A Reinvestigation of Phase Equilibria in the System Al_2O_3-SiO_2-ZnO

ROBERT HANSSON, BAOJUN ZHAO, PETER C. HAYES, and EVGUENI JAK

The phase equilibria and liquidus temperatures in the binary SiO_2-ZnO system and in the ternary Al_2O_3-SiO_2-ZnO system at low Al_2O_3 concentrations have been experimentally determined using the equilibration and quenching technique followed by electron probe X-ray microanalysis. In the SiO_2-ZnO system, two binary eutectics involving the congruently melting willemite (Zn_2SiO_4) were found at 1448 ± 5 °C and 0.52 ± 0.01 mole fraction ZnO and at 1502 ± 5 °C and 0.71 ± 0.01 mole fraction ZnO, respectively. The two ternary eutectics involving willemite previously reported in the Al_2O_3-SiO_2-ZnO system were found to be at 1315 ± 5 °C and 1425 ± 25 °C, respectively. The compositions of the eutectics are 0.07, 0.52, and 0.41 and 0.05, 0.28, and 0.67 mole fraction Al_2O_3, SiO_2, and ZnO, respectively. The results of the present investigation are significantly different from the results of previous studies.

I. INTRODUCTION

SILICA-CONTAINING slags are formed during the pyrometallurgical processing of zinc and lead. The chemistry of both the complex sinters and slags formed in the different processes used can only be fully explained by high-order systems including several different elements. The development of thermodynamic computer models enables these complex predictions of phase equilibria in both lower- and higher-order systems to be carried out but requires precise information, especially on the lower-order systems. One of the several ternary systems relevant to the zinc/lead smelting using the Imperial smelting process (ISP) includes the Al_2O_3-SiO_2-ZnO system. Both the ZnO and SiO_2 are main components of the ISP sinters and slag, while Al_2O_3 is also present, but at lower concentrations (the main sources of Al_2O_3 are coke ash and, in some cases, fluxing). The previously available phase-equilibria data on the ternary Al_2O_3-SiO_2-ZnO system have been evaluated during optimization of a thermodynamic model using the FactSage[1] computer package. Possible discrepancies in previous data have been suggested, since no reasonable thermodynamic parameters could be found to describe previous experimental information. These discrepancies prompted the present experimental study.

The phase equilibria in the Al_2O_3-SiO_2 system have been extensively studied.[2–7] The only binary compound (mullite ($Al_6Si_2O_{13}$)) formed in the system has been suggested to melt both incongruently[2–5] and congruently.[6,7] An assessment performed by Eriksson and Pelton[8] of the Al_2O_3-SiO_2 system concludes that mullite melts congruently at 1890 °C, resulting in eutectics between both mullite and corundum (Al_2O_3) and mullite and cristobalite (SiO_2). Bunting[9] used a quenching technique and optical metallography to investigate phase equilibria in the binary SiO_2-ZnO system. A complete phase diagram including the liquidus temperatures was reported. Willemite (Zn_2SiO_4) was found to melt congruently at 1512 ± 3 °C, and the melting point of ZnO was found to be 1975 ± 25 °C.[9] Eutectics were reported between both tridymite (SiO_2) and willemite and between willemite and zincite (ZnO). A liquid miscibility gap forming above 1695 °C in the silica-rich part of the binary system[9] was also reported.

Solidus temperatures in the Al_2O_3-ZnO system were measured by Bunting.[10] The solidus data in the Al_2O_3-ZnO system were used to suggest that gahnite ($ZnAl_2O_4$) melts congruently, at temperatures close to 1950 °C. Hansson *et al.*[11] studied phase equilibria in the Al_2O_3-ZnO system at subsolidus conditions using a quenching technique followed by electron probe X-ray microanalysis. The solubility of Al_2O_3 in the spinel (gahnite) below 1500 °C was found to be low and increased dramatically at higher temperatures, approaching that of pure Al_2O_3. Hansson *et al.* used a combination of Bunting's solidus temperatures and the experimentally determined subsolidus data to construct a binary diagram suggesting that gahnite melts incongruently at temperatures close to 1950 °C. Bunting performed the only study on phase equilibria in the ternary Al_2O_3-SiO_2-ZnO system using a quenching technique and metallographic examination. The liquidus temperatures were investigated mainly at low Al_2O_3 concentrations. Mixtures of known compositions were prepared and equilibrated at given temperatures, quenched in water, and investigated microscopically for identification of phases. No ternary compounds were found, two ternary eutectics were located, and a phase diagram was reported.[10]

Attempts to thermodynamically model these systems indicated the need to confirm the results[10] of the aforementioned studies. The development of new analytical and experimental techniques enables accurate information on phase equilibria to be obtained. The reinvestigation of phase equilibria in the Al_2O_3-SiO_2-ZnO system at low Al_2O_3 concentrations using these new techniques is described in the present article.

