THERMODYNAMIC PROPERTIES AND STRUCTURAL ASSESSMENT OF BORON OXIDE IN $CaO-SiO_2$ AND $CaO-SiO_2$ -CaF_2 SLAGS FOR SILICON REFINING

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ABSTRACT

New production process for polycrystalline silicon is necessary in order to increase the actual feed stock of this material for the solar cell market. Metallurgical grade silicon can be used for the production of solar cells if the required degree of purity is achieved. The slag refining of silicon for boron removal using silicate slags is one of the available techniques. In this work, the thermodynamics of $CaO-SiO_2$ *and* $CaO-SiO_2-CaF_2$ *slags were evaluated at 1823 K using metal-slag equilibration method. The activity coefficient of boron oxide and the borate capacity of the slag were calculated for low boron containing slags (boron concentration lower than 0.25%).*

For basicities lower than 0.8 in the $CaO-SiO_2$ *binary system, as the content of silica increases, an unexpected decrease in the activity coefficient of boron oxide was observed. To explain this decrease, a model where the boron in slag phase is incorporated in the silicate network was proposed.* ^{11}B *solid state NMR analyses and quantum chemical calculations have shown that this boron exists in tetrahedral form connected to four silica groups and having a* Ca^{2+} *coordinated close to it.*

INTRODUCTION

Nowadays, the use of clean energy has become crucial, and it can be perceived in the increase of the production of solar cell for the past few years. Due to this increase in the demand, the price of the high purity silicon, that is the main substrate for solar cell has also increased. New production routes for solar grade silicon (99.9999%Si) are required in order to increase the feedstock of polycrystalline silicon for the solar cell production. The refining of metallurgical grade silicon (99.8%Si) is an available option, but the removal of boron, the most difficult impurity to be removed from silicon, is still a problem. The oxidation using plasma combined with water vapor has shown good results, but this process requires longer treatment time with considerable amount of energy. Alternatively the oxidation of boron using silicate slags is possible, and will be effective if a high boron partition ratio is attained. The partition ratio is considered to be affected by the activity coefficient of boron oxide in slag, as well as the oxygen partial pressure between slag and silicon. Therefore, the basicity and the structure of the slag are the important parameters for such refining process.

The basicity of the slag is defined in this work as the ratio alkaline oxide/silica, and will increase as the CaO amount increases. For the binary system CaO-SiO_2 at 1823 K, the ratio CaO/SiO_2 can only exceed 1.2 if a flux, such as CaF_2 is used [1]. Silicate slags can have its structure changed as the ratio network-former/network-modifier changes [2]. As the amount of SiO_2 (network-former) increases, polymeric structures are formed in the slag. The formation of such structures may affect the behavior of boron in slag. In the present work, thermodynamic properties of boron oxide in silicate slags at 1823 K are shown together with the definition for borate capacity of slags. The major local structures of boron for CaO-SiO_2 slags with CaO/SiO_2 ratio lower than 0.8 was evaluated using ^{11}B solid state NMR analysis supported by quantum chemical calculations.

METHODOLOGY

High purity silicon was doped with 150 ppm of boron using an induction furnace. Three grams of silicon was equilibrated with 6.7 grams of slags of various compositions in a graphite crucible at 1823 K in argon atmosphere using a $MoSi_2$ resistance furnace. Slags were prepared from reagent grade SiO_2, CaF_2 and CaO calcined from $CaCO_3$ in air. The temperature was controlled using a Pt-6%Rh/Pt-30%Rh thermocouple, having an accuracy of ±2K.

After 18 hours the sample was quenched in a flushing argon gas. The slag was physically separated from the silicon, crushed in a ball mill and both phases were subjected to chemical analysis using ICP-AES.

Samples for structural analysis were quenched in water and ground into fine powder. ^{11}B analyses were done in a Chemagnetics CMX400 solid state NMR. The sample rotation was 3kHz, the reference was $BF_3.Et_2O$, and the Lamour frequency was 128.4 MHz.

RESULTS AND DISCUSSION

In order to confirm if the equilibrium was successfully attained, the calcium content of samples of the binary CaO-SiO_2 system were compared with the data provided by Morita [3].

