	0.0	29.5
188	liquid	1433	56.6	1.9	4.3	37.2
	fayalite		69.5	0.1	0.0	30.4
190	liquid	1413	51.1	5.4	4.1	39.4
	fayalite		69.5	0.4	0.0	30.1
191	liquid	1338	38.5	18.2	4.6	38.7
	fayalite		51.5	17.1	0.0	31.4
192	liquid	1393	46.8	7.9	4.1	41.2
227	liquid	1323	35.7	11.7	6.1	46.5
	fayalite		68.3	1.3	0.0	30.4
	wollastonite		34.3	17.2	0.2	48.3
228	liquid	1353	40.2	9.9	4.3	45.6
	fayalite		68.9	0.9	0.0	30.2
	silica		0.8	0.1	0.1	99.0
229	liquid	1353	40.8	12.8	4.2	42.2
	fayalite		67.8	1.8	0.0	30.4
231	liquid	1393	47.4	4.8	4.9	42.9
	fayalite		69.5	0.3	0.0	30.2
	silica		1.0	0.0	0.1	98.9
232	liquid	1373	42.7	7.8	4.9	44.6
	fayalite		69.2	0.6	0.0	30.2
	silica		1.0	0.0	0.1	98.9
233	liquid	1373	43.3	8.6	4.1	44.0
	fayalite		68.3	0.8	0.0	30.9
235	liquid	1433	53.3	10.8	4.0	31.9

Figures 2(a) through (d), respectively. In these figures, light lines represent isotherms, and heavy lines represent boundaries between the fayalite and wollastonite, and between the fayalite and tridymite primary phase fields. It can be seen from Figures 2(a) through (d) that the fayalite primary phase field is bounded by the wollastonite and tridymite primary phase fields in the composition range investigated, and that the addition of up to 6 wt pct of alumina does not introduce any new primary phases in this region.

The EPMA measurements show little or no alumina dissolved in fayalite (2FeO·SiO₂). The composition of fayalite does not lie in the alumina-containing sections of the quaternary system. Note that these sections are not true ternary diagrams, and caution should be exercised in predicting subliquidus phase relations.

The results of Bowen *et al.*^[11] on the “FeO”-CaO-SiO₂ system in equilibrium with metallic iron are shown as dashed lines in Figure 2(a), for comparison. There were only two isotherms, at 1473 and 1423 K, determined by Bowen *et al.* in the fayalite primary phase field. It can be seen from Figure 2(a) that there is good agreement between the results of the present studies and those obtained by Bowen *et al.*

The present results are compared to those of Schairer and

Table IV. Experimental Results on the Al₂O₃-CaO-“FeO”-SiO₂ System with Al₂O₃ in Liquid Close to 6 Wt Pct in Equilibrium with Metallic Iron

