Distribution of Boron Between Silicon and CaO-MgO-Al_2O_3-SiO_2 Slags

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Production of solar-grade silicon through metallurgical refining methods can be less expensive than current production methods both in terms of energy use and capital cost. Slag refining is a potential metallurgical refining method for removal of boron from silicon. The distribution of boron between silicon and binary CaO-SiO_2 and MgO-SiO_2 slags, and between silicon and ternary CaO-MgO-SiO_2 and CaO-Al_2O_3-SiO_2 slags has been investigated in this work at 1873 K (1600 °C). The distribution coefficient of boron has been found to be between 2 and 2.5 in the binary CaO-SiO_2 and MgO-SiO_2 systems. It has also been found to be in the same range across the entire CaO-MgO-SiO_2 system. In these systems the distribution coefficient is unaffected by slag composition. The distribution coefficient has been found to decrease with increasing Al_2O_3 content in the slag in the ternary CaO-Al_2O_3-SiO_2 system.

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I. INTRODUCTION

SOLAR cells are considered to be one of the most promising energy sources in the future. The Earth receives energy from the sun that is orders of magnitude higher than both current and projected future energy demand. Solar cells are, however, too expensive at present to compete with fossil fuels in most countries. Crystalline silicon solar cells dominate the solar cell market and have proven to maintain high efficiency for decades. More advanced solar cell technologies may become more competitive in the future but crystalline silicon solar cells are predicted to have significant share of the market for many years to come since it is a well-established technology and based on abundant raw materials.

Solar-grade silicon contributes significantly to the cost of the final solar module and this silicon is at present mainly produced through the Siemens process which is an expensive process both in terms of energy use and capital cost. Production of solar-grade silicon directly by use of metallurgical refining methods can reduce the cost and hence make energy from solar cells more attractive. It has, however, proven to be very challenging to bring the boron content in silicon to a sufficiently low level by these methods.

Slag refining has been proposed as a potential metallurgical refining method for removal of boron from silicon. A limited number of studies have been conducted on slag refining of silicon for boron removal and the literature data is widely scattered. The ability of a slag for boron removal is given by the distribution coefficient of boron:

$$L_B = \frac{w_{(B)}}{w_{[B]}}, \quad [1]$$

where $w_{(B)}$ is the mass fraction of boron in the slag and $w_{[B]}$ is the mass fraction of boron in silicon. The value of the distribution coefficient has in the binary CaO-SiO_2 system been found to be in the range from 0.5 to more than 5 in different works.[1–7] The literature values in the ternary CaO-MgO-SiO_2 and CaO-Al_2O_3-SiO_2 systems are also widely scattered.[3,8–11] The aim of this work has been to determine the distribution coefficient of boron for binary and ternary slags in the CaO-MgO-Al_2O_3-SiO_2 system at 1873 K (1600 °C). All compositions are given on mass basis in the text and tables while mole fractions are used in the figures.

II. EXPERIMENTAL

Master slags were made from oxides with a purity of at least 99 pct bought from commercial suppliers. The base oxides were: 99.9 pct SiO_2 (Aldrich), 99.9 pct CaO (Aldrich), ≥99 pct MgO (Sigma-Aldrich), and 99.5 pct Al_2O_3 (Alfa Aesar). Each master slag had a weight of approximately 300 g and was made by melting a mixture of the oxides in a graphite crucible by induction heating under argon atmosphere. They were quenched in a water-cooled copper mold remelted at least two more times to ensure homogeneous composition. The slags were crushed to a powder in a tungsten carbide disk mill between each melting and crushed to −0.25 mm after the final melting. Approximately 100 to 140 mg/kg boron was added as pure B_2O_3 (99.98 pct, Alfa Aesar) to the binary 50 pctCaO-50 pctSiO_2 and ternary MgO-A_2O_3-SiO_2 master slags after the first melting. The composition of all the master slags was measured by XRF to be at least 99.8 pct in total of CaO, MgO, Al_2O_3, and SiO_2. A content of approximately 0.1 pct Fe_2O_3 was also measured while the total content of

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Table I. Results for Different Holding Times with the Most Silica-Rich Master Slag in the Binary $CaO\text{-}SiO_2$ System

ID.	Time (h)	SiO_2 (pct)	CaO (pct)	B in Slag (mg/kg)	B in Si (mg/kg)
CS0	0	63.7	36.2	<3	118.2 ± 24.0[†]
CS1	0.6	63.2	36.3	21.2 ± 5.0	102.1 ± 2.0
CS2	3	62.3	37.4	74.4 ± 3.1	45.1 ± 3.1
CS3	6	60.3	39.4	81.5 ± 3.0	36.0 ± 3.7
CS4*	9	57.7	42.1	57.3 ± 8.1	26.8 ± 3.4
CS5**	6	62.1	37.7	98.8 ± 4.1	46.4 ± 3.6

CS0 is the initial slag composition and initial boron concentration in slag and silicon.
*Silicon from the batch given in MS0 in Table III.
**Pure silicon and a separately made boron-doped slag.
[†] Boron content in silicon based on two replicate splits.

other impurities was 0.1 pct or less. The composition of the master slags are given as the initial composition of CS0, CS10/CS11, MS0, CMS13/CMS14, CAS0, CAS6, and MAS0 in Tables I, II, III, IV, V, VI, and VII. Intermediate slag compositions were made by mixing of the master slags. Four batches of silicon doped with 90 to 120 mg/kg boron was made by adding boron (99.6 pct, Goodfellow) to pure silicon (≥99.999999 pct, REC). The boron-silicon mixtures were melted one time by induction heating in a graphite crucible under argon atmosphere and quenched in the same way as the master slags. The boron-doped silicon was then crushed in a tungsten carbide disk mill to a size fraction between 0.125 and 2.0 mm and cleaned by etching in hydrofluoric acid. The first silicon batch was used in the binary $CaO\text{-}SiO_2$ system, the second batch was used in the binary $MgO\text{-}SiO_2$, and ternary $CaO\text{-}MgO\text{-}SiO_2$ system, the third batch was used in the ternary $CaO\text{-}Al_2O_3\text{-}SiO_2$ system, and the fourth batch was used in the ternary $MgO\text{-}Al_2O_3\text{-}SiO_2$ system.

Graphite crucibles (outer diameter 40 mm, height 54 mm, and wall thickness 4 mm) were filled with 15 g of boron-doped silicon and 15 g of slag. The crucible was then inserted into a graphite resistance tube furnace and heated from room temperature to 1873 K (1600 °C) in approximately 15 minutes under 99.99 or 99.999 pct argon atmosphere. The furnace was evacuated to less than 3 mbar pressure and refilled with argon gas three times before heating was started. An argon gas flow of approximately 5 L/h was maintained throughout the experiment. The furnace was shut down after the targeted holding time and cooled down to the melting point of silicon within 2 minutes where the cooling followed a negative exponential trend. The temperature was 150 K (150 °C) below the melting point of silicon another 2 minutes later. Accurate control of temperature was achieved using a dual thermocouple placed just below the crucible where one was connected to the regulator and the other was connected to the temperature logger. The calibration of the temperature logger was checked against a calibrated temperature logger and no significant deviation was found (less than 0.3 K). B-type thermocouples (Pt-6 pctRh/Pt-30 pctRh) were used and they were calibrated against an UKAS calibrated B-type thermocouple and a deviation of 0.4 K (0.4 °C) was observed. A detailed drawing of the furnace is shown in Figure 1. Most of the experiments in the $MgO\text{-}SiO_2$ system were conducted under somewhat different conditions; 5 g of silicon and 5 g of slag were heated in a graphite crucible with lid using an alumina tube furnace. Other conditions were the same as in the other experiments.