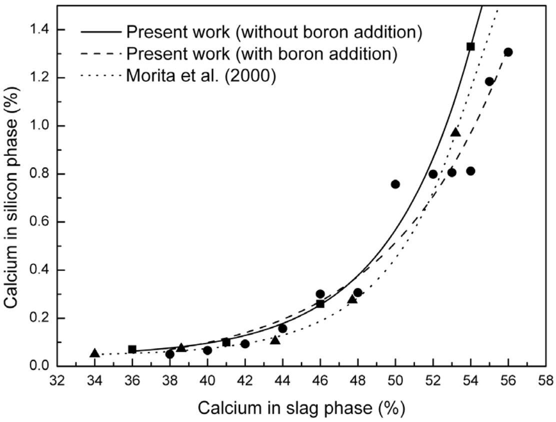

Figure 1: Calcium concentration in samples of CaO-SiO$_2$ slags equilibrated with silicon for 18 hours at 1823 K

From the equilibration results, the partition ratio of boron (LB = (B)/[B]) between silicon and slag phase was clarified for the CaO-SiO$_2$ and CaO-SiO$_2$-(25%CaF$_2$ and 40%CaF$_2$) slag systems. The result is illustrated in Figure 2. The addition of CaF$_2$ increased the attainable basicity of the slag (1.2 for CaO-SiO$_2$, 4.0 for CaO-SiO$_2$-25%CaF$_2$ and 7.0 for CaO-SiO$_2$ -40%CaF$_2$). The highest partition ratio was obtained for CaO-SiO$_2$ slags at basicity 1.2.

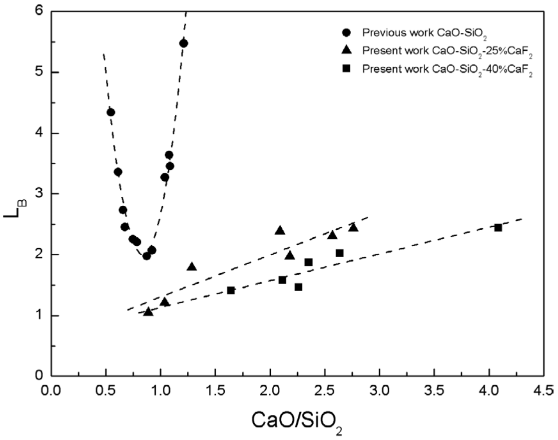

Figure 2: Partition ratio of boron between silicate slags and silicon equilibrated at 1823 K

Calcium fluoride has neither the oxidation potential of silica nor the strong basicity character of CaO. Since the same ratio of slag/silicon (2.3) was kept constant for all the experiments, the addition of CaF$_2$ promoted the dilution of the other two components. In order to confirm the state of boron in slag phase, a series of experiments were conducted where the boron concentration in the premelted silicon was raised from 150 ppm to 1.0 wt%. The maximum concentration of boron obtained in the slag phase was below 0.25 wt%, and could be regarded as a Henrian solution, as shown in Figure 3.

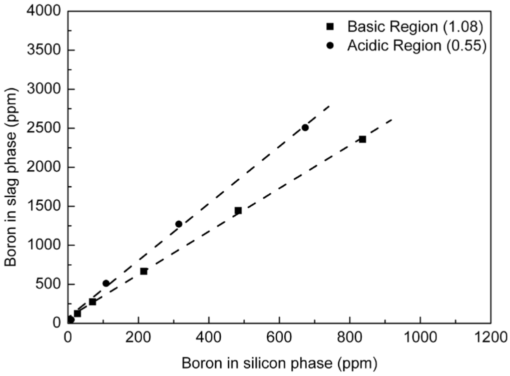

Figure 3: Boron dependence with its content between silicon and slag phase for the binary system SiO_2-CaO at 1823 K. The max concentration of boron in slag was 0.25 wt%

Based on reaction 1, the activity coefficient of boron oxide can be calculated as shown by Equation 2.

$$\underline{B} + \frac{3}{4}\, SiO_{2(l)} = BO_{1.5(l)} + \frac{3}{4}\, Si_{(l)} \tag{1}$$

$$\gamma_{BO_{1.5}} = \frac{K\, a_B \left(a_{SiO_2}\right)^{\frac{3}{4}}}{X_{BO_{1.5}} \left(a_{Si}\right)^{\frac{3}{4}}} \tag{2}$$

where K is the reaction constant.

The activity of silicon was calculated using Gibbs-Duhem equation combined with the data published by Inoue [4]. The boron activity was evaluated based on the work of Yoshikawa [5] and the silica activity was taken from Morita [3]. The activity coefficient of boron oxide is shown in Figure 4A.