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
57	liquid	1433	60.7	2.7	5.5	31.1
	fayalite		69.4	0.3	0.1	30.2
58	liquid	1423	54.7	0.0	5.3	40.0
	fayalite		70	0.0	0.0	30.0
	silica		1.2	0.0	0.0	98.8
62	liquid	1413	53.6	0.0	6.3	40.1
	fayalite		69.9	0.0	0.0	30.1
	silica		1.4	0.0	0.1	98.5
69	liquid	1418	53.9	0.0	6.2	39.9
	silica		1.3	0.0	0.0	98.7
70	liquid	1428	54.8	0.0	5.4	39.8
	fayalite		70.7	0.0	0.0	29.3
	silica		1.3	0.0	0.0	98.7
81	liquid	1413	52.7	5.9	6.6	34.8
	fayalite		70	0.6	0.0	29.4
82	liquid	1413	57.3	4.9	7.2	30.6
	fayalite		70	0.6	0.1	29.3
83	liquid	1393	43.2	6.8	6.0	44.0
	silica		0.7	0.1	0.3	98.9
84	liquid	1393	46.3	10.4	6.1	37.2
86	liquid	1393	54.7	8.6	6.2	30.5
	fayalite		68.3	2.0	0.1	29.6
87	liquid	1388	43	6.6	6.0	44.4
	silica		1	0.1	0.2	98.7
88	liquid	1388	46.1	10.3	6.1	37.5
92	liquid	1373	40.3	19.7	7.2	32.8
	fayalite		40.2	27.8	0.0	32.0
95	liquid	1373	43.5	13.4	6.0	37.1
96	liquid	1373	52.5	11.1	6.0	30.4
97	liquid	1351	34.9	12.3	6.0	46.8
	silica		0.8	0.1	0.1	99.0
98	liquid	1351	40.3	16.1	6.0	37.6
99	liquid	1353	47.7	14.6	6.1	31.6
	wustite		99	0.6	0.2	0.2
100	liquid	1373	39.1	9.7	6.1	45.1
104	liquid	1343	44.9	15.3	6.7	33.1
	fayalite		58.2	11.2	0.0	30.6
106	liquid	1373	53.1	10.8	6.0	30.1
	wustite		99	0.0	0.6	0.4
110	liquid	1393	44.5	6.5	5.9	43.1
111	liquid	1393	46.8	10.0	5.9	37.3
112	liquid	1373	40	9.3	5.9	44.8
113	liquid	1373	44.2	13.1	5.9	36.8
114	liquid	1351	36.4	11.7	5.8	46.1
115	liquid	1351	41.5	16.2	6.0	36.3
127	liquid	1358	35.2	21.3	5.9	37.6
	wollastonite		4.4	44.8	0.3	50.5
	fayalite		40.5	27.5	0.0	32.0
129	liquid	1353	49.6	12.5	6.9	31.0
	wustite		99.0	0.0	0.7	0.3
	fayalite		65.0	4.9	0.1	30.0
130	liquid	1393	46.2	4.5	6.1	43.2
	silica		0.9	0.0	0.1	99.0
131	liquid	1393	49.7	8.2	6.1	36.0
	fayalite		68.8	1.0	0.0	30.2
133	liquid	1373	52.7	10.5	6.2	30.6
	fayalite		67.1	2.9	0.1	29.9
135	liquid	1373	39.9	8.9	5.9	45.3
	silica		1.0	0.1	0.1	98.8
136	liquid	1345	47.1	14.7	6.5	31.7
	wustite		99.0	0.1	0.6	0.3

Table IV. Continued

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
138	fayalite	1351	57.3	12.0	0.0	30.7
	liquid		40.1	9.2	5.9	44.8
139	fayalite	1351	69.1	0.8	0.0	30.1
	liquid		42.2	13.8	6.2	37.8
147	fayalite	1393	67.1	3.0	0.0	29.9
	liquid		49.5	2.4	6.2	41.9
148	fayalite	1373	70.0	0.1	0.0	29.9
	silica		1.2	0.0	0.1	98.7
149	liquid	1373	43.2	6.7	6.0	44.1
	fayalite		69.4	0.5	0.0	30.1
150	liquid	1359	44.2	10.4	6.7	38.7
	fayalite		68.1	1.3	0.0	30.6
151	liquid	1337	40.7	7.8	6.4	45.1
	fayalite		69.3	0.5	0.0	30.2
152	silica	1337	0.9	0.1	0.2	98.8
	liquid		34.5	12.2	5.9	47.4
154	silica	1337	0.7	0.1	0.1	99.1
	liquid		40.2	16.6	5.9	37.3
179	fayalite	1413	62.4	6.9	0.0	30.7
	liquid		57.6	5.3	6.2	30.9
180	fayalite	1323	69.0	0.8	0.2	30.0
	liquid		33.2	12.5	6.5	47.8
181	wollastonite	1323	32.5	18.3	0.1	49.1
	silica		1.0	0.2	0.2	98.6
182	liquid	1333	35.9	14.3	6.2	43.6
	wollastonite		30.0	20.8	0.1	49.1
183	fayalite	1333	67.2	2.2	0.0	30.6
	liquid		41.1	16.5	8.7	33.7
184	fayalite	1333	45.1	22.4	0.0	32.5
	liquid		41.4	16.2	8.4	34.0
185	fayalite	1333	46.9	20.3	0.0	32.8
	spinel		46.5	0.0	53.2	0.3
186	liquid	1313	36.7	10.4	6.0	46.9
	fayalite		68.4	0.9	0.0	30.7
187	silica	1323	0.8	0.1	0.2	98.9
	liquid		35.5	16.3	6.3	41.9
188	fayalite	1323	65.7	3.5	0.0	30.8
	liquid		38.9	16.8	9.4	34.9
189	fayalite	1313	44.6	22.5	0.1	32.8
	spinel		45.2	0.0	54.6	0.2
190	liquid	1413	32.5	12.2	7.4	47.9
	wollastonite		33.9	17.5	0.2	48.4
191	silica	1413	0.9	0.1	0.3	98.7
	liquid		52.2	2.3	7.2	38.3
192	fayalite	1413	69.4	0.1	0.0	30.5
	liquid		52.4	4.1	6.8	36.7
193	fayalite	1393	69.4	0.3	0.1	30.2
	liquid		47.3	4.9	7.2	40.6
194	fayalite	1393	69.6	0.3	0.0	30.1
	liquid		47.6	6.6	6.9	38.9
195	fayalite	1312	69.1	0.6	0.0	30.3
	liquid		33.4	12.1	7.4	47.1
196	fayalite	1312	68.3	1.2	0.0	30.5
	wollastonite		34.2	17.4	0.1	48.3
197	silica	1312	0.9	0.1	0.2	98.8
	fayalite		66.5	3.2	0.0	30.3
198	wollastonite	1304	27.1	23.8	0.2	48.9
	mullite		1.5	19.4	35.4	43.7
199	liquid	1353	31.4	12.2	8.8	47.6
	fayalite		68.5	1.3	0.0	30.2
200	wollastonite	1353	34.4	17.5	0.1	48.0
	silica		0.8	0.1	0.2	98.9
201	liquid		34.2	19.0	6.1	40.7