III. ANALYSIS

The boron content in the slag and silicon samples was analyzed by ICP-MS. The instrument *Element 2* from Thermo Scientific was used for these analyses. A small amount of slag and silicon had to be sampled and dissolved

Table II. Equilibrium Experiments in the Binary $CaO\text{-}SiO_2$ System

	Before (pct)		After (pct)			
ID.	SiO_2	CaO	SiO_2	CaO	B in Slag (mg/kg)	B in Si (mg/kg)
CS6	59.1	40.7	53.8	45.9	82.4 ± 6.7	36.6 ± 7.7
CS7	54.6	45.2	48.6	51.1	82.7 ± 7.0	34.7 ± 4.9
CS8*	50.0	49.7	47.7	51.9	90.4 ± 1.9	36.9 ± 2.2
CS9			46.3	53.4	90.7 ± 5.3	38.9 ± 1.9
CS10*	45.5	54.2	44.3	55.3	85.6 ± 2.4	34.0 ± 3.6
CS11			43.1	56.6	90.0 ± 8.3	35.6 ± 0.7
CS12**[,†]	~65	~35	68.4	31.2	43.9 ± 1.3	21.5 ± 4.3
CS13**	45.5	54.2	42.6	56.8	128.3 ± 5.3	61.3 ± 17.8
FS5**	50.5	48.9	48.2	51.3	66.0 ± 3.0	25.7 ± 2.9

*3 h holding time.
**Boron-doped slag.
[†] Silica crucible and 18 h holding time.

Table III. Results in the Binary MgO-SiO_2 system

	Time (h)	SiO_2 (pct)	MgO (pct)	B in Slag (mg/kg)	B in Si (mg/kg)
MS0	0	65.5	33.9	69.7 ± 1.1	101.1 ± 10.7
MS1	1	65.3	34.0	67.3 ± 2.2	94.0 ± 9.5
MS2	2	64.1	35.2	74.3 ± 11.5	92.7 ± 11.1
MS3	3	63.8	35.4	79.6 ± 8.5	83.1 ± 3.1
MS4	6	62.7	36.6	110.5 ± 2.4	52.8 ± 0.8
MS5	9	58.6	40.6	125.2 ± 1.9	52.0 ± 1.5
MS6*	6	58.9	40.5	99.9 ± 4.3	51.8 ± 2.2
MS7*,**	6	60.4	38.6	47.6 ± 7.4	21.6 ± 2.7
MS8†	12	62.2	37.0	112.2 ± 17.1	53.4 ± 9.7

MS0 is the initial slag composition and the initial concentration of boron in slag and silicon.
*15 g silicon and 15 g slag.
**No lid and starting with pure silicon.
†Silicon coated crucible walls.

Table IV. Results in the Ternary CaO-MgO-SiO_2 System

	Before (pct)			After (pct)				
ID.	SiO_2	CaO	MgO	SiO_2	CaO	MgO	B in Slag (mg/kg)	B in Si (mg/kg)
CMS1	59.1	34.8	6.0	54.5	38.6	6.7	65.1 ± 1.6	30.0 ± 4.3
CMS2	54.5	33.5	11.8	49.6	37.0	13.2	72.8 ± 6.0	33.9 ± 3.0
CMS3	49.9	32.2	17.7	46.8	36.7	16.3	83.1 ± 6.5	36.8 ± 2.9
CMS4	45.3	36.7	17.7	45.1	41.0	13.6	82.6 ± 5.6	37.7 ± 2.7
CMS5	45.5	48.3	6.0	43.7	52.0	4.1	69.6 ± 3.2	29.2 ± 2.8
CMS6	60.5	13.8	25.5	53.9	16.8	29.1	90.3 ± 5.4	38.0 ± 5.2
CMS7	45.4	42.5	11.9	44.5	46.2	9.0	78.7 ± 1.0	32.5 ± 2.7
CMS8	55.5	27.3	17.0	49.8	32.0	18.0	80.9 ± 6.6	33.6 ± 1.9
CMS9	50.5	40.7	8.5	46.9	44.8	8.0	71.1 ± 2.5	28.6 ± 1.4
CMS10	50.3	23.2	26.2	47.6	25.8	26.4	104.7 ± 9.3	42.3 ± 3.2
CMS11	55.4	15.6	28.8	50.1	18.0	31.7	99.9 ± 6.8	43.6 ± 1.0
CMS12	60.4	8.0	31.3	52.7	9.3	37.7	110.6 ± 6.0	43.9 ± 3.9
CMS13	45.3	30.8	23.6	46.5	34.4	18.9	102.3 ± 4.5	44.2 ± 1.4
CMS14*				45.4	33.7	20.7	37.3 ± 2.4	16.0 ± 0.9
CMS15	64.1	27.2	8.5	57.8	32.6	9.4	67.0 ± 1.8	29.4 ± 1.8
CMS16*				61.8	28.3	9.6	14.1 ± 2.1	7.7 ± 1.1
CMS17	64.6	18.3	17.0	58.6	22.0	19.2	75.1 ± 3.2	33.6 ± 0.8
CMS18*				57.0	23.2	19.6	23.4 ± 1.3	9.8 ± 1.0
CMS19	65.0	9.3	25.4	58.9	11.3	29.6	94.1 ± 10.4	38.3 ± 1.8
CMS20*				61.3	10.0	28.4	40.6 ± 1.8	16.1 ± 4.0

*Starting with pure silicon.

before the ICP-MS analysis could be performed. The graphite crucible was at first completely removed by grinding before slag and silicon was manually separated. Any slag remaining on silicon and silicon remaining on slag was removed by grinding before both the slag and silicon pieces were cleaned. As much slag and silicon as possible was collected from the crucible. Sealed plastic bags and nitrile gloves were used after cleaning to avoid surface contamination. All slag and silicon excavated from the crucible were crushed separately in a tungsten carbide grinder to make a homogeneous powder. Silicon with 99.9999999 pct purity was crushed three times to clean the milling chamber before the silicon samples were crushed. The slag samples were crushed after the silicon samples and the milling chamber was cleaned with acetone between each crushing of both the silicon and slag samples.

Three samples of 20 to 45 mg of silicon were taken from the powder and dissolved using 0.5 mL 40 pct HF (Suprapur®, Merck) and 1.5 mL 68 pct HNO_3 (ultra-pure). High dissolution rates were observed when a fine powder of silicon was dissolved in this acid mixture, and therefore 0.5 mL deionized water was added to the acid solution to achieve a less vigorous dissolution and thereby reduce the maximum temperature of the solution due to the exothermic reaction. The powdered slag was also sampled in three replicate splits of 20 to 45 mg and dissolved in the same acid mixture, but no water was added. An additional treatment in an UltraCLAVE was necessary to completely dissolve the slag. The sample vial with acids and powdered slag was heated by microwaves at 513 K (240 °C) and a pressure of 100 bars for 10 minutes. The total treatment time including heating and cooling time was 2 hours. The dissolved slag and silicon samples were diluted to 220 or 250 mL before the ICP-MS analysis. The slag composition was determined by XRF on glass disks made with 0.5 g sampled slag and a

Table V. Results for Different Holding Times with a Selected CaO-Al_2O_3-SiO_2 Slag

ID.	Time (h)	SiO_2 (pct)	CaO (pct)	Al_2O_3 (pct)	B in Slag (mg/kg)	B in Si (mg/kg)
CAS0	0	24.4	35.5	39.9	7.3 ± 1.2	84.4 ± 7.3
CAS1	3	26.9	34.9	38.0	51.1 ± 3.3	44.3 ± 19.8
CAS2	5.8	26.6	35.1	38.2	52.4 ± 3.8	39.3 ± 3.0
CAS3	9	25.7	35.6	38.5	52.7 ± 1.9	38.2 ± 1.3

CAS0 is the initial slag composition and the initial boron concentration in slag and in silicon.

