

# Experimental Study of Silicon Refining by Slag Treatment: Distribution of Boron and Phosphorus

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**Abstract.** Current production of metallurgical-grade Si relies on an energy-intensive process based on complex solid-liquid-gas reactions in an electric submerged arc furnace using graphite electrodes. This is followed by a slow Siemens process to grow ultra-high purity solar-grade silicon. Due to increasing decarbonization and environmental pressures that the metal industry is facing, new sustainable process technologies are required. This study is part of a broader investigation on pyrometallurgical electrorefining of silicon in the presence of slag and provides the basis for impurity behaviour in Si-slag system without an imposed electromotive force. For the first time, experimental technique of drop-quenching followed by direct phase analysis techniques of electron microprobe analyzer (EPMA) and laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) were employed in silicon processing environment. The experiments were carried out to define the distribution coefficients of minor elements (B, P) between Si and SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> at silica and alumina crucibles under inert Ar gas at 1500 °C. The results presented are highly novel and show the influence of slag composition and process conditions on the element properties. The experimental results were compared to the computational simulation results by FactSage© using its FToxid and FSupsi databases. The results can be utilized to design Si-slag process for primary ore resources and for secondary silicon-rich scraps in pyrometallurgical smelting environment, as well as to potentially improve the thermochemical databases of computational simulation programs.

## 1 Introduction

In metallurgical grade silicon (98 % purity), as the source for solar-grade silicon, boron and phosphorus concentrations are typically between 10-100 ppm [1–2] with the maximum accepted levels being 800 ppm B and 500 ppm P [3]. Their removal is inherently difficult, and they possess high segregation coefficients between solid and liquid silicon [2]. In general, boron behaviour in different Si-slag systems have been studied rather broadly [3–4], but only limitedly in Si – SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> system and with rather inconsistent results [4–10]. Phosphorus is less investigated element in Si-slag systems and most studies has adopted alloyed Si with fluoride/chloride containing slags, for example [10–14].

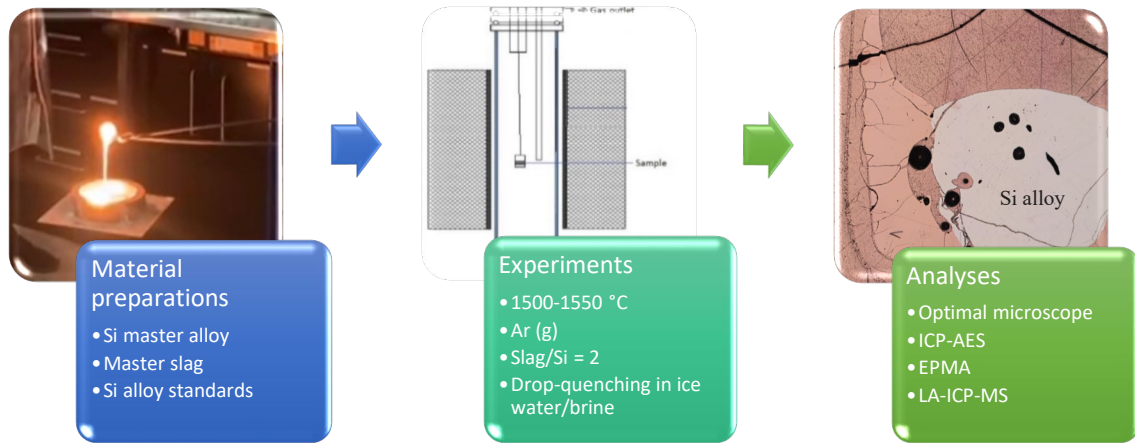
All the previous studies have been conducted with a more traditional technique where tens of grams of Si and slag have been melted, and then quenched under Ar in the cooling coin of the furnace followed by bulk chemical analyses to measure the phase compositions. This study aimed to reach a full equilibrium within the Si-slag-crucible system (0.6 g sample) under inert gas atmosphere by using drop-quenching technique followed by direct phase analyses of EPMA and LA-ICP-MS. This technique has been used successfully for minor element investigations before, for example in copper and nickel smelting systems [15–17] but was now adopted for the first time for silicon-slag system.

## 2 Experimental and analytical techniques

The reagent materials used were high-purity metals and oxides (99.9 % or above) supplied by Thermo Fisher Scientific Inc., Waltham, MA, USA, and Merck KGaA, Darmstadt, Germany. Master silicon alloy (Si-B-P) was prepared by melting Si and P in boron nitride painted alumina crucibles under Ar at 1500 °C. The master alloy composition was measured to contain 150 ppmw P and 570 ppm B by ICP-AES. Additionally, master slag was prepared by melting SiO<sub>2</sub>-CaO-10 wt%Al<sub>2</sub>O<sub>3</sub> slag in Pt crucible under air for 60 min at 1500 °C and casted to a steel rail. The composition after melting was analysed with ICP-AES as 46.7 wt% CaO–42.9 wt% SiO<sub>2</sub>–9.6 wt% Al<sub>2</sub>O<sub>3</sub>. Si alloy standards for LA-ICP-MS were prepared by drop-quenching 1 g of Si with different B and P concentrations (1500 °C, under Ar, Al<sub>2</sub>O<sub>3</sub> crucible). The standards were then analysed with ICP-AES and further used for LA-ICP-MS analyses of Si phase in the Si-Slag samples.