Table IV. Continued

Experiment Number	Phases	Temperature (K)	Composition (Wt Pct)			
			FeO	CaO	Al ₂ O ₃	SiO ₂
202	wollastonite	1323	18.7	31.6	0.0	49.7
	liquid		35.7	11.7	6.1	46.5
203	fayalite	1353	68.3	1.3	0.0	30.4
	wollastonite		34.3	17.2	0.2	48.3
204	liquid	1353	45.4	15.5	5.7	33.4
	fayalite		55.5	13.2	0.0	31.3
205	liquid	1373	46.8	15.0	5.6	32.6
	fayalite		52.2	16.0	0.0	31.8
206	liquid	1373	42.9	6.1	6.8	44.2
	fayalite		69.4	0.3	0.0	30.3
207	silica	1373	0.9	0.1	0.1	98.9
	liquid		42.9	8.0	6.1	43.0
208	fayalite	1413	68.7	0.8	0.0	30.5
	liquid		52.0	2.4	6.1	39.5
209	fayalite	1393	69.3	0.1	0.0	30.6
	liquid		47.3	5.7	5.9	41.1
210	fayalite	1353	68.9	0.4	0.0	30.7
	liquid		40.0	10.1	6.0	43.9
211	fayalite	1333	68.5	1.0	0.0	30.5
	liquid		37.3	12.5	6.0	44.2
212	fayalite	1333	68.3	1.4	0.0	30.3
	liquid		43.8	15.5	8.2	32.5
213	fayalite		51.8	16.8	0.0	31.4
	wustite		99.0	0.0	0.8	0.2
214	spinel		47.3	0.0	52.6	0.1

Yagi,^[14] as shown in Figure 3. The temperatures of the univariant points, representing the equilibrium of liquid with tridymite and fayalite in the Al₂O₃-“FeO”-SiO₂ system, are plotted against the alumina content. It can be seen from Figure 3 that the difference in this region between the present work and the results of Schairer and Yagi is less than 10 K.

The liquidus temperatures in the fayalite primary phase field are reduced by the addition of alumina to slag, as shown in Figure 4. Three typical slag compositions in the fayalite primary phase field were chosen to determine the effect of an Al₂O₃ addition on liquidus temperatures. The initial compositions were selected near silica saturation and are given in the Figure 4 caption. The liquidus temperatures of these slags were compared to the slags having 2, 4, and 6 wt pct Al₂O₃ and the same “FeO”/CaO/SiO₂ ratios. It can be seen from Figure 4 that the additions of up to 6 wt pct Al₂O₃ decrease the liquidus temperatures for all fayalite slags. The effect of each Al₂O₃ weight percent addition to the slag is estimated to decrease the liquidus temperature by approximately 3 K.