II. EXPERIMENTAL

The experimental procedure used in this study for the sample preparation, equilibration, quenching, and examination

---

ROBERT HANSSON, formerly Research Scholar, PYROSEARCH, Pyrometallurgy Research Centre, The University of Queensland, is Laboratory Manager, ALcontrol AB, 581 10 Linkoping, Sweden. BAOJUN ZHAO, Research Fellow, PETER C. HAYES, Professor and Director, and EVGUENI JAK, Associate Professor and Research Director, are with PYROSEARCH, Pyrometallurgy Research Centre, School of Engineering, The University of Queensland, St Lucia, Queensland, 4072, Australia. Contact e-mail: e.jak@minmet.uq.edu.au

Manuscript submitted March 3, 2004.

of the samples is similar to that described by Jak *et al.*[12] Powders of the oxides Al_2O_3 and ZnO (99.5+ wt pct purity and <5 μm, produced by Aldrich Chemical Company, Inc.) and fused SiO_2 (99.5+ wt pct purity, produced by Aldrich Chemical Company, Inc.) were used as starting materials. The fused SiO_2 granules were ground to powder in an agate mortar prior to use. Pure powders were weighed and mixed thoroughly in an agate mortar. The mixture compositions selected were those that would result in the formation of one or two condensed phases at equilibrium with liquid. The mixtures were pelletized prior to equilibration, and the 0.2 g samples were placed in platinum crucibles at predetermined temperatures in air. The temperature was controlled to within ±1 °C. A working thermocouple calibrated against a standard thermocouple was positioned next to the sample in the furnace. The overall temperature accuracy was estimated to be ±5 °C. Following equilibration in air, the samples were directly quenched in water. The sample weight was recorded before and after the experiments using an analytical balance with an accuracy of ±0.1 mg. The samples were mounted and polished following the final quenching. The microstructures were examined in detail using optical and scanning electron microscopy coupled with energy-dispersive spectroscopy analysis. Phase compositions were determined using a JEOL* 8800L electron probe X-ray microanalyzer (EPMA) with wavelength-dispersive detectors. The instrument was operated at a 15 kV accelerating voltage with a probe current of 15 nA. Powders of Al_2O_3, SiO_2 (Charles M. Taylor Co., Stanford, CA) and ZnO (prepared "in-house" by sintering 99.9+ purity ZnO powder and verified against a willemite (Zn_2SiO_4) standard supplied by Micro-Analysis Consultants Ltd., Cambridge, United Kingdom) were used as standards for the EPMA measurements of aluminium, silicon, and zinc, respectively. The Duncumb–Philibert ZAF correction procedure supplied with the JEOL-8800L apparatus was applied. From analysis of the willemite standard, it was found that the concentration of SiO_2 was systematically overestimated by the standard ZAF correction procedure in the presence of ZnO. A secondary correction procedure was, therefore, applied. A symmetric parabolic function was chosen for the correction, with the maximum at a 1:1 mole ratio of SiO_2 and ZnO, respectively, and at zero at pure SiO_2 and ZnO. The magnitude of the correction was 0.02 mole fraction at its maximum. In the presence of Al_2O_3, the correction was applied only to the SiO_2 + ZnO fraction. The average accuracy of the EPMA measurements after the secondary correction is estimated to be within ±1 wt pct.

III. RESULTS AND DISCUSSION

A. *The Binary SiO_2-ZnO Phase Diagram*

The compositions of the phases obtained as a result of experiments in the binary SiO_2-ZnO system are given in Table I. The constructed binary-phase diagram is shown in Figure 1. Silica exists in two different polymorphs at the conditions studied. Tridymite is transformed to cristobalite at 1465 °C at 1 atm pressure.[1] Both forms of SiO_2 dissolve about 0.01 mole fraction of ZnO at all temperatures investigated. No significant solid solubility was observed in the willemite or the zincite phases.

The eutectic reaction between tridymite, willemite, and liquid was found to occur at 1448 ± 5 °C and at 0.52 ± 0.01 mole fraction ZnO. The intersection between the extrapolated SiO_2 and willemite liquidus was used for the estimation of the eutectic temperature and composition. No liquid was observed in a sample (experiment 26) equilibrated at 1442 °C with a bulk composition between the tridymite and the willemite. Samples with bulk compositions both in the tridymite (experiment 1) and the willemite (experiment 9) primary-phase fields equilibrated at 1450 °C were found to contain liquid. These experiments confirm both the temperature and the composition of the invariant point.