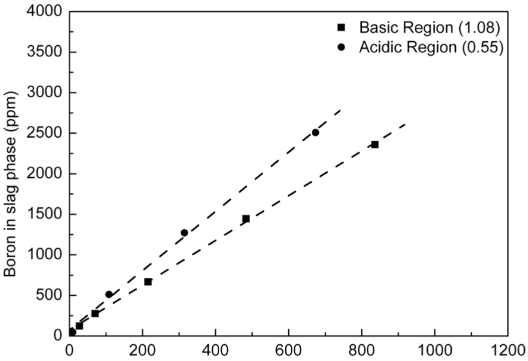

Figure 4: A) Activity coefficient of boron oxide for silicate slags at 1823 K compared with the data from Noguchi. B) Relation between activity coefficient of boron oxide and basicity for samples of CaO/SiO_2 ratio higher than 0.8

The difference between the activity coefficients calculated in the present work and the work done by Noguchi [6] may be due to the difference in the boron activity in silicon phase adopted for both works. As expected, the activity coefficient of boron oxide decreases with increase in basicity except for the silica rich region ($CaO/SiO_2<0.8$), where the activity coefficient decreases as we increase the silica content. As will be present later in this paper, the behavior of boron oxide in slag is similar to the behavior of sulfide. However, the decrease in the activity coefficient of boron oxide with increase of the silica content in slags with CaO/SiO_2 ratio lower than 0.8 was unexpected. A linear relation between basicity and the activity coefficient of boron oxide is present in Figure 4B, giving the following relation:

$$\ln \tilde{a}_{BO_{1.5}} = -4.00(CaO/SiO_2) + 3.67 \tag{3}$$

In order to explain the behavior of boron oxide in silica rich slags, the structure of such slag was investigated. The XRD analyses of the binary system containing a CaO/SiO_2 ratio lower than 0.8 have indicated the presence of an amorphous structure in the slag phase. Since boron oxide is also a network former (as silica) the possibility of boron incorporation by the silicate network was investigated using ^{11}B solid state NMR analysis, as well as quantum chemical calculations. The result is shown in Figure 5 together with the quantum chemical calculation results (vertical lines) for five different species: $^{[3]}B$ - $^{[3]}B$ (boron oxide connected to boron oxide in an open threefold structure), $^{[3]}B$ - 1Si-2NBO (boron in threefold structure connected to one silica group, having 2 non bridging oxygen), $^{[3]}B$-2Si-1NBO (boron in threefold structure connected to two silica groups, having 1 non bridging oxygen), $^{[3]}B$-3Si (boron in threefold structure connected with 3 silica groups) and $^{[4]}B$-4Si-Ca (boron in fourfold structure connected to 4 silica groups and having a Ca^{+2} coordinate close to the boron atom). The result for $^{[4]}B$-4Si-Ca (-1.7 ppm of chemical shift) is coincident with the result obtained from NMR and consistent with the result published by Lin-Shu Du [7]. This result is also in agreement with the data available for reedmergnerite [8].

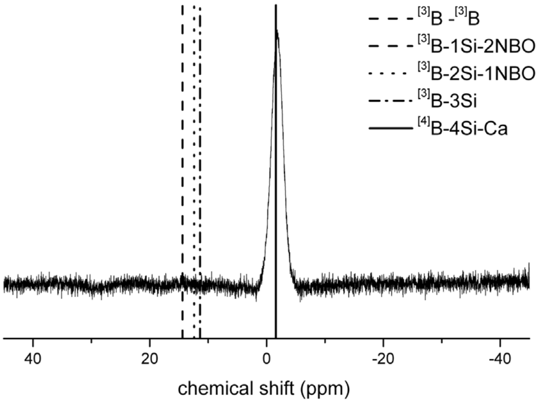

Figure 5: Result of ^{11}B solid state NMR analysis for a sample of the CaO-SiO_2 binary system with CaO/SiO_2 ratio of 0.55 containing a boron concentration around 0.25%. The vertical lines represent the values obtained by quantum chemical calculations for several possible structures

This result suggests that boron was incorporated by the silicate network as a fourfold structure, being a part of a large silicate structure (Figure 6). This result is valid for samples of low CaO/SiO_2 ratio and low boron content.