Table VI. Results in the ternary CaO-Al_2O_3-SiO_2 system

		Before (pct)			After (pct)				
ID.	Time (h)	SiO_2	CaO	Al_2O_3	SiO_2	CaO	Al_2O_3	B in Slag (mg/kg)	B in Si (mg/kg)
CAS4	6	39.5	50.4	9.8	39.9	50.6	9.4	68.9 ± 11.0	33.2 ± 5.7
CAS5	6	25.1	50.3	24.3	32.1	45.4	22.3	66.5 ± 3.9	39.0 ± 1.0
CAS6	6	10.7	50.1	38.9	21.7	42.4	35.7	56.2 ± 9.2	42.3 ± 7.2
CAS7	9	54.1	35.7	10.1	49.5	39.6	10.8	60.9 ± 8.6	31.2 ± 6.7
CAS8	9	38.8	35.7	25.4	37.2	37.8	24.9	59.4 ± 6.1	38.0 ± 8.4

Table VII. Results in the Ternary MgO-Al_2O_3-SiO_2 System

ID.	Time (h)	SiO_2 (pct)	MgO (pct)	Al_2O_3 (pct)	B in Slag (mg/kg)	B in Si (mg/kg)
MAS0	0	49.8	22.6	27.1	139.4 ± 14.3	<1
MAS1	3	49.4	22.6	27.4	94.7 ± 4.4	41.9 ± 10.5
MAS2	6	48.5	23.0	28.1	85.9 ± 15.9	44.9 ± 10.3
MAS3	9	47.7	23.3	28.7	88.9 ± 8.5	47.7 ± 14.5
MAS4*	6	—	—	—	108.8 ± 6.3	60.1 ± 7.0

MAS0 is the initial slag composition and the initial boron content in slag and silicon.
*Boron-doped silicon.

9.5 g mixture of 50 pct sodium metaborate and 50 pct sodium tetraborate. The XRF instrument was calibrated against certified reference materials for the whole range of compositions in this work.

IV. RESULTS

The results for each slag system are given separately starting with the binary CaO-SiO_2 system. An initial series of experiments were conducted to determine the equilibrium time for each slag system. The slag compositions given in the tables are normalized to the total content of oxides. About 0.1 pct is Fe_2O_3 and less than 0.1 pct is other impurities while the rest is different amounts of CaO, MgO, Al_2O_3, and SiO_2. The uncertainty of the measured boron concentration is given in the figures and tables as 95 pct confidence intervals based on the standard deviation of the three replicate splits.

A. *The Binary CaO-SiO_2 System*

The most silica-rich master slag was chosen for determination of equilibrium time in the binary CaO-SiO_2 slag system because the equilibrium time was expected to be the longest for this system. The viscosity is known to increase with increasing silica content in the slag[12] and diffusivity is known to be inversely proportional to viscosity. Hence mass transfer should be slower the more viscous the slag is. The results from these experiments are shown in Figure 2 and Table I.

The silicon content was measured simultaneously with the boron content by ICP-MS and found to be between 90 and 100 pct in most of the analyses. An accurate measurement of the silicon content is not expected since silicon is the sample matrix. However, the first replicate split of CS0 had a measured silicon content of 73 pct which is considerably lower than expected. The boron content in this replicate split was measured to be 96.1 mg/kg, which is considerably lower than the measured boron content of 120.1 and 116.3 mg/kg in the two other replicate splits. The lower measurement values for the first replicate split indicated a possible error during the sample preparation, and the first replicate spilt was therefore disregarded.

It is seen in Figure 2 that the system reaches equilibrium within 6 hours. One experiment was conducted with boron oxide-doped slag and pure silicon to approach equilibrium by mass transfer in the opposite

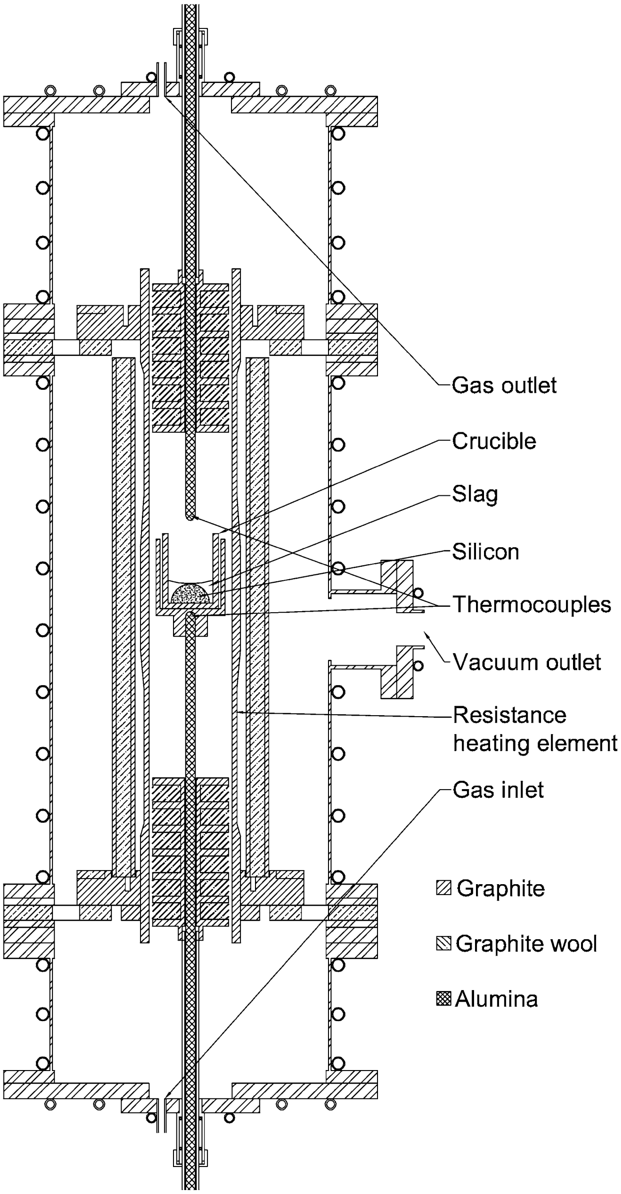

Fig. 1—Drawing of furnace where the bottom thermocouple was used for measurement of temperature throughout the experiments. A second thermocouple could be inserted from the top and used for calibration.

direction and this experiment verifies the equilibrium time of 6 hours. Most of the equilibrium experiments were thus performed with a holding time of 6 hours based on these results. The recovery of boron relative to the total initial boron content in slag and silicon is also indicated in Figure 2 and is seen to be close to 100 pct for most experiments. Some SiO_2 is lost from the slag in reaction with carbon from the crucible. A mass loss that increased approximately linearly with time was observed where the mass loss was measured by weighing the graphite crucible before and after the experiments. The reaction

$$SiO_2 + C = CO(g) + SiO(g) \qquad [2]$$

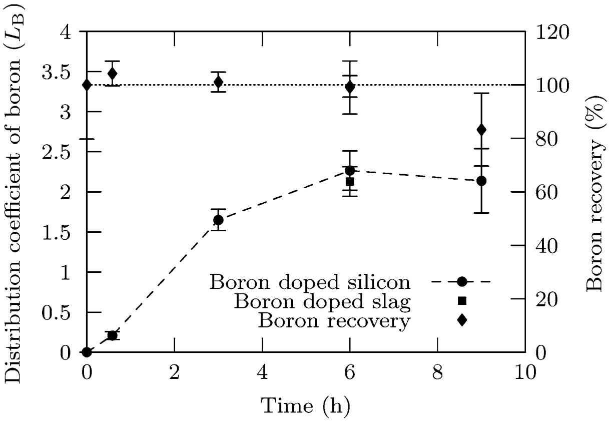

Fig. 2—Distribution coefficient of boron as a function of time for a 38 pctCaO-62 pctSiO_2 slag. Recovery of boron as compared to the total initial content in silicon and slag is shown on the secondary axis.