The experiments included high-temperature equilibration of Si-slag samples under Ar gas atmosphere at 1500 °C, followed by quick quenching to an ice-water mixture. The experiments were carried out in a vertical tube furnace in Nabertherm RHTV 120-300/18 with the controller unit C42. The samples were

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**Figure 1.** The experimental method and analytics used.

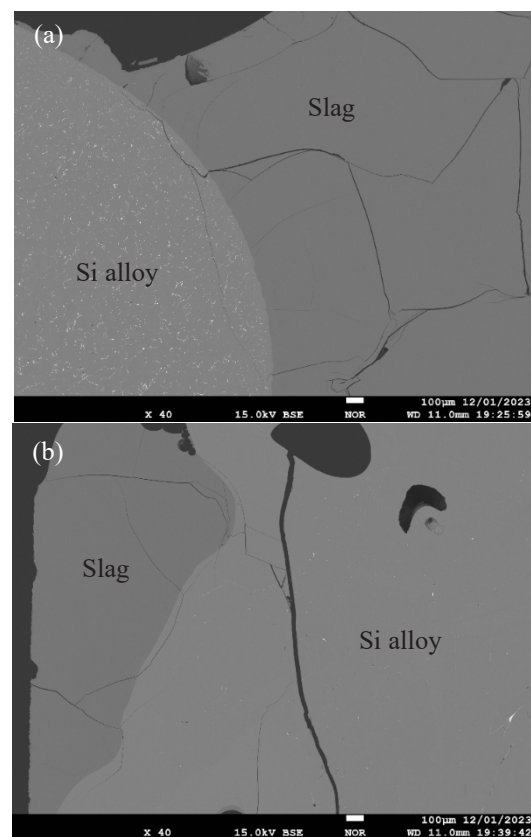
melted from 30 min to 16 h at different primary saturation phases, *i.e.*, using 99.53 % pure  $\text{Al}_2\text{O}_3$  and 99.99 % pure  $\text{SiO}_2$  crucibles (supplied by Nanyang Xinyu New Material Technology Co. Ltd., Nanyang, China). The equilibrated samples were mounted in epoxy resin and ground/polished to expose the cross-section. The microstructure of the samples was examined by both optical and electron microscopy. The phase compositions were measured with microanalysis techniques including EPMA and LA-ICP-MS.

### 3 Results and discussion

Figure 2 shows BSE images of the microstructures of silica and alumina-saturated samples. As shown silicon alloy phase included brighter segregations, especially at alumina-saturation. All the major elements and phosphorus was measured in silicon and slag phase by EPMA. Other impurities, such as Mg, Zr, Y, Fe and Mo, were additionally found and measured in some samples, mainly in the alumina-saturated systems. The Si alloys at silica-saturation included less segregations and less impurities. LA-ICP-MS was used primarily to measure boron, but also other elements, including P, to verify and compare with the probe results.

FactSage© simulations using FToxid and FSups databases were conducted for the same initial compositions with the same boundary conditions as in the experimental systems. Table 1 shows and compares the experimentally determined distribution coefficients of B and P after 4 h compared to the simulation results. Silica-saturated system was fully equilibrated at 4 h, but alumina-saturate system required longer equilibration time. The comparison is still made for the 4 h experiments in this extended abstract. It seems that alumina-saturated system had slightly higher distribution coefficient for both elements compared to silica-saturated system.

As it can be seen, most experimental results for distribution coefficients are significantly different from the simulation results, with only  $L^{\text{slag/SiB}}$  at silica-saturation relatively close to the predicted value. The influence of increasing alumina in slag on the boron distribution coefficient and boron dissolution in slag is found to be highly overestimated by FactSage simuli-



**Figure 2.** Microstructures of Si alloy –  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$  slag systems at alumina-saturation (a) and silica-saturation (b) at 1500 °C after 4 h smelting.

**Table 1.** Experimental and simulation results for 4 h samples.

	Experimental		Simulation	
	$\text{SiO}_2\text{-sat.}$	$\text{Al}_2\text{O}_3\text{-sat.}$	$\text{SiO}_2\text{-sat.}$	$\text{Al}_2\text{O}_3\text{-sat.}$
$L^{\text{slag/SiB}}$	$2.3 \pm 0.2$	$2.6 \pm 0.5$	1.5	13.6
$L^{\text{slag/SiP}}$	$0.17 \pm 0.05$	$0.41 \pm 0.16$	$1.3\text{E-}17$	$6.3\text{E-}19$
$\text{Al}_2\text{O}_3$ in slag (wt%)	$5.6 \pm 0.1$	$36 \pm 0.5$	5.4	44

ons compared to the experimental results. On the other hand, the phosphorus distribution coefficient was significantly lower and practically no dissolution of P in slag occurred based on the simulations compared to the experimental findings.

The experimental results for  $L^{\text{slag/SiB}}$  were similar to a few previous studies [4–6]. Additionally,  $L^{\text{slag/SiP}}$  obtained was in the same range to part of the values found in literature (for different systems; various Si alloys or slags) [10–13]. Even though more experimental results are needed, it is evident that both databases FSupsi and FToxid used for the simulations require re-assessing and optimizing of these systems.

## 4 Conclusions and summary

New experimental and analytical techniques were employed to measure phosphorus and boron in Si–SiO<sub>2</sub>–CaO–Al<sub>2</sub>O<sub>3</sub> systems at 1500 °C. The distribution coefficients of P and B between slag and Si were calculated and compared to FactSage© calculations. The experimental and simulation results had radical differences, and it is considered that the databases used require re-assessing. The experimental results are promising, but more experimentation, standards and analyses are required to verify the results.

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