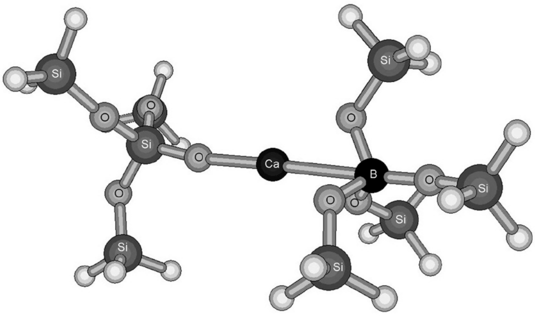

Figure 6: Boron incorporation in the silicate network for CaO-SiO$_2$ slags with CaO/SiO$_2$ ratio lower than 0.8 and boron content up to 0.25%

Based on the slag-metal equilibrium data (Equation 4), the borate capacity of slag systems was defined in this work as shown in Equation 5:

$$\underline{B} + \frac{3}{4}O_2 + \frac{3}{2}O^{2-} = BO_3^{3-} \tag{4}$$

$$C_{BO_3^{3-}} = \frac{(\text{mass\%}BO_3^{3-})}{a_{\underline{B}}P_{O_2}^{\frac{3}{4}}} = \frac{K_1 a_{O^{2-}}^{\frac{3}{2}}}{f_{BO_3^{3-}}} \tag{5}$$

where K_1 is the reaction constant. The capacity of the slag is increased with increase in basicity, as expected for an acidic oxide. If the borate capacity data is treated in the same way adopted for the activity coefficient, it can be fitted by a linear relation (Equation 6) as shown in Figure 7. Since there is no data available on the borate capacity of the slags, it will be compared with the sulfide capacity [9], in Equation 7.

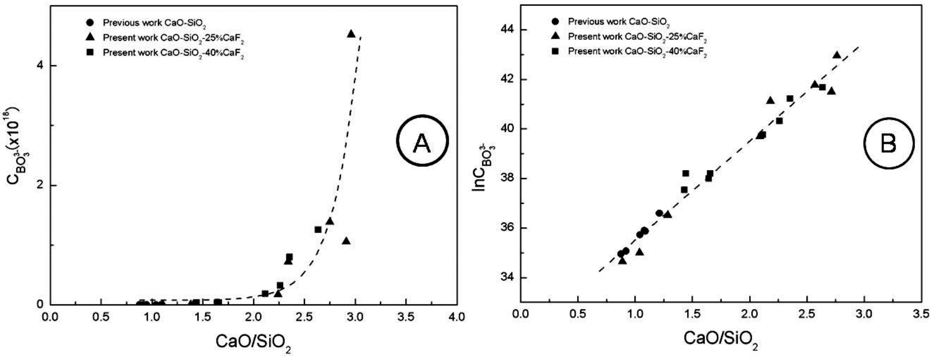

Figure 7: A) Borate capacity for silicate slags at 1823 K. B) Relation between borate capacity for samples of CaO/SiO$_2$ ratio higher than 0.8

$$\ln C_{BO_3^{3-}} = 4.00\,(CaO/SiO_2) + 31.51 \tag{6}$$

The relation between borate capacity and sulfide capacity [10] can be expressed by Equation 8, and the expected slope of the plot in Figure 8 is 3/2. The obtained slope was 1.43 and 1.88, revealing an agreement between both properties of the slag.

$$C_{S^{2-}} = \frac{(\text{mass\%}S^{2-})\,P_{O_2}^{\frac{1}{2}}}{P_{S_2}^{\frac{1}{2}}} = \frac{K_2 a_{O^{2-}}}{f_{S^{2-}}} \tag{7}$$

$$\log C_{BO_3^{3-}} = \frac{3}{2}\log C_{S^{2-}} + \log\frac{K_1}{K_2^{\frac{3}{2}}} + \log\frac{f_{S^{2-}}^{\frac{3}{2}}}{f_{BO_3^{3-}}} \tag{8}$$

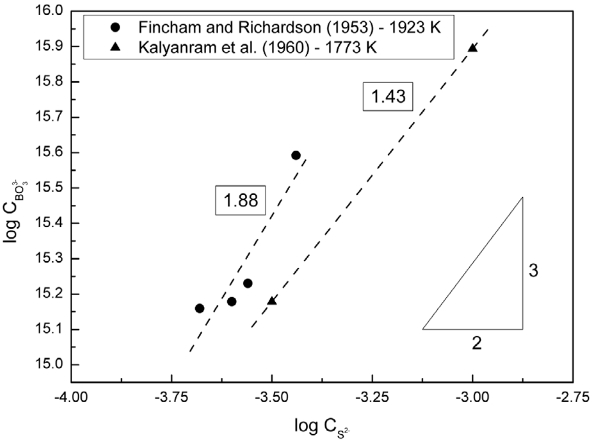

Figure 8: Relation between borate capacity and sulfide capacity of silicate slags

CONCLUSIONS

Boron exists as a monomer in $CaO\text{-}SiO_2$ slags containing up to 0.25 wt% boron.