The eutectic temperature between willemite and zincite was found to be at 1502 ± 5 °C, and the composition at the invariant point was found to be 0.71 ± 0.01 mole fraction ZnO. A sample of a bulk composition in-between that of willemite and zincite (experiment 27) equilibrated at 1500 °C was found to be completely solid. A sample with a bulk composition in the zincite primary-phase field equilibrated at 1503 °C contained both zincite and liquid (experiment 17).

The melting temperature of the congruently melting willemite was previously reported to be 1512 ± 3 °C.[9] One sample on the SiO_2-rich side of willemite (experiment 28) and another on the ZnO-rich side of willemite (experiment 29) were equilibrated at 1509 °C and 1512 °C, respectively. After equilibration, they were found to be fully glassy following quenching. A sample in the willemite primary-phase field (experiment 16) equilibrated at 1510 °C contained both willemite and liquid. These experimental results support the previously reported melting temperature of willemite.[9]

The experimental results from the present study are compared to the binary SiO_2-ZnO phase diagram reported by Bunting[9] in Figure 1. The reported compositions of both eutectic reactions are significantly different in the present and previous study. Bunting reported the tridymite and willemite eutectic to be at 1432 °C and 0.491 mole fraction ZnO. This is 16 °C and 0.03 mole fraction ZnO lower than the values found in the present investigation. The willemite and zincite eutectic was previously reported to occur at 1507 °C and 0.775 mole fraction ZnO.[9] The temperature of this eutectic reaction agrees, within experimental errors, with the findings of the present study. The previously reported eutectic composition is 0.06 mole fraction richer in ZnO, a significantly higher ZnO concentration in comparison to the present findings. Bunting did not perform any postanalysis of the composition of samples following equilibration. Significant evaporation of ZnO was found to occur at elevated temperatures. All samples were weighed before and after equilibration in the present study. As much as approximately 20 wt pct losses from the total sample weight were recorded in samples in the ZnO primary-phase field at temperatures around 1550 °C. The weight loss increased with increasing ZnO concentration at each given temperature. Evaporation of ZnO did not affect the accuracy of the final results of the present study, since the compositions of phases were measured after the experiments. Evaporation of ZnO could account for uncertainties of the data reported by Bunting for the ZnO-rich part of the system. The difference in liquidus temperatures in the SiO_2 (tridymite and cristobalite) primary-phase fields between the previous[9] and the present study may be

---

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

Table I. Compositions of Phases Present in the Binary SiO_2-ZnO System

				EPMA		
Experiment	Temperature (°C)	Equilibrium Time (Min)	Phase(s)	Pretreatment (°C)	SiO_2 (Mole Fraction)	ZnO (Mole Fraction)
SiO_2 primary-phase field						
1	1450	300	L	1550	0.478	0.522
	1450	300	SiO_2	1550	0.987	0.013
2	1500	240	L	1550	0.493	0.507
	1500	240	SiO_2	1550	0.987	0.013
3	1500	95	L	—	0.499	0.501
	1500	95	SiO_2	—	0.989	0.011
4	1550	240	L	—	0.512	0.488
	1550	240	SiO_2	—	0.987	0.013
5	1550	110	L	—	0.514	0.486
	1550	110	SiO_2	—	0.986	0.014
6	1600	180	L	—	0.529	0.471
	1600	180	SiO_2	—	0.988	0.012
7	1600	75	L	—	0.541	0.459
	1600	75	SiO_2	—	0.989	0.011
8	1658	60	L	—	0.575	0.425
	1658	60	SiO_2	—	0.994	0.006
Willemite primary-phase field						
9	1450	30	L	1520	0.455	0.545
	1450	30	W	1520	0.333	0.667
10	1455	150	L	—	0.475	0.525
	1455	150	W	—	0.336	0.664
11	1461	95	L	—	0.481	0.519
	1461	95	W	—	0.336	0.664
12	1468	960	L	—	0.448	0.552
	1468	960	W	—	0.331	0.669
13	1477	60	L	—	0.439	0.561
	1477	60	W	—	0.334	0.666
14	1480	180	L	1400	0.438	0.562
	1480	180	W	1400	0.336	0.664
15	1500	300	L	—	0.390	0.610
	1500	300	W	—	0.331	0.669
16	1510	240	L	—	0.387	0.613
	1510	240	W	—	0.335	0.665
Zincite primary-phase field						
17	1503	330	L	—	0.291	0.709
	1503	330	Z	—	0.001	0.999
18	1505	1140	L	—	0.284	0.716
	1505	1140	Z	—	0.001	0.999
19	1506	60	L	—	0.281	0.719
	1506	60	Z	—	0.000	1.000
20	1515	1005	L	—	0.282	0.718
	1515	1005	Z	—	0.001	0.999
21	1519	1045	L	—	0.284	0.716
	1519	1045	Z	—	0.001	0.999
22	1527	125	L	—	0.279	0.721
	1527	125	Z	—	0.001	0.999
23	1550	120	L	—	0.279	0.721
	1550	120	Z	—	0.001	0.999
24	1557	90	L	1650	0.275	0.725
	1557	90	Z	1650	0.000	1.000
25	1613	60	L	1650	0.256	0.744
	1613	60	Z	1650	0.001	0.999
Subsolidus						
26	1442	105	SiO_2	—	0.983	0.017
	1442	105	W	—	0.343	0.657
27	1500	120	W	—	0.335	0.665
	1500	120	Z	—	0.001	0.999
Liquid						
28	1509	70	L	—	0.438	0.562
29	1512	75	L	—	0.312	0.688