The addition of alumina leads to the expansion of the fayalite primary phase field toward lower “FeO” concentrations. This can be illustrated by Table V. In the composition range investigated, there is a point A representing equilibrium of liquid with wollastonite, tridymite, fayalite, and metallic iron. The compositions and temperatures of point A, from Figures 2(a) through (d), are listed in Table V. It can be seen from Table V that the position of point A changes with the addition of alumina to the slag. The SiO₂ content of the point-increases from 44.2 to 47.2 wt pct with the addition of 6 wt pct of Al₂O₃, while the “FeO” content decreases significantly from 42.3 to 35.6 wt pct. Thus, the fayalite primary phase field expands toward higher silica and lower iron oxide concentrations with the addition of

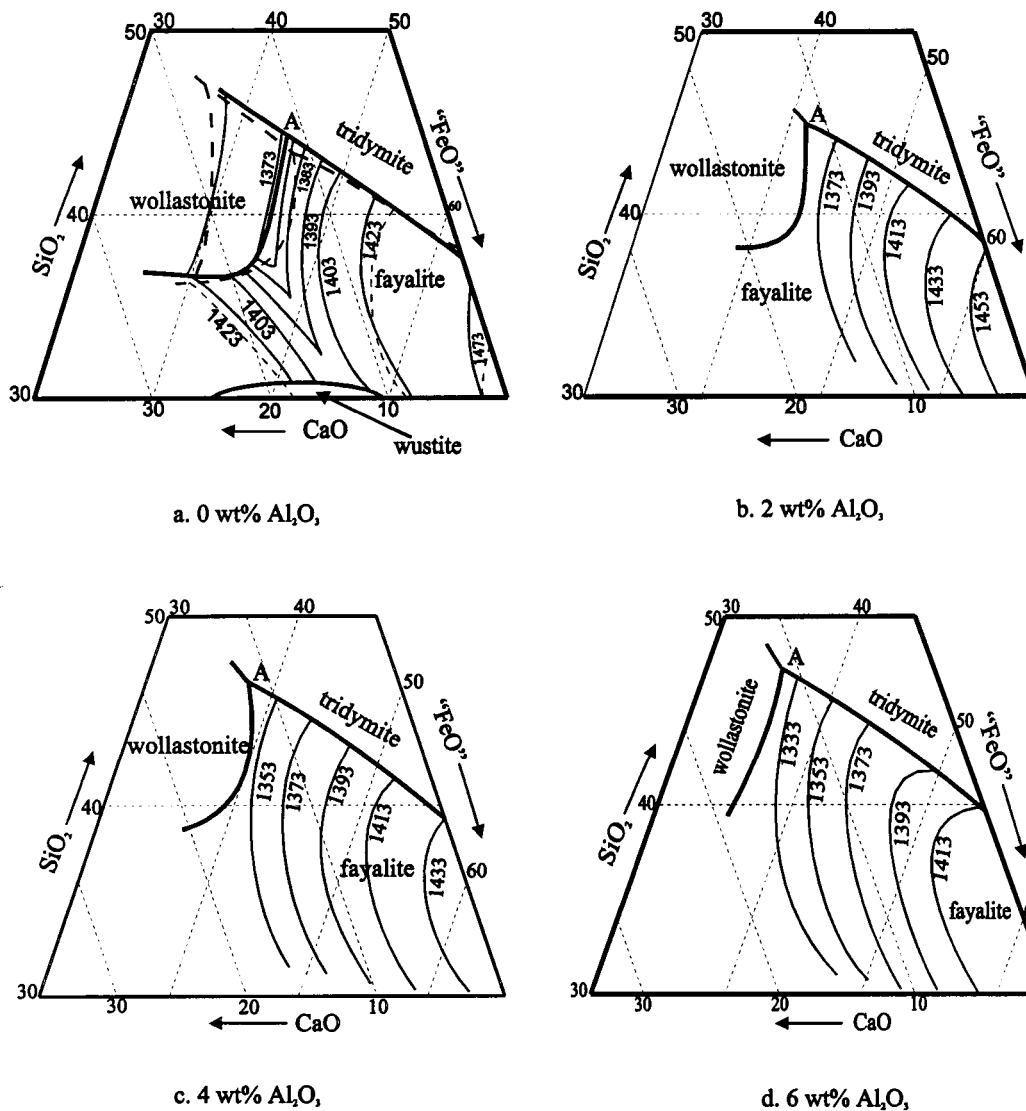


Fig. 2—(a) through (d) Experimentally determined liquidus isotherms in the fayalite primary field of the Al_2O_3 -“FeO”-CaO- SiO_2 system in equilibrium with metallic iron (temperature in K).