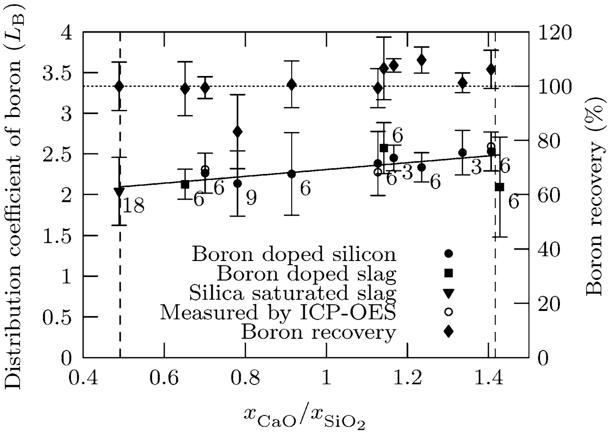

Fig. 3—Distribution coefficient of boron as a function slag composition in the binary CaO-SiO_2 system. Holding time is shown beside the data points. Recovery of boron relative to the total initial content in silicon and slag is shown on the secondary axis. The liquidus lines at 1873 K (1600 °C) according to Jung *et al.*[13] are indicated as dashed vertical lines.

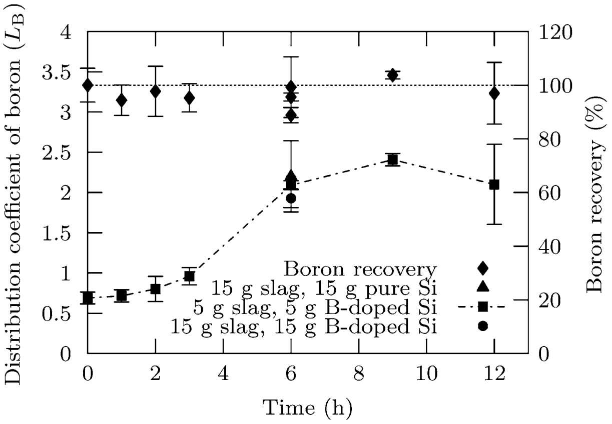

Fig. 4—Distribution coefficient of boron as a function of time in the binary MgO-SiO_2 system. Recovery of boron relative to the total initial content in silicon and slag is shown on the secondary axis.

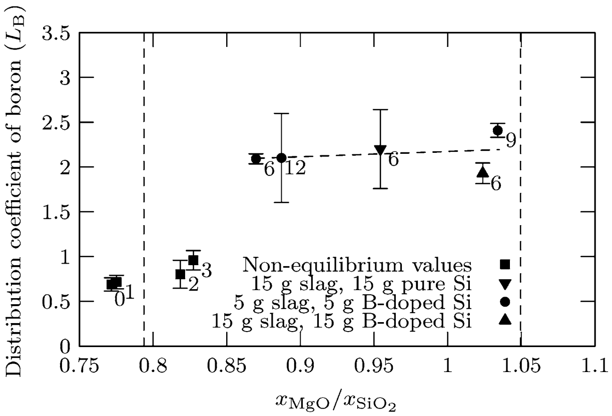

Fig. 5—Distribution coefficient of boron in the MgO-SiO_2 system as a function of slag composition. Holding time is shown beside the data points and the liquidus lines at 1873 K (1600 °C) according to Wu *et al.*[14] are shown as vertical dashed lines.

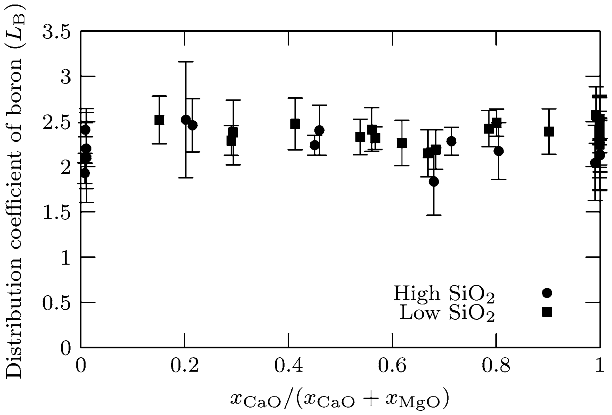

Fig. 6—Distribution coefficient of boron as a function of mole fraction of CaO relative to the sum of mole fractions of CaO and MgO.

was the main cause of this mass loss. The slag composition after 6 hours was hence measured to be somewhat different from the initial composition. A loss of SiO_2 was measured in all investigated slag systems. All compositions in this work are therefore given as measured by XRF after the experiments.

The results from the equilibrium experiments in the binary CaO-SiO_2 system are shown in Figure 3 and Table II. Also the experiments with 6 and 9 hours holding time from the initial series above are included in the figure. The distribution coefficient of boron is seen to be between 2 and 2.5 across the entire liquid region of the binary CaO-SiO_2 system at 1873 K (1600 °C). A small but not significant increase of the distribution coefficient is seen with increasing CaO content in the slag. Two experiments were performed in the CaO-rich part of the system with a holding time of 3 hours and equilibrium was reached within that time as can be seen in Figure 3. A shorter equilibrium time than 6 hours for these slags is expected since CaO-rich slags are less viscous than SiO_2-rich slags causing a faster mass transfer. One experiment was performed in a SiO_2 crucible and hence the slag was saturated with SiO_2. It was therefore more viscous than the most SiO_2-rich master slag and an 18 hours holding time was used in this experiment to ensure equilibrium between slag and silicon with respect to boron. A boron-doped slag and pure silicon was used in this experiment. The distribution coefficient of boron from this experiment is shown in Figure 3 and is seen to fit with the trend found for the experiments performed in graphite crucibles. Four experiments altogether were performed in the binary CaO-SiO_2 slag system with boron oxide doped slag and pure silicon. The recovery of boron was determined in the same way as already described in the initial series above and is seen in Figure 3 to be close to 100 pct for most experiments.

The most CaO-rich slag is seen to be slightly outside the liquid region given by Jung *et al.*[13] The slag in this experiment may therefore have been partially solid Ca_2SiO_4 before the experiment was finished. The solid Ca_2SiO_4 may not incorporate boron and therefore give a lower apparent distribution coefficient of boron than for a slag that is entirely liquid. This experiment is therefore not evaluated in the discussion of the results.