L = Liquid, W = Willemite, and Z = Zincite.

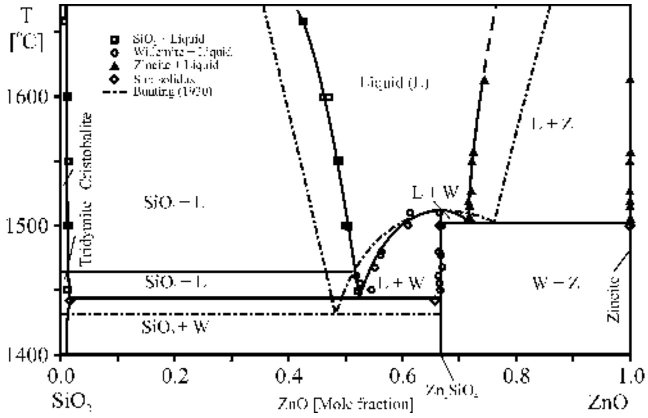

Fig. 1—The binary SiO_2-ZnO phase diagram; L = liquid, W = willemite, and Z = zincite.

a result of metastability. Precipitation of tridymite or cristobalite from the high-SiO_2 slag was found to be a very slow process. In the present study, experiments were deliberately performed starting from a high SiO_2 concentration in the bulk (0.80 mole fraction) to retain seeding SiO_2 crystals. This is not possible in the experimental technique used by Bunting. The compositions of phases in samples (following equilibration and quenching) were analyzed by EPMA in the present investigation. The EPMA enables the compositions of the liquid (glass) at various distances from the solid phase(s) to be measured, ensuring that liquid is homogeneous in composition. These measurements of the glass compositional profile confirmed the achievement of equilibria and the absence of crystallization during quenching. The advantages given by the present experimental technique are believed to make the present approach more reliable than the technique used previously.

IV. THE TERNARY SYSTEM Al_2O_3-SiO_2-ZnO

The compositions of the phases obtained as a result of experiments in the ternary Al_2O_3-SiO_2-ZnO system are given in Table II. The experimental data were used to construct the liquidus surface in the ternary-phase diagram shown in Figure 2. Solid lines in the diagram were drawn using experimental data obtained in the present investigation. Dashed lines were drawn using information from the binary Al_2O_3-SiO_2[8] and the Al_2O_3-ZnO[10,11] systems. The binary SiO_2-ZnO data were obtained in the present investigation. Some typical microstructures observed in the samples in the Al_2O_3-SiO_2-ZnO system are presented in Figure 3.

The binary compounds gahnite ($ZnAl_2O_4$), mullite ($Al_6Si_2O_{13}$), and willemite (Zn_2SiO_4) are formed in the ternary Al_2O_3-SiO_2-ZnO system. No ternary compounds have been observed. Two ternary eutectics in the composition triangles SiO_2-Zn_2SiO_4-$ZnAl_2O_4$ and ZnO-Zn_2SiO_4-$ZnAl_2O_4$, marked A and B, respectively, in Figure 2, were found in the present study.