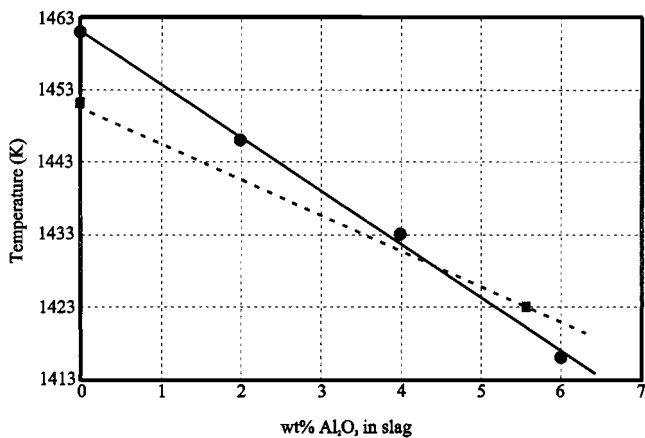


Fig. 3—The relationship between liquidus temperature and alumina content along the boundary line of tridymite and fayalite in the Al_2O_3 -“FeO”- SiO_2 system in equilibrium with metallic iron: solid lines—experimental work; and dashed lines—results of Schairer and Yagi.^[14]

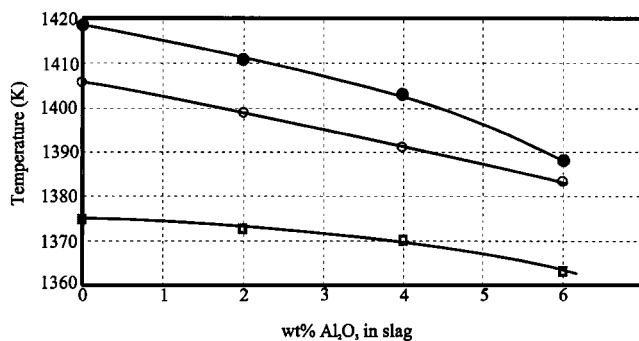


Fig. 4—The effect of Al_2O_3 on liquidus temperatures for the following slags: (□) 45 pct “FeO,” 11 pct CaO, and 44 pct SiO_2 ; (○) 50 pct “FeO,” 10 pct CaO, and 40 pct SiO_2 ; and (●) 55 pct “FeO,” 10 pct CaO, and 35 pct SiO_2 .

alumina. It also can be seen from Table V that the liquidus temperature of point A is decreased from 1361 to 1318 K by the addition of 6 wt pct alumina.

One of the systems which is similar to Al_2O_3 -CaO-“FeO”- SiO_2 is Al_2O_3 -CaO-MgO- SiO_2 . Osborn *et al.*^[29] constructed

Table V. Experimentally Determined Point A—Equilibrium of Liquid + Wollastonite + Tridymite + Fayalite + Metallic Iron (Figure 2)

Section Al ₂ O ₃ in Slag (Wt Pct)	Point A (Fig. 2)			Temperature (K)
	Composition (Wt Pct)			
	CaO	"FeO"	SiO ₂	
0	13.5	42.3	44.2	1361
2	11.8	41.3	44.9	1353
4	11.5	38.0	46.5	1333
6	11.2	35.6	47.2	1318

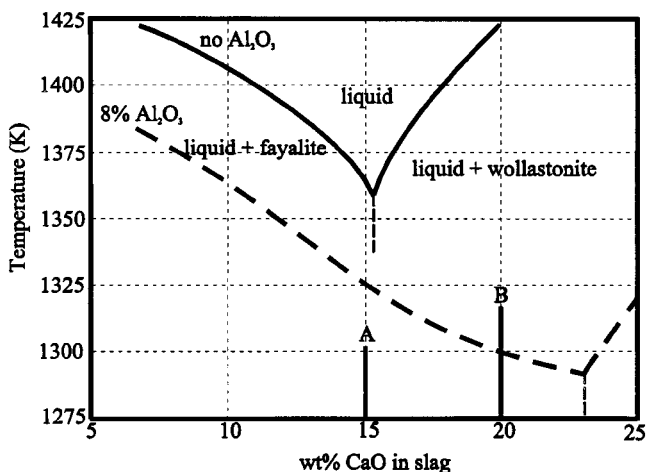


Fig. 5—Liquidus surfaces in the pseudobinary CaO-“FeO” system at 40 pct SiO₂: solid line—without Al₂O₃; and dashed line—with 8 pct Al₂O₃.