Silicon and slag from the samples labeled CS0, CS3, CS7, and CS11 in Tables I and II was also analyzed at an external laboratory by ICP-OES. The boron content in slag was measured to 1.1 mg/kg for CS0, 67 mg/kg for CS3, 66 mg/kg for CS7, and 70 mg/kg for CS11. In silicon the boron content was measured to 83 mg/kg for CS0, 29 mg/kg for CS3, 29 mg/kg for CS7, and 27 mg/kg for CS11. The distribution coefficient of boron calculated from these samples are shown in Figure 3 and they are seen to be in close agreement with the values measured using ICP-MS. The total boron content in slag and silicon found by ICP-OES is significantly lower than the total boron content found by ICP-MS. This may indicate a bias in the boron content as measured by one or both of the instruments. Such a bias will however not affect the measured distribution coefficient of boron provided that the bias is the same for both the slag and silicon samples. The close agreement of the measured distribution coefficient of boron with the two different instruments indicates that this probably have been the case.

B. *The Binary MgO-SiO_2 System*

The binary MgO-SiO_2 system was investigated with different holding times up to 12 hours where most experiments were carried out with a lid on the crucible to decrease mass loss. Most of the experiments in this binary system also differed from experiments in other slag systems in terms of mass and type of furnace; they were performed with 5 g of slag and 5 g of silicon in an alumina tube furnace. The boron-doped silicon was in these experiments premelted in the graphite crucible and cooled to room temperature before slag was added. In the 12 hours experiment the inner wall of the crucible was observed to be wetted with silicon after premelting boron-doped silicon. This layer of silicon was observed to still be present after the experiment and mass loss was lower than after the experiments with 6 and 9 hours holding time. The silicon-covered crucible wall is there-

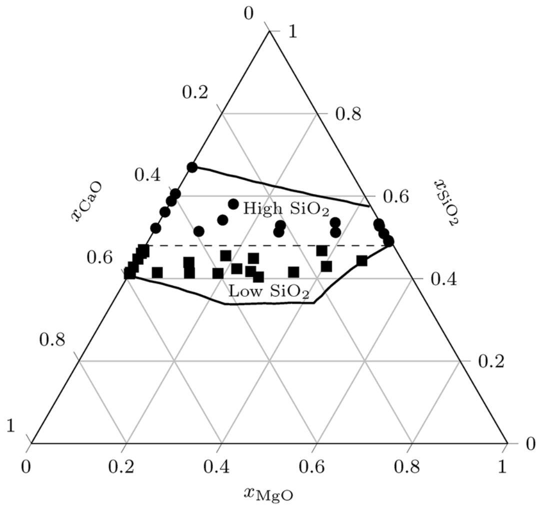

Fig. 7—Slag compositions as measured after experiments in the CaO-MgO-SiO_2 system.

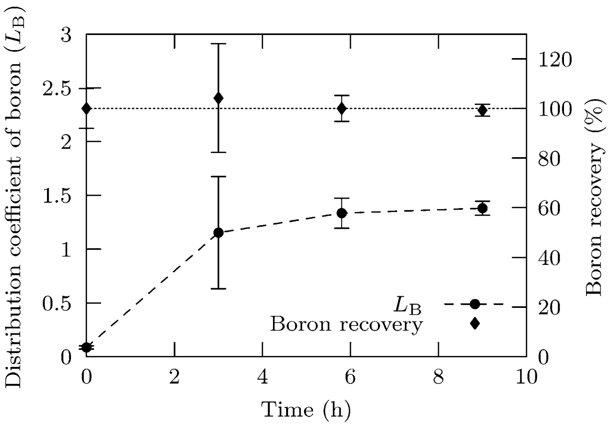

Fig. 8—Distribution coefficient of boron as a function of time in the ternary 35.7 pctCaO-40 pctAl_2O_3-24.3 pctSiO_2 system. Recovery of boron relative to the total initial content in silicon and slag is shown on the secondary axis.

fore believed to have prevented reaction between carbon and SiO_2 in the slag.

Equilibrium was found to be reached within 6 hours in the binary MgO-SiO_2 system as can be seen in Figure 4. The results in this system are also given in Table III. It is seen that almost no transfer of boron had occurred after 3 hours. This was probably caused by the slag composition being slightly outside the liquid region in the MgO-SiO_2 system as can be seen in Figure 5. Loss of SiO_2 with time did, however, bring the slag composition inside the liquid region for holding times of 2 hours and longer. Some MgO was also lost from the slag according to the mass balance, but at a much lower rate than SiO_2. Also in this system one experiment was conducted with pure silicon to approach equilibrium by mass transfer in the opposite direction. Doping of the slag with boron oxide was not necessary since the slag initially contained boron oxide. This experiment was performed with 15 g slag and 15 g silicon and a holding time of 6 hours in the above described graphite tube furnace and it confirmed an equilibrium time of 6 hours. The 12 hours experiment and another experiment with 15 g boron-doped silicon and 15 g slag was also performed in the graphite tube furnace while the other experiments in the binary MgO-SiO_2 system were performed in the alumina tube furnace. The distribution coefficient of boron is seen to have a value between 2 and 2.5 also in this system. The recovery of boron was also in this system found to be close to 100 pct for most experiments.

C. *The Ternary CaO-MgO-SiO_2 System*

The viscosity is unchanged when CaO is replaced with MgO (on equal mass basis) in the ternary CaO-MgO-SiO_2 system.[12] The rate of mass transfer in the ternary CaO-MgO-SiO_2 system was therefore considered to be similar as in the binary CaO-SiO_2 and MgO-SiO_2 systems. An equilibrium time of 6 hours was therefore deemed to be sufficient for this system and all 20 experiments were performed with this holding time. The three most viscous ternary slags were performed by equilibration with mass transfer of boron in both directions to assure that equilibrium was reached. In addition the slag with the lowest SiO_2 content (in mole basis) was equilibrated in both directions. Equilibrium was in these experiments confirmed to be reached in 6 hours.

All results in the ternary CaO-MgO-SiO_2 system are shown in Figure 6 and Table IV. The separation between high and low SiO_2 containing slags can be seen in Figure 7. The distribution coefficient of boron is seen to be the approximately same across the entire system with most values in the range between 2 and 2.5. Replacing CaO with MgO is seen to have no influence on the distribution coefficient of boron. The SiO_2 content was not found to influence the distribution coefficient significantly either as can be seen by the similar values of the distribution coefficient of boron with high and low SiO_2 content, respectively.

D. *The Ternary CaO-Al_2O_3-SiO_2 System*

Six different slag compositions were investigated in the ternary CaO-Al_2O_3-SiO_2 system. Three of the slags contained approximately 35 pct CaO and different levels of Al_2O_3 while the three other slags contained approximately 50 pct CaO and different levels of Al_2O_3. Experiments with holding times up to 9 hours were performed with the slag containing least CaO and most Al_2O_3. This slag system was chosen to see if the Al_2O_3 content influenced the equilibrium time. The equilibrium time for a slag with similar CaO content in the binary CaO-SiO_2 system has been determined above to be 6 hours. The viscosity is approximately the same with constant CaO content in the CaO-Al_2O_3-SiO_2 system[12] and a similar equilibrium time as in the binary CaO-SiO_2 system was therefore expected for the investigated ternary CaO-Al_2O_3-SiO_2 system. The results are shown in Table V.