The temperature and composition of the ternary eutectic A at 1315 ± 5 °C with a composition of 0.07, 0.52, and 0.41 mole fraction Al_2O_3, SiO_2, and ZnO, respectively, were determined from the intersection of the primary-phase boundaries between tridymite and gahnite and willemite and gahnite, shown in Figures 2 and 4, respectively. A sample prepared with a composition similar to the eutectic composition and equilibrated at 1310 °C for 6 hours did not contain any noticeable amounts of liquid after quenching. Another sample of the same composition equilibrated at 1320 °C for 3 hours contained liquid following quenching. This confirms the eutectic temperature.

A sample with a bulk composition in the zincite primary-phase field equilibrated at 1400 °C for 6 hours contained the crystalline phases gahnite, willemite, and zincite in equilibrium. Samples with bulk compositions in the zincite and the gahnite primary-phase fields equilibrated at 1450 °C were found to contain liquid after quenching. The temperature of the ternary eutectic B was, therefore, estimated to be 1425 ± 25 °C at the compositions of 0.05, 0.28, and 0.67 mole fraction Al_2O_3, SiO_2, and ZnO, respectively, determined by extrapolation of the gahnite and zincite boundary to 1425 °C.

A small solubility of ZnO was observed in both the tridymite and cristobalite SiO_2 polymorphs. Gahnite was found to become nonstoichiometric, containing additional Al_2O_3 with increasing temperature, as reported previously.[11] Both zincite (ZnO) and willemite have insignificant solubilities of Al_2O_3 and SiO_2.

Details of the liquids surrounding the eutectics A and B in Figure 2 are shown in Figures 5 and 6, respectively. Experimentally determined liquidus compositions are given in Figures 5 and 6 using squares and circles for bivariant and univariant conditions, respectively. The figures illustrate that many of the univariant liquidus determinations have been performed in several replicates starting from different bulk compositions and equilibrated for different times at each temperature. Equilibrium is achieved since the compositions of the replicates are the same within experimental errors. Determined isotherms and primary-phase boundaries are given using solid lines, and the previously reported data by Bunting[10] are given using the dotted lines in Figures 5 and 6.

The position of the ternary eutectic A found in the present study confirms the previous findings by Bunting[10] within experimental errors (Figure 5). However, the presently estimated temperature for the invariant reaction is 10 °C higher than that reported by Bunting. The position of the boundary between the gahnite and tridymite primary-phase fields shows a reasonable agreement. The positions of the boundaries between the willemite and tridymite primary-phase fields and between the gahnite and willemite primary-phase fields are significantly different. The present and previously reported compositions of the liquids along the 1400 °C liquidus isotherm in the willemite primary-phase field agree within experimental error. Both the location and direction of the liquidus isotherms in the tridymite and cristobalite primary-phase fields and the gahnite primary-phase field are significantly different between the present study and previous one by Bunting. The diagram proposed by Bunting results in a much wider composition range of the liquid above the eutectic A at given temperatures than is the case in the present study.

The eutectic B was previously reported[10] to exist at 1440 ± 5 °C with a composition of 0.103, 0.185, and 0.713 mole fraction Al_2O_3, SiO_2, and ZnO, respectively (Figure 6). Whilst the eutectic temperature of 1425 °C obtained in the present study is close to the 1440 °C temperature determined