pseudoternary sections on the base of CaO-MgO-SiO₂ at 5 pct Al₂O₃ intervals, from 5 to 35 pct Al₂O₃. Similarly, their results showed that addition of Al₂O₃ to slag decreases the liquidus temperature in the olivine primary-phase field. It was observed that a new primary-phase spinel (MgAlO₄) appeared between the olivine and MgO primary-phase fields with a 15 pct addition of Al₂O₃. With a 25 pct Al₂O₃ addition, the olivine primary-phase field is completely replaced by the spinel primary-phase field. In the present investigation, the spinel (Fe_xAl_{3-x}O_{4+y}) phase was only found at the lower-silica region in samples containing more than 8.0 pct Al₂O₃ in the liquid phase (Table IV).

It has been found by Verney^[6] that the better smelting conditions (lower fuel consumption) can be obtained with a final slag composition of 40 wt pct SiO₂, 32 wt pct “FeO”, 20 wt pct CaO, and 8 wt pct Al₂O₃ (slag B) rather than with another slag composition of 42 wt pct SiO₂, 35 wt pct “FeO”, 15 wt pct CaO, and 8 wt pct Al₂O₃ (slag A). This fact can be explained by the results obtained in the present work. Figure 5 shows the effect of Al₂O₃ on the fayalite primary-phase field and liquidus temperatures at 40 pct SiO₂. The solid line represents the results from the CaO-“FeO”-SiO₂ system (Figure 2(a)). The dashed line is obtained from the Al₂O₃-CaO-“FeO”-SiO₂ system (Figures 2(b) through (d)) by extrapolation of the present results at 0 to 6 pct Al₂O₃ to 8 pct Al₂O₃. It can be seen from Figure 5 that two primary phase fields, fayalite and wollastonite, exist in the composition range investigated. With increasing CaO contents, the liquidus temperature decreases in the fayalite primary-phase

field and increases in the wollastonite primary-phase field. However, with an 8 pct addition of alumina, the fayalite primary-phase field extends so that the liquidus temperature continuously decreases with increasing CaO content up to 23 pct CaO. The addition of 8 pct Al₂O₃, therefore, results in the location of both slags A and B in the fayalite primary phase field, and the liquidus temperature of slag B (~1300 K) is lower than that of slag A (~1325 K). This lower liquidus temperature with an alumina addition explains the better smelting conditions (lower fuel consumption) observed by Verney^[6] for slag B rather than slag A.

IV. SUMMARY

Liquidus temperatures in the fayalite primary-phase field and boundary lines in the Al₂O₃-“FeO”-CaO-SiO₂ system at Al₂O₃ contents from 0 to 6 wt pct, in equilibrium with metallic iron, have been experimentally determined. It has been found that an Al₂O₃ addition expands the fayalite primary phase field toward lower iron oxide concentrations. The liquidus temperatures of the fayalite slags are decreased by approximately 3 K for each 1 wt pct of Al₂O₃ added.