Equilibrium was found to be reached within 3 to 6 hours as can be seen in Figure 8. The recovery of

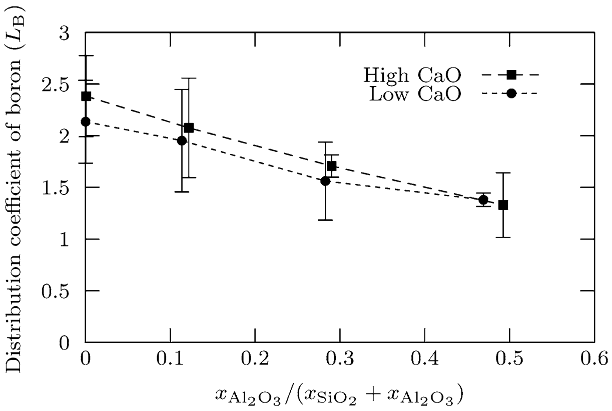

Fig. 9—Distribution coefficient of boron as a function of the mole fraction of Al_2O_3 relative to the sum of mole fractions of Al_2O_3 and SiO_2.

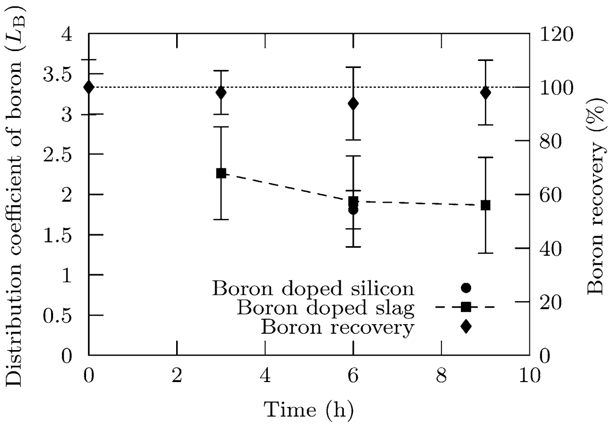

Fig. 10—Distribution coefficient of boron as a function of time in the $MgO-Al_2O_3-SiO_2$ system. Recovery of boron relative to the total initial content of boron in slag and silicon is shown on the secondary axis.

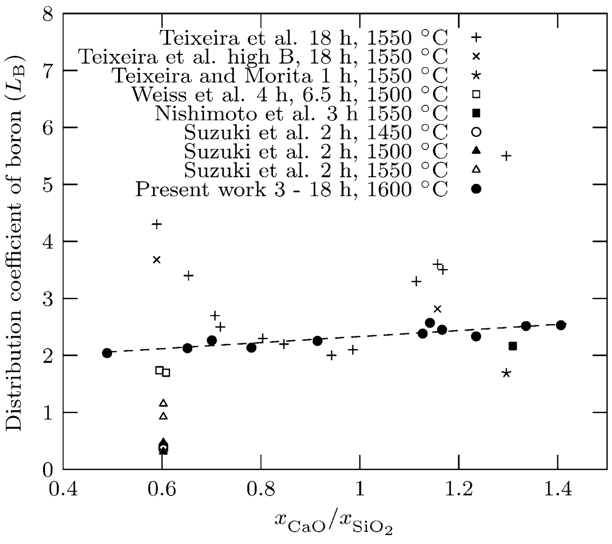

Fig. 11—Distribution coefficient of boron in the binary $CaO-SiO_2$ system as found in the present work compared with previous works.

boron in this system is seen to be 100 pct for all three holding times. The SiO_2 content in the slag was found to increase after the three first hours of holding time. This was caused by a significant amount of calcium and aluminium being reduced into the molten silicon. The concentration of calcium and aluminium in silicon after 3 hours was measured to be 0.8 and 1.2 pct, respectively. From 3 hours holding time the SiO_2 content in the slag is seen Table V to decrease in the same way as in the other slag systems. An equilibrium time of 9 hours was chosen to be sure that equilibrium was reached for the slags with approximately 35 pct CaO while an equilibrium time of 6 hours was chosen for the slags containing approximately 50 pct CaO.

The distribution coefficient of boron was found to decrease with increasing Al_2O_3 content in the slag as can be seen in Figure 9 and Table VI. The CaO content in the slag was not found to influence the distribution coefficient of boron significantly in this system either as can be seen by the small difference between slags with high and low CaO content, respectively.

One ternary $MgO-Al_2O_3-SiO_2$ slag was also investigated with holding times up to 9 hours where the slag initially contained approximately 140 mg/kg boron. The investigation of this system was performed by a master student under the supervision of the present authors.[15] The results are shown in Table VII and Figure 10. Pure silicon was used and equilibrium is seen to be reached within 6 hours. This equilibrium time was confirmed by one experiment with a holding time of 6 hours where equilibrium was approached by mass transfer in the opposite direction by use of boron-doped silicon. This is on the low side of the values found in the ternary $CaO-MgO-SiO_2$ system indicating that Al_2O_3 also decrease the distribution coefficient when added to a binary $MgO-SiO_2$ slag.

V. DISCUSSION

The recovery of boron is seen to be close to 100 pct for most experiments indicating that boron remains in the slag-silicon system. A complete recovery of boron also indicates that the sampling and analytical procedure works well for determination of boron in all slag systems. Each slag system is compared with previous works below.

A. *The Binary $CaO-SiO_2$ System*

The distribution coefficient of boron in the binary $CaO-SiO_2$ system is compared with previous works in Figure 11. Teixeira *et al.*[1] investigated the whole liquid region of this system at 1823 K (1550 °C). A good agreement with the present work is seen in the mid-range of this slag system. Teixeira *et al.* found higher values of the distribution coefficient of boron for slags with a high CaO content and slags with a high SiO_2 content. The work by Teixeira *et al.* was conducted for 18 hours in graphite crucibles under argon atmosphere. Temperature may have some influence on the distribution coefficient, but a change in the trend from quadratic to linear with just a 50 K (50 °C) change in temperature is not expected. Teixeira *et al.* also investigated the concentration dependence of the distribution coefficient of boron up to 0.08 pct in silicon and 0.8 pct B_2O_3 in slag and found it to behave as a Henrian solute in this range.

Teixeira and Morita[2] investigated a slag with a CaO/SiO_2 mass ratio of 1.21 using a holding time of 1 hour. The other conditions were the same as in the work by Teixeira *et al.* discussed above. They found the distribution coefficient to be 1.69 which is somewhat lower than found in the present work. It is also significantly lower than found in their work for the same composition with a holding time of 18 hours which indicates that equilibrium has not been reached for a holding time of 1 hour.

The distribution coefficient of boron found in the present work is on the other hand higher than found in the work by Suzuki *et al.*[3] They used both argon atmosphere and argon mixed with 12.5 pct CO_2 but did not find the atmosphere to influence the distribution coefficient of boron. A holding time of 6 hours was found to be necessary to reach equilibrium for a similar slag composition at 1873 K (1600 °C) in the present work. Suzuki *et al.* used 10 g of slag and 10 g of silicon which is close to the 15 g of slag and silicon used in the present work. Hence, a holding time of 2 hours as used by Suzuki *et al.* for temperatures between 1723 K and 1823 K (1450 and 1550 °C) may not have been sufficiently long to reach equilibrium. Suzuki *et al.* used boron-doped silicon and equilibrium was hence approached by mass transfer of boron from silicon to slag, which will give a lower value of the distribution coefficient than the true value if equilibrium was not reached. The final slag composition was not determined and the initial composition was therefore used in Figure 11. They used graphite crucibles and the slag composition had probably changed somewhat toward a more CaO-rich slag due to the reaction between carbon and SiO_2.