Table II. Liquidus Compositions in the Ternary System Al_2O_3-SiO_2-ZnO

Experiment	Temperature (°C)	Equilibrium Time (Min)	Phases	Premelting (°C)	Liquidus Compositions by EPMA		
					Al_2O_3	Mole Fraction SiO_2	ZnO
Bivariant equilibria							
SiO_2 (Cristobalite and Tridymite) primary-phase field							
30	1500	45	L + SiO_2	—	0.084	0.354	0.562
31	1400	120	L + SiO_2	—	0.093	0.578	0.329
32	1400	300	L + SiO_2	—	0.062	0.526	0.412
33	1450	120	L + SiO_2	—	0.061	0.515	0.423
34	1450	120	L + SiO_2	—	0.066	0.564	0.370
35	1450	65	L + SiO_2	—	0.088	0.603	0.310
36	1500	240	L + SiO_2	—	0.053	0.582	0.365
37	1500	240	L + SiO_2	—	0.085	0.668	0.247
38	1550	60	L + SiO_2	—	0.033	0.589	0.378
39	1550	65	L + SiO_2	—	0.053	0.659	0.288
Spinel primary-phase field							
40	1500	240	L + S	—	0.132	0.572	0.296
41	1400	300	L + S	—	0.094	0.508	0.397
42	1500	240	L + S	—	0.104	0.477	0.419
43	1500	180	L + S	—	0.089	0.411	0.500
44	1500	120	L + S	—	0.140	0.714	0.146
45	1550	120	L + S	—	0.197	0.599	0.204
Willemite primary-phase field							
46	1400	185	L + W	—	0.055	0.446	0.499
47	1450	120	L + W	—	0.033	0.404	0.562
Univariant equilibria							
48	1320	355	L + SiO_2 + W	—	0.061	0.516	0.423
49	1350	200	L + SiO_2 + W	—	0.061	0.515	0.423
50	1325	120	L + S + SiO_2	—	0.077	0.524	0.399
51	1350	115	L + S + SiO_2	—	0.086	0.541	0.373
52	1400	60	L + S + SiO_2	—	0.103	0.602	0.295
53	1400	300	L + S + SiO_2	—	0.096	0.604	0.300
54	1325	90	L + S + W	—	0.076	0.474	0.449
55	1375	70	L + S + W	—	0.075	0.442	0.483
56	1350	120	L + S + W	—	0.078	0.474	0.449
57	1350	120	L + S + W	—	0.077	0.470	0.453
58	1375	65	L + S + W	—	0.076	0.437	0.487
59	1375	60	L + S + W	—	0.076	0.432	0.491
60	1400	55	L + S + W	—	0.073	0.396	0.531
61	1415	60	L + S + W	—	0.070	0.379	0.551
62	1450	60	L + S + Z	1650	0.053	0.263	0.684
63	1450	60	L + S + Z	1650	0.054	0.262	0.684
64	1500	50	L + S + Z	1650	0.062	0.236	0.702
65	1500	60	L + S + Z	1650	0.062	0.235	0.703
66	1500	45	L + S + Z	1650	0.065	0.243	0.693
67	1550	60	L + S + Z	1650	0.077	0.207	0.717
68	1450	360	L + W + Z	—	0.026	0.265	0.708

L = Liquid, S = Spinel, SiO_2 = Cristobalite or Tridymite, W = Willemite, and Z = Zincite.

by Bunting,[10] the composition is significantly different from previous findings. A comparison of both measured and estimated liquidus isotherms from the present investigation with the previous diagram in the gahnite and zincite primary-phase fields shows that the composition ranges of the liquid above eutectic B at each temperature are significantly smaller in the present study. The gahnite, willemite, and zincite liquidus surfaces are all very steep close to the composition of the eutectic B, making the liquidus in the Al_2O_3-SiO_2-ZnO system strongly dependent on composition in this region.

The largest differences between the present and the previous[10] investigation on phase equilibria in the Al_2O_3-SiO_2-ZnO system were found at compositions close to the eutectic B, as shown in Figures 2 and 6. Since the eutectic B is located in the ZnO-rich region of the composition range, these differences most likely result from the ZnO evaporation. The evaporation of ZnO was not accounted for in the previous investigation,[10] but did not affect the accuracy of the present data, as discussed in the previous section. The smaller deviations encountered at compositions surrounding the eutectic A, as shown in Figures 2 and 5, could not be explained.

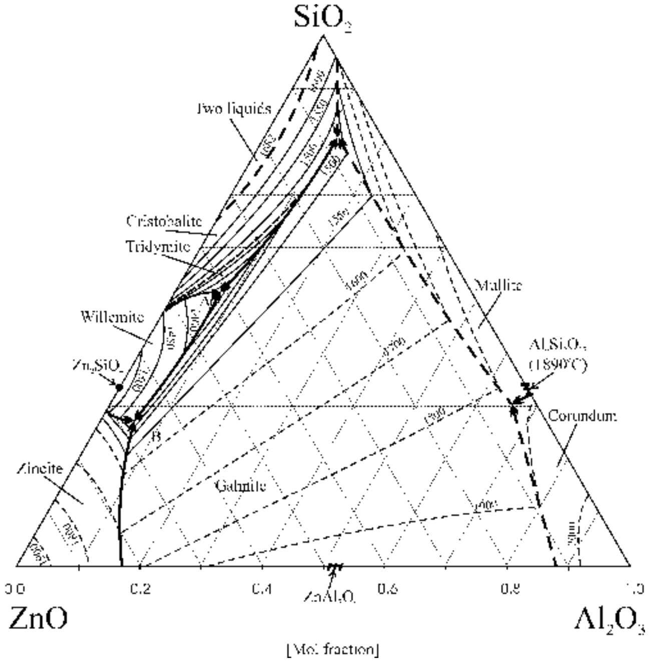

Fig. 2—The ternary Al_2O_3-SiO_2-ZnO phase diagram.