The activity coefficient of boron oxide for $CaO\text{-}SiO_2$ and $CaO\text{-}SiO_2\text{-}CaF_2$ slags at 1823 K was determined, and its dependence with basicity (for samples with $CaO/SiO_2 > 0.8$) is given by:

$$\ln \tilde{a}_{BO_{1.5}} = -4.00\,(CaO/SiO_2) + 3.67$$

An unexpected low activity coefficient of boron oxide in $CaO\text{-}SiO_2$ slags was observed for slags with CaO/SiO_2 ratio lower than 0.8. This behavior was attributed to the incorporation of boron by the silicate network. This result was confirmed by ^{11}B solid state NMR analysis (resonance detected at -1.7ppm).

The borate capacity was defined in this work as:

$$C_{BO_3^{3-}} = \frac{(\text{mass\%}BO_3^{3-})}{a_{\underline{B}}P_{O_2}^{\frac{3}{4}}} = \frac{K_1 a_{O^{2-}}^{\frac{3}{2}}}{f_{BO_3^{3-}}}$$

Its dependence with basicity (for samples with $CaO/SiO_2 > 0.8$) is given by:

$$\ln C_{BO_3^{3-}} = 4.00(CaO/SiO_2) + 31.51$$

The relation between borate capacity and sulfide capacity is given by:

$$\log C_{BO_3^{3-}} = \frac{3}{2}\log C_{S^{2-}} + \log \frac{K_1}{K_2^{\frac{3}{2}}} + \log \frac{f_{S^{2-}}^{\frac{3}{2}}}{f_{BO_3^{3-}}}$$

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REFERENCES

Suzuki, K., Sugiyama, T., Takano, K. & Sano, N. (1990). Thermodynamics for Removal of Boron from Metallurgical Silicon by Flux Treatment. *Journal of the Japan Institute of Metals*, Vol. 54(2), pp. 168-172. [1]

Richardson, F. D. (1974). *Physical Chemistry of Melts in Metallurgy*. Vol. 1, Academic Press London - New York. [2]

Morita, K., Kume, K. & Sano, N. (2000). *A Newly Developed Method for Determining SiO_2 Activity of the Silicate Slags Equilibrated with Molten Silicon Alloys*. ISIJ International Vol. 40, pp. 554-560. [3]

Inoue, G., Yoshikawa, T. & Morita, K. (2003). *Effect of Calcium on Thermodynamic Properties of Boron in Molten Silicon, High Temperature Materials and Processes*. Vol. 22, pp. 221-226. [4]

Yoshikawa, T. & Morita, K. (2005). *Thermodynamic Property of B in Molten Si & Phase Relations in the Si-Al-B Systems*. Materials Transactions JIM, Vol. 46, pp. 1335-1340. [5]

Noguchi, R., Suzuki, K., Tsukihashi, F. & Sano, N. (1994). *Thermodynamics of Boron in a Silicon Melt*, Metallurgical & Materials Transactions B, Vol. 25B, pp. 903-907. [6]

Du, L. S. & Stebbins, J. F. (2003). Solid-state NMR Study of Metastable Immiscibility in Alkali Borosilicate Glasses. *Journal of Non-Crystalline Solids*. Vol. 315, pp. 239-255. [7]

Mackenzie, K. J. D. & Smith, M. E. (2002). *Multinuclear Solid-state NMR of Inorganic Materials*. Pergamon, Tokyo, pp. 421. [8]

Finchan, C. J. B. & Richardson, F. D. (1953). *The Behavior of Sulfur in Silicate & Aluminate Melts*. Proceeding of the Royal Society of London, Series A, pp. 40-62. [9]

Kalyanram, M. R., MacFarlane, T. G. & Bell, H. B. (1960). The Activity of Calcium Oxide in Slags in the Systems CaO-MgO-SiO_2, CaO-Al_2O_3 - SiO_2 and CaO-MgO-Al_2O_3-SiO_2 at 1500 °C. *The Journal of the Iron & Steel Institute*. Vol. 195, pp. 58-64. [10]