Weiss and Schwerdtfeger[4] investigated one slag composition in the binary calcium silicate system at 1773 K (1500 °C) using a boron-doped slag. Equilibrium was hence approached by mass transfer in the opposite direction as when using boron-doped silicon. The experiments were conducted under argon atmosphere in silica crucibles. Silica saturation of the slag was hence attained throughout their experiments. The boron concentration in slag was 1.25 pct B_2O_3 while it was 0.23 pct elemental boron in silicon. This may be somewhat outside the Henrian solute range of boron in the system and the results are seen to be somewhat lower than found in the present work. They used holding times of 4 and 6.5 hours and found the distribution coefficient to be 1.74 and 1.70, respectively, which indicates that equilibrium were reached after 4 hours in their experiments.

Nishimoto *et al.*[5] also investigated one slag composition in the binary calcium silicate system at 1823 K (1550 °C) where the CaO/SiO_2 mass ratio was equal to 1.22. The experiments were conducted in graphite crucibles under argon atmosphere. They found the equilibrium time to be 2 hours and determined the distribution coefficient to be 2.16 which is in good agreement with the present work. The initial slag composition is used in Figure 11 since the final slag composition was not measured.

The distribution coefficient in the binary calcium silicate system has also been determined in some other works but the values have not been included since the systems are considered not to be in equilibrium. Luo *et al.*[6] did one experiment under argon atmosphere at 1773 K (1500 °C) with a CaO/SiO_2 mass ratio of 1.21 and found the distribution coefficient of boron to be 2.2. This value is in good agreement with the present work, but the final slag composition was not measured. The system was held at in a silica crucible and the slag composition has therefore changed toward silica saturation during their experiment. Ding *et al.*[7] published one value of the distribution coefficient of boron at 1823 K (1550 °C). The distribution coefficient was found to be 1.0 but the holding time was not stated and it is therefore not possible to evaluate if the system has reached equilibrium. The amount of silicon used for their experiments was not stated either and argon gas was bubbled through water before it entered the furnace. Moisture has previously been shown by Nordstrand and Tangstad[16] to remove boron from silicon. The system in the study by Ding *et al.* may therefore be a non-equilibrium system with a concentration gradient of boron in slag and silicon throughout the experiment.

A summary of the observations discussed above is that the present work is in good agreement with the work by Teixeira *et al.*[1] for slag compositions in the mid-range of the liquid region and Nishimoto *et al.*[5] for high CaO content in the slag. The values found by Weiss and Schwerdtfeger[4] is somewhat lower than found in the present work while the values found by Suzuki *et al.*[3] much lower than found both in the present work and found in the work by Weiss and Schwerdtfeger. The system may, however, as discussed above, not have reached equilibrium in the work by Suzuki *et al.* No obvious explanation has been found, even if there is a 50 K (50 °C) difference in temperature, for the discrepancy between the present work and the work by Teixeira *et al.* for high and low SiO_2 content in the slag.

B. *The Ternary CaO-MgO-SiO$_2$ System*

There are no previous works in the binary $MgO-SiO_2$ system. Two works have been conducted before the present work in the ternary $CaO-MgO-SiO_2$ system and they are compared with the present work in Figure 12. Also the values from the present work in the binary $CaO-SiO_2$ and $MgO-SiO_2$ systems have been included in the plot of the present work. The trend found in the present work is shown as a dashed line in Figure 12 and it is seen to be almost horizontal with a small but not significant increase of the distribution coefficient with decreasing SiO_2 content in the slag.

Suzuki *et al.*[3] determined the distribution coefficient of boron at 1723 K (1450 °C) under CO atmosphere using CaO-10 pctMgO-SiO_2 slags, and the values are seen to be lower than found in the present work. They

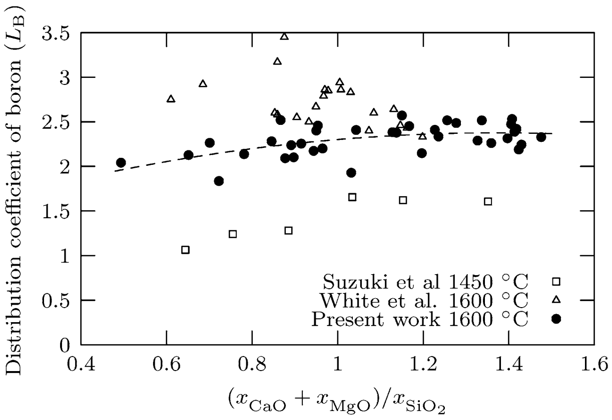

Fig. 12—Distribution coefficient of boron in the ternary CaO-MgO-SiO_2 system as found in the present work compared with previous works.

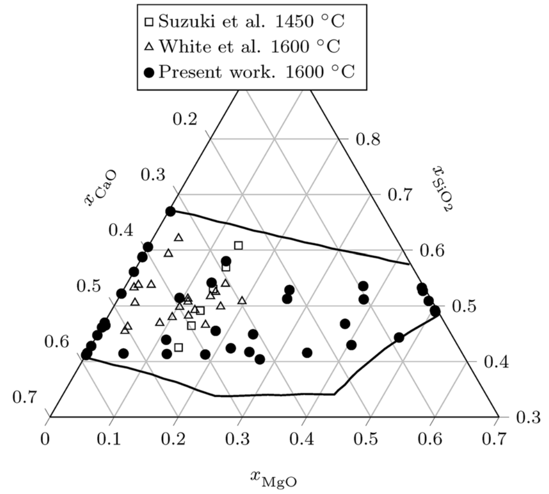

Fig. 13—Investigated slag compositions in the ternary CaO-MgO-SiO_2 system.

used a holding time of 2 hours, which is somewhat short considering that the equilibrium time in the binary CaO-SiO_2 system has been found to be between 2 and 6 hours at 1823 K to 1873 K (1550 °C to 1600 °C). The system may therefore not have reached equilibrium giving values lower than the equilibrium value in the same way as in the binary CaO-SiO_2 system. They also investigated the temperature dependence of the distribution coefficient for a 29 pctCaO-20 pctMgO-51 pct-SiO_2 slag and found the distribution coefficient to increase with temperature. This trend may, however, also be caused by the system not being in equilibrium. A higher temperature gives faster mass transfer possibly yielding values closer to equilibrium with increasing temperature.

White *et al.*[8] equilibrated CaO-MgO-SiO_2 slags with silicon under CO gas at atmospheric pressure. They used a holding time of 48 hours at 1873 K (1600 °C) and their results are seen to be in relatively close agreement with the present work. It is seen that White *et al.* obtained somewhat higher values than found in the present work for slags with a higher SiO_2 content. The MgO content in the slags investigated by White *et al.* ranged from 1.0 to 14.3 pct. The final slag composition in the present work and the work by White *et al.* is shown in Figure 13 together with the initial composition in the work by Suzuki *et al.* White *et al.* also investigated the influence of reduced partial pressure of CO where argon was used as a diluent. This caused the mean value of the distribution coefficient of boron to be lowered from 2.7 at atmospheric pressure of CO to 2.6 at a CO pressure of 0.6 atm balanced with 0.4 atm argon.

White *et al.* also investigated the influence of nitrogen atmosphere on the distribution coefficient of boron.[9] They used mixtures of nitrogen and CO gas under atmospheric pressure where the nitrogen content was varied between 0.1 and 0.4 atm. The distribution coefficient was found to increase under nitrogen atmosphere where the mean value of the distribution coefficient under 0.4 atm nitrogen gas was 3.1. They also investigated four calcium silicate slags with 0.3 to 0.5 pct MgO under 0.99 atm nitrogen gas and 0.01 atm CO. The distribution coefficient was found to be in the range from 1.8 to 2.2 which is much lower than any other values they found. The final composition of these slags was, however, outside the liquid region on the CaO-rich side of the slag system. The slag may therefore have been partially solid before the experiment was finished and the solid part would then have been dicalcium silicate. Such a boron-deficient solid would give a lower distribution coefficient of boron than in a completely liquid slag.