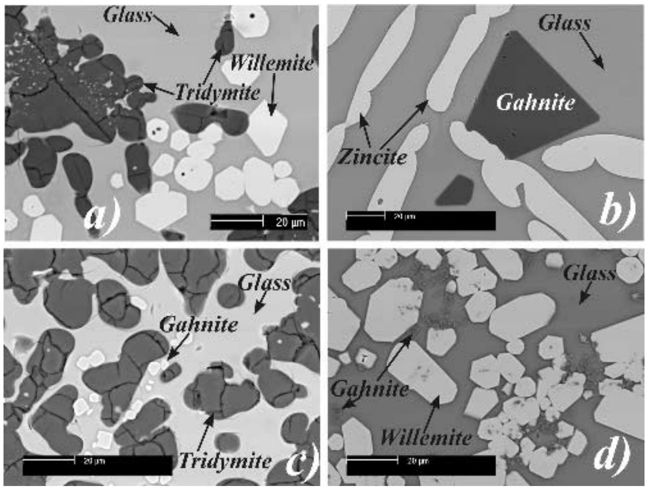

Fig. 3—Typical scanning electron microscopy microstructures observed in the Al_2O_3-SiO_2-ZnO system.

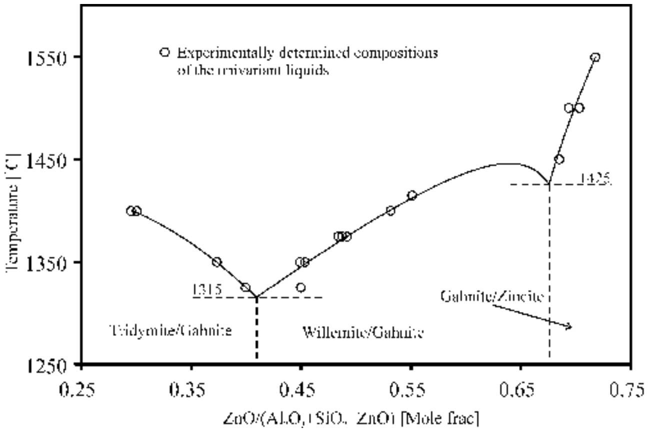

Fig. 4—The temperature dependence of univariant liquid compositions in the system Al_2O_3-SiO_2-ZnO.

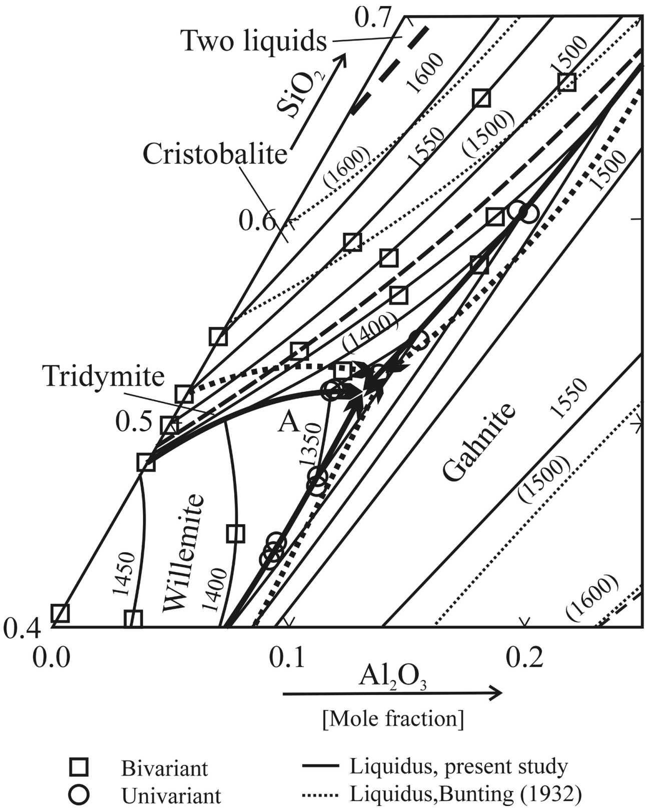

Fig. 5—An enlarged area of the liquidus in the ternary Al_2O_3-SiO_2-ZnO phase diagram (temperatures are in degrees Celsius).