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REFERENCES

1. A.K. Biswas and W.G. Davenport: *Extractive Metallurgy of Copper*, 3rd ed., Pergamon Press, New York, NY, 1994, pp. 74-98.
2. P.J. Mackey: *Can. Metall. Q.*, 1982, vol. 21, pp. 221-60.
3. D. Santander: *The Future of Copper Pyrometallurgy*, Proc. Symp. held during the First Latin American Congress of Mining and Extractive Metallurgy, Santiago, Chilean Institute of Mining Engineers, Chile, 1974, pp. 31-89.
4. J.M. Toguri, N.J. Themelis, and P.H. Jennings: *Can. Metall. Q.*, 1964, vol. 3, pp. 197-220.
5. R.W. Ruddle: *The Physical Chemistry of Copper Smelting*, Institution of Mining and Metallurgy, London, 1993, pp. 40.
6. L.R. Verney: *Trans. Inst. Min. Metall.*, 1960, vol. 69, pp. 211-36.
7. F.E. Lathe: *Trans. Can. Inst. Min. Metall.*, 1951, vol. 54, pp. 95-104.
8. L.R. Verney: *Trans. Inst. Min. Metall.*, 1969, vol. 78, pp. C28-C42.
9. C.R. Fountain, M.D. Coulter, and J.S. Edwards: *Copper 1991*, COBRE 91 Int. Symp. Proc., Pergamon Press, New York, NY, 1991, vol. IV, pp. 359-73.
10. C.R. Fountain, J.M.I. Tuppurainen, N.R. Whitworth, and J.K. Wright: *The Paul E. Queneau Int. Symp.*, TMS, Warrendale, PA, 1993, vol. II, pp. 1461-76.
11. N.L. Bowen, J.F. Schairer, and E. Posnjak: *Am. J. Sci.*, 1933, vol. 26, pp. 193-284.
12. W.C. Allen and R.B. Snow: *J. Am. Ceram. Soc.*, 1955, vol. 38, pp. 264-80.
13. A. Muan and E.F. Osborn: *Phase Equilibria among Oxides in Steelmaking*, Addison-Wesley Publishing Company, Reading, MA, 1965, pp. 54 and 113.
14. J.F. Schairer and K. Yagi: *Am. J. Sci.*, 1952, Bowen volume, part 2, pp. 471-512.
15. R.B. Snow and W.J. McCaughey: *J. Am. Ceram. Soc.*, 1942, vol. 25, pp. 151-60.
16. R. Hay, J. White, and T.H. Caulfield: *J. Soc. Glass Technol.*, 1937, vol. 21, pp. 270-80.
17. C. Henrich: *AIIME Trans.*, 1916, vol. 56, pp. 621-26.
18. J. Newton and C.L. Wilson: *Metall. Copper*, 1942, p. 126.
19. W.T. Lankford, N.L. Samways, R.F. Craven, and H.E. McGannon: *The Making, Shaping and Treating of Steel*, 10th ed., United States Steel, Pittsburgh, PA, 1985, p. 326.
20. J.F. Schairer: *J. Am. Ceram. Soc.*, 1942, vol. 25, pp. 241-74.

21. A. Muan and E.F. Osborn: *Yearbook Am. Iron Steel Inst.*, 1951, pp. 325-59.
22. E. Jak, N. Liu, and P.C. Hayes: *Metall. Trans. B*, 1998, vol. 29B, pp. 541-53.
23. E. Jak, H.G. Lee, and P.C. Hayes: *Kor. IMM J.*, 1995, vol. 1, pp. 1-8.
24. E. Jak, S. Degterov, B. Zhao, A.D. Pelton, and P.C. Hayes: *Proc. Zinc and Lead Processing Symp.*, Calgary, Canada, Can. Inst. Min. Met. and Petr., Montreal, Quebec, Canada, 1998, pp. 313-33.
25. E. Jak, B. Zhao, and P.C. Hayes: *Proc. 5th Int. Symp. on Metallurgical Slags and Fluxes*, ISS-AIME, Sydney, 1997, pp. 719-26.
26. E. Jak, N. Liu, H.G. Lee, and P.C. Hayes: *Proc. Lead & Zinc '95 Int. Symp.*, Sendai, Min. Mat. Inst. of Japan, Japan, 1995, pp. 747-51.
27. E. Jak, N. Liu, P. Wu, A.D. Pelton, H.G. Lee, and P.C. Hayes: *Proc. 6th AusIMM Extractive Metallurgy Conf.*, Brisbane, AusIMM, Parkville, Victoria, Australia, 1994, pp. 253-59.
28. E. Jak, N. Liu, H.G. Lee, and P.C. Hayes: *Proc. 6th AusIMM Extractive Metallurgy Conf.*, Brisbane, AusIMM, Parkville, Victoria, Australia, 1994, pp. 261-68.
29. E.F. Osborn, R.C. DeVries, K.H. Gee, and H.M. Kraner: *Trans. AIME*, 1954, vol. 200, pp. 33-45.