C. *The Ternary CaO-Al_2O_3-SiO_2 System*

Several studies have been conducted to determine the distribution of boron between silicon and ternary CaO-Al_2O_3-SiO_2 slags. Two of these works are compared with the present work in Figure 14. Fujiwara *et al.*[10] investigated the system using alumina crucibles at 1873 K (1600 °C) under argon atmosphere. Their work is seen to agree with the trend found in the present work where the distribution coefficient decreases with increasing Al_2O_3 content in the slag. The slag compositions in their work have been calculated here based on the assumption that the slag composition is fixed at the liquidus line as shown in Figure 15.

Johnston and Barati[11] investigated the system under argon atmosphere at 1773 K (1500 °C) and their results also agree with the trend found in the present work, even if the temperature is 100 K (100 °C) lower than in the present work. They used alumina crucibles and a holding time of 2 hours. An equilibrium time of 2 hours had been found using a 30 pctAl_2O_3-40 pctCaO-10 pctMgO-20 pctSiO_2 slag. More viscous slags may have longer equilibrium times. Their work has been divided into low and high CaO slags, respectively, where the compositions of slags are shown in Figure 15. The slags also contained 2.1 to 4.2 pct MgO and this is probably the reason why the final slag compositions are close to the liquidus line at 1873 K (1600 °C). The CaO

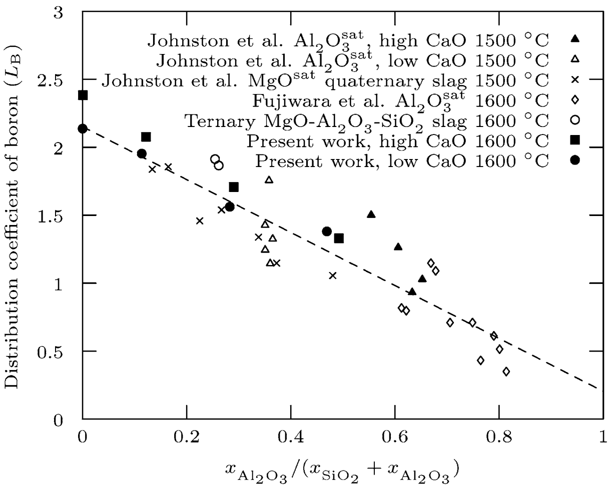

Fig. 14—Distribution coefficient of boron in the ternary $CaO-Al_2O_3-SiO_2$ system as found in the present work compared with previous works.

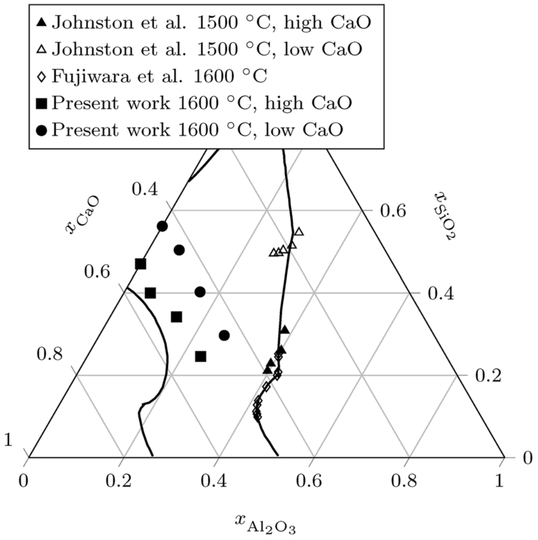

Fig. 15—Investigated slag compositions in the ternary $CaO-Al_2O_3-SiO_2$ system.

content in the slag is seen not to influence the distribution coefficient significantly which also has been found to be the case in the present work. Replacing CaO with MgO was in the present work found to not influence the distribution coefficient of boron significantly in the ternary $CaO-MgO-SiO_2$ system. A series with quaternary $CaO-MgO-Al_2O_3-SiO_2$ slags from the study by Johnston and Barati was also included in Figure 14 and it is seen to follow the same trend as the ternary $CaO-Al_2O_3-SiO_2$ slags. This series was conducted in magnesia crucibles using the same conditions as a described for the ternary $CaO-Al_2O_3-SiO_2$ system. This supports the finding that replacing CaO with MgO does not influence the distribution coefficient of boron.

Luo *et al.*[6] did also investigate the ternary $CaO-Al_2O_3-SiO_2$ system where they found the distribution coefficient to increase both with time and temperature. The values they found in these experiments were in the range from 4.8 to 6.5. The longest holding time they used was 2 hours and an increasing distribution coefficient with time indicates that their system had not reached equilibrium. Mass transfer rate increases with temperature and this may explain the increase of the distribution coefficient of boron with increasing temperature. They also did a series of experiments with fixed CaO/SiO_2 mass ratio and increasing Al_2O_3 content in the slag. They used silica crucibles and a holding time of 1 hour and found the distribution coefficient to increase with increasing Al_2O_3 content in the slag where the values were in the range between 4.5 and 9.3. This is opposite of the trends fond in the present and other previous works. The use of a silica crucible means that the silica content in the slag probably changed significantly toward silica saturation, but the final slag composition was not measured. It is therefore not possible to plot the results in terms of final slag composition and a plot in terms of initial composition could be somewhat misleading when comparing with other works. A holding time of 1 hour may be insufficient for the system to reach equilibrium considering that SiO_2-rich slags have been found in the present study to need up to 6 hours to reach equilibrium. The study was for these reasons not included in Figure 14.

A linear fit to all plotted data from the present and previous works is also shown in Figure 14 and extrapolates to a value close to zero when the SiO_2 content in the slag is zero. At this point the metal will no longer contain any silicon and the partial pressure of oxygen in the system is therefore too low to oxidize boron. It is therefore expected that the distribution coefficient should decrease to zero as the SiO_2 content in the slag decreases to zero. The distribution coefficient of boron in the $CaO-Al_2O_3-SiO_2$ system can therefore be expressed by

$$L_B = L_B^0 \frac{x_{SiO_2}}{x_{SiO_2} + x_{Al_2O_3}}, \qquad [3]$$

where L_B^0 is the distribution coefficient of boron for a slag not containing Al_2O_3. The quaternary $CaO-MgO-Al_2O_3-SiO_2$ slags in the study by Johnston and Barati are also seen to follow this trend. More data is needed to determine if a $MgO-Al_2O_3-SiO_2$ slag follows this trend.

VI. CONCLUSIONS

The distribution coefficient of boron is independent of slag composition in the binary $CaO-SiO_2$ and $MgO-SiO_2$ systems and the ternary $CaO-MgO-SiO_2$ system. The distribution coefficient has been found in the present work to be between 2 and 2.5 across the entire liquid region of these systems at 1873 K (1600 °C). The distribution coefficient decreases with increasing Al_2O_3 content in the ternary $CaO-Al_2O_3-SiO_2$ system. This decrease of the distribution coefficient of boron also agrees with previous works in the ternary $CaO-Al_2O_3$-

SiO_2 system and the quaternary CaO-MgO-Al_2O_3-SiO_2 system.

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