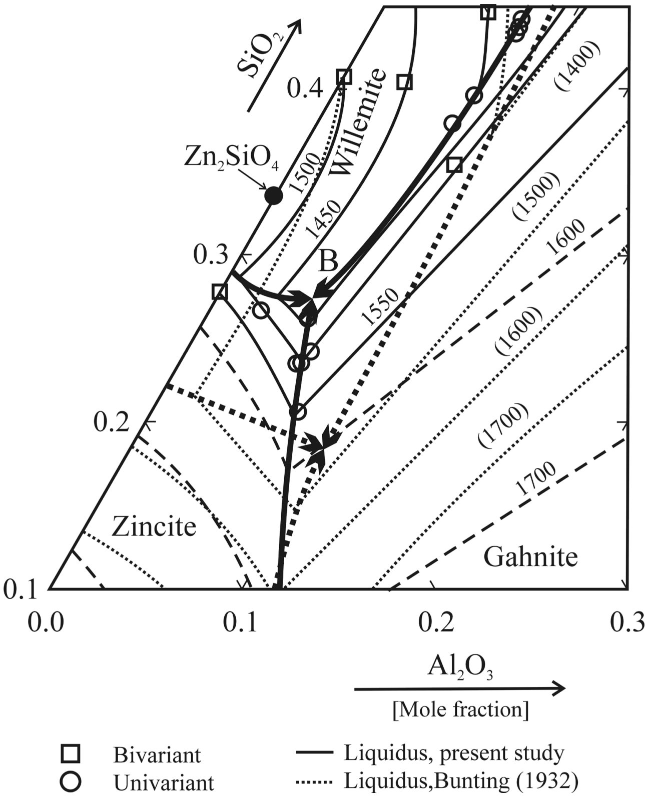

Fig. 6—An enlarged area of the liquidus in the ternary Al_2O_3-SiO_2-ZnO phase diagram (temperatures are in degrees Celsius).

V. CONCLUSIONS

The phase equilibria and liquidus of the binary SiO_2-ZnO system have been investigated, and significant differences from previously reported data were observed. The temperatures and compositions of the two eutectics between tridymite and willemite and between willemite and zincite with liquid were estimated to be 1448 ± 5 °C and 0.52 ± 0.01 mole fraction ZnO and 1502 ± 5 °C and 0.71 ± 0.01 mole fraction ZnO, respectively.

Two ternary eutectics, A and B, were found in the ternary system Al_2O_3-SiO_2-ZnO at 1315 ± 5 °C and 1425 ± 25 °C, respectively. The compositions of the eutectics A and B, respectively, are 0.07, 0.52, and 0.41 and 0.05, 0.28, and 0.67 mole fractions of Al_2O_3, SiO_2, and ZnO, respectively. The eutectic temperature A and the composition of eutectic B are significantly different from previously reported data.

ACKNOWLEDGMENTS

Mr. Stephen Bonner is gratefully acknowledged for his help with the experimental work as part of his undergraduate thesis. The authors thank the Australian Research Council for ongoing support for this research. We also thank ISP Smelting, Britannia Zinc Ltd., Portovesme SRC, MIM Huttenwerke Duisburg GmbH, Hachinohe Smelting Company Ltd., and Pasminco Smelter Technical Support for financial support of this project.

REFERENCES

1. C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R.B. Mahfoud, J. Melançon, A.D. Pelton, and S. Petersen: *CALPHAD*, 2002, vol. 26 (2), pp. 189-228.
2. N.L. Bowen and J.W. Greig: *J. Am. Ceram. Soc.*, 1924, vol. 7, pp. 238-54.
3. E.C. Shears and W.A. Archibald: *Iron and Steel, London*, 1954, vol. 27, pp. 26-30 and 61-66.
4. F.J. Klug, S. Prochazka, and R.H. Doremus: *J. Am. Ceram. Soc.*, 1987, vol. 70 (10), pp. 750-59.
5. J.W. Welch: *Nature*, 1960, vol. 186, pp. 546-47.
6. S. Aramaki and R. Roy: *J. Am. Ceram Soc.*, 1962, vol. 45, pp. 229-42.
7. N.A. Toropov and F.Y. Galakhov: *Dokl. Akad. Nauk SSSR*, 1951, vol. 78, pp. 299-302.
8. G. Eriksson and A.D. Pelton: *Metall. Trans. B*, 1993, vol. 24B, pp. 807-16.
9. E.N. Bunting: *Bur. Stand. J. Res.*, 1930, vol. 4, pp. 131-36.
10. E.N. Bunting: *Bur. Stand. J. Res.*, 1932, vol. 8 (2), pp. 279-87.
11. R. Hansson, P.C. Hayes, and E. Jak: *Metall. Mater. Trans. B*, 2004, vol. 35B, pp. 633-42.
12. E. Jak, P.C. Hayes, and H.G. Lee: *Kor. IMM J.*, 1995, vol. 1 (1), pp. 